Thermal degradation of Triethylene glycol used in dehydration of natural gas

A study of degradation rate and products

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Department of Chemical Engineering, CE 3+4, 2024-25

Master's Thesis

Thermal Degradation of TEG

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Abstract:

Triethylene glycol (TEG) is widely used in natural gas dehydration systems due to its hygroscopic nature and relatively low toxicity. However, when exposed to high temperatures, TEG begins to degrade, forming by-products like monoethylene glycol (MEG) and diethylene glycol (DEG). These degradation compounds can reduce system efficiency, leading to issues such as foaming, corrosion, and reduced dehydration performance. A detailed understanding of the degradation pathways and the accurate quantification of byproducts is essential to optimize the dehydration process and ensuring system reliability. This study examines the thermal degradation behavior of TEG under controlled heating conditions, with a primary focus on the identification and quantification of degradation products. GC-FID was selected as the principal analytical tool because of its high accuracy in detecting degraded by-products MEG and DEG. GC-MS was also used to confirm the identities of degraded compounds, but lacked the precision needed for reliable quantification. Although Raman spectroscopy was explored as a potential technique, it proved ineffective in detecting degradation compounds in this case. Overall, our findings highlight GC-FID as a reliable method for monitoring thermal degradation in glycol systems and provide useful insights into how TEG behaves under thermal conditions.

Contents

Preface

This project has been carried out by Satwik Saswat Mahapatra and Bilal Ahmad as part of the third and fourth semesters of the Master's programme in Chemical Engineering. The project period extended from September 2024 to June 2025 and will be presented in June 2025.

We would like to express our gratitude to our supervisor, Associate Professor Marco Maschietti, at the Department of Chemical Engineering and Biotechnology, for his excellent supervision, encouragement, and critical insights throughout the project. We are especially thankful for his thoughtful suggestions, which contributed significantly to both the direction and quality of the work.

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Aalborg University, June 2, 2025

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Chapter 1

Introduction

Natural gas, like most natural resources, contains impurities that need to be removed. This is to ensure the gas sent through the pipeline meets certain specifications of purity agreed by the client, as well as to avoid fouling, clogging, damage to equipment and meet emission standards. Water is one of the major impurities that is removed during processing through dehydration. This is crucial to avoid condensation of water and formation of gas hydrates in the pipeline, which can lead to clogging and corrosion, especially in the presence of acidic components in the gas. Typically, dehydration of natural gas is accomplished by absorption using glycols, most commonly by tri-ethylene glycol (TEG). This method is able to meet the desired water content that is required for gas transmission pipelines, which is typically 70-140 mg/Nm^3. After absorption, TEG is recovered through a regenerator that operates at high temperatures (204 °C). This process achieves around 99% TEG. [1]

Exposure to high temperature, water and oxygen for a prolonged period of time is known to cause TEG to degrade. TEG, which is originally a colourless liquid, becomes dark-brown or even black after degradation. This can cause issues related to dehydration performance, as well as fouling in the system. Literature is scarce regarding the products and mechanism of TEG degradation. It is known that TEG can break down into MEG and DEG when degraded, and is also known to form other compounds such as organic acids, in the presence of oxygen. Analysis of this process can be achieved by either monitoring the reduction in the amount of TEG over time, or the formation of known degradation products within the sample.

The current challenge is to identify degradation products of TEG under different conditions in order to better understand the reaction mechanism. This requires selecting appropriate analytical tools. The effect of water, oxygen and other compounds absorbed by TEG during the dehydration process is also worth exploring. In this study, we aim to tackle some of these challenges.

Chapter 2

Literature Review

2.1 Overview

Natural gas has only seen widespread use in recent history. Its discovery can be dated back to ancient Greece, and its first usage can be dated back to 500 BC in China. Around the late 18th century and early 19th century, natural gas began to be used commercially, mainly for lighting houses and streets. It was after the invention of the Bunsen burner, followed by the development of pipeline systems, that natural gas became a prominent source of energy. There are some advantages of using natural gas that set it apart from other fossil fuels, such as coal and petroleum. The most important factor is clean combustion, as it is considerably less polluting than other fossil fuels.

Today, Natural gas as a global energy source is just as prominent as ever 2.1. North America leads in production with around 31% of global production, mainly coming from the US. This is followed by the CIS (Commonwealth of Independent States), the Middle East, and the Asia-Pacific. A detailed overview of global production and consumption by region can be seen in the Figure 2.2. Norway is the leading producer of natural gas in Europe by far, accounting for almost three-quarters of the total production within Europe and 3 % of the global production as per 2023. All of it is produced from reservoirs under the seabed through offshore installations [2].

Global production of natural gas has increased by about 1.9% in the last decade (2013-2023), while the consumption has grown by around 1.7%, as shown in the Figure 2.3. In Europe, there has been a decline in both production and consumption of natural gas in recent years due to an increasing focus on renewable energies. A growth in demand for Liquefied Natural GAS (LNG) was seen primarily by the Asia-Pacific countries like China, India, and other non-OECD countries. Europe and OECD Asia-Pacific countries, on the other hand, saw a decline in LNG demand [2].

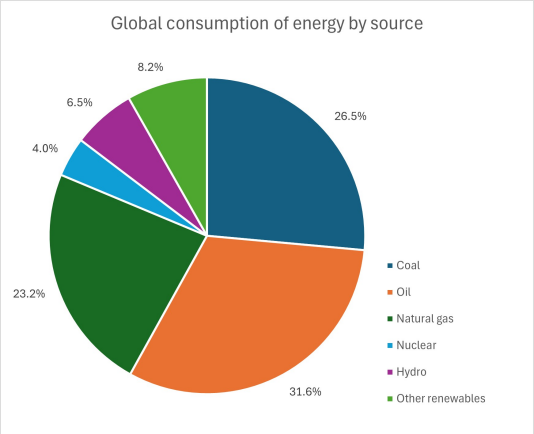

Figure 2.1: Distribution of global energy consumption by source by Statistical Review of World Energy 2024 [2] .

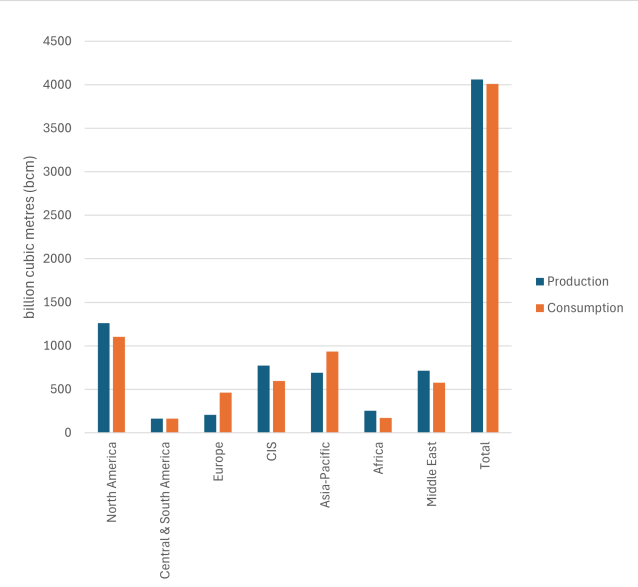

Figure 2.2: Global production and consumption of natural gas by region. (The data represented above in cubic metres is measured at 15 °C and 1.013 Bar) [2]

The composition of natural gas depends on its origin. Natural gas that is associated with an oil reservoir is also called "wet gas", and it is richer in higher molecular weight hydrocarbons and leaner in methane. It is therefore typically richer in Natural Gas Liquids (NGLs), which contain C_2+ compounds. Whereas, natural gas that is not associated with much, if any, crude oil or gas liquids, is called "dry gas". It is richer in methane and has a much lower concentration of higher hydrocarbons [3]. A detailed composition of natural gas can be seen in the

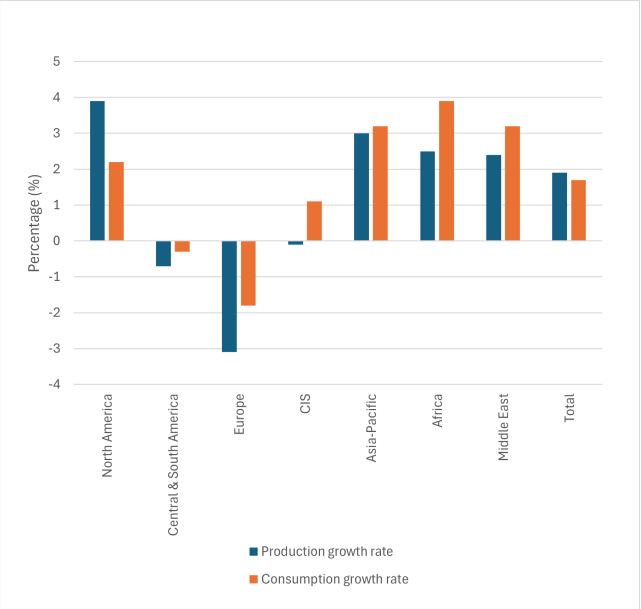

Figure 2.3: Growth of global production and consumption of natural gas by region between 2013-2023. [2]

Table 2.1.

Constituent	Composition (vol%)	
	Wet gas	Dry gas
Hydrocarbons		
Methane	84.6	96
Ethane	6.4	2
Propane	5.3	0.6
Isobutane	1.2	0.18
n-butane	1.4	0.12
Isopentane	0.4	0.14
n-pentane	0.2	0.06
Hexanes	0.4	0.1
Heptanes	0.1	0.8
Non-hydrocarbons		
Carbon Dioxide	< 5	
Helium	< 0.5	
Hydrogen Sulfide	< 5	
Nitrogen	< 10	
Argon	< 0.05	
Radon, Krypton, Xenon	Traces	

Table 2.1: Typical composition of wet and dry gas [3].

2.2 Processing Natural gas

Raw natural gas needs to be processed to remove impurities before it can be transported through the pipeline. This involves a number of processes to make sure the pipeline gas meets both environmental regulations and pipeline-quality criteria. The removal of different components is discussed below in detail, and a general schematic diagram representing a typical gas processing unit is shown in the Figure 2.4.

2.2.1 Separation of liquid hydrocarbons

A valuable part of natural gas is Natural Gas Liquids, also abbreviated as NGL. As discussed earlier, they consist of higher molecular weight hydrocarbons and are found generally in wet natural gas, but also occur in lower quantities in dry natural gas [3]. There are multiple ways to separate NGLs.

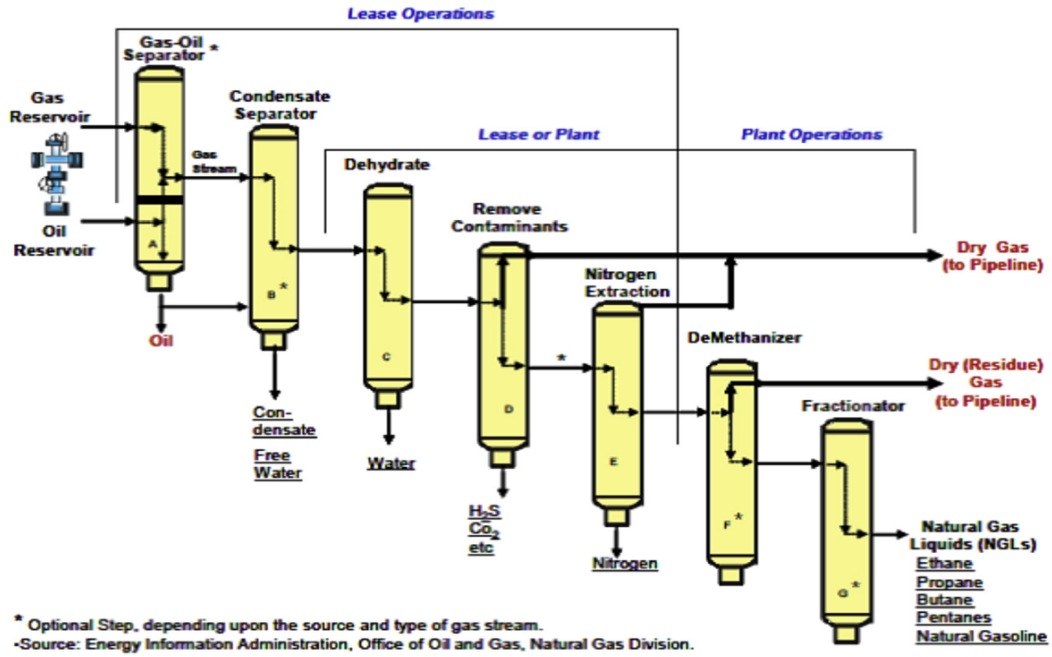

Figure 2.4: Schematic representation of general gas processing units [3].

2.2.2 Removal of Mercury

The presence of Mercury in extracted gas creates a two-pronged issue. Firstly, it can corrode heat exchangers. The second issue is with the disposal of any solid or liquid material that is used to remove mercury from the gas, which poses an environmental and health safety hazard.

Mercury can be removed by either a regenerative or a non-regenerative process. Most of the non-regenerative methods use sulphur in some form, which can react with mercury to form a stable compound. Regenerative methods use silver to form an amalgam with mercury, which can then be decomposed and regenerated. [3]

2.2.3 Removal of trace components

1. **Nitrogen** - Nitrogen content in the gas can reduce its heating value since it is non-combustible. It can be removed by cryogenic distillation, pressure swing adsorption, or membrane separation. [3]

2. **Helium** - Although it needs to be removed, helium is a desirable product and can be separated using nitrogen injection. [3]

3. **Oxygen** - Lower concentrations of oxygen can be removed by using non-regenerative scavengers. When dealing with high concentrations, catalytic

reaction can be used to convert it into water, which can then be removed during dehydration. [3]

4. **Arsenic compounds** - Arsenic is a health and safety hazard, and its combustion can cause environmental pollution. Additionally, it can also poison other catalysts downstream. Removing arsenic compounds can be achieved by a non-regenerative adsorption process. [3]

5. **Naturally occurring radioactive materials (NORM)** - Radioactive elements like ^{226}Ra, ^{214}Bi, and ^{214}Pb have been detected in the scales and sludge of gas processing units in some reservoirs. [4] NORM emissions can be inhibited by using filter assemblies or by using scale inhibitors. [3]

2.2.4 Removal of acid gases

H_2S and CO_2 present in natural gas are termed "acid gases" due to the fact that they can combine with water and form weak acids. These acidic solutions can be very corrosive and cause damage to the pipeline. Natural gas that has sulphur compounds like H_2S in concentrations typically higher than around 4 ppm, is called "sour gas". Otherwise, if it mostly has CO_2, it is called "sweet gas" [5]. Removal of H_2S from natural gas is challenging because it is toxic and lethal to humans. H_2S gas can damage aquatic life if released into the sea, and combustion of sulphur-containing compounds can cause acid rain if released into the atmosphere. On the other hand, the presence of CO_2 can affect the combustion quality of the natural gas because it is non-flammable. Furthermore, the presence of H_2S and CO_2 also affects hydrate formation by any water present in the gas. CO_2 has a relatively smaller effect and inhibits hydrate formation, whereas H_2S promotes hydrate formation and can cause operational issues [5].

The method for removing acid gases depends on the composition and quantity of raw gas to be processed. Either absorption or adsorption processes can be used.

Chemical absorption

Amine compounds such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyl diethanolamine (MDEA), di-isopropanolamine (DIPA), and diglycolamine (DGA) are widely used to absorb H_2S and CO_2 from the gas stream. Their selection depends on the operating conditions and composition of the gas. Their selectivity for either component can be improved by using sterically hindered amines.

Potassium carbonate is also used as a mild alkali to absorb acid gases. Caustic bases like NaOH can also be used, but additional washing with water is needed to remove any caustic substance entrained in the gas. [3]

Physical solvent

Methanol was the first commercial, organic physical solvent ever used for hydrate inhibition, dehydration, gas sweetening, and liquid recovery. This process is known as Rectisol and was developed and licensed by Lurgi Oel Gas Chemie GmbH and Linde AG. Similarly, the Selexol process (by Allied Chemical Corporation), the Purisol process (by Lurgi Oel Gas Chemie), and Fluor solvent (by Fluor Corporation), along with a hybrid solvent process called Sulfinol (by Shell Global Solutions), are also used.[3]

Adsorption Process

The adsorption process is another alternative to remove acid gases and other sulfur contaminants. These can be regenerative, like molecular sieves, or non-generative, like activated carbon. Membranes can also be used for the removal of CO_2, however, they can be weak to high pressure, temperatures, and have weak mechanical strength. [3]

H_2S scavenger process

H_2S and other sulphur compounds can be scavenged by reaction with a solid medium like metal oxides or by liquid scavengers like MEA-Triazine. Higher concentrations can be tackled by a continuous process like the Ferrox process or the Stretford process. [3]

2.2.5 Removal of water

Natural gas extracted from a well is saturated with water at the conditions of the well. The water content depends on the pressure, temperature, and composition. Acidic gas components such as CO_2 and H_2S increase the solubility of water in the gas due to their affinity for water.

2.3 Dehydration

Removal of water is necessary to prevent liquid water condensation and the formation of gas hydrates in the pipeline system during transportation. A gas hydrate is a physical combination of water and other small molecules, forming a solid which has an "ice-like" appearance but with a dissimilar structure. Natural gas hydrates are predominantly methane hydrates, since it is the primary component of natural gas. The structure of a hydrate is determined by the composition of the gas. Smaller molecules like CO_2 and H_2S form hydrates that are structurally different from hydrates formed by larger hydrocarbon molecules like C_3H_8 and C_4H_{10}.

Formation of hydrates in Natural Gas Liquid (NGL) systems can cause clogging and fouling, which can restrict flow or damage equipment and the pipeline system. The structure of the hydrate itself affects the temperature and pressure at which hydrate forms. Preventing the formation of hydrates can be achieved by keeping the gas stream at or above the dew point or saturation condition. Another method is by using a chemical inhibitor in the stream. However, a better solution, which is most commonly used, is to remove the water from the natural gas before transporting, i.e., dehydration.

Another problem associated with the condensation of water in a natural gas pipeline is corrosion, particularly when acidic components such as H_2S and CO_2 are also present.

Finally, contract specifications for dew-point requirements are also required to be met before sending the gas through the pipeline.

2.3.1 Dehydration Methods

The removal of water from natural gas and natural gas liquids (NGLs) is called dehydration. There are two major ways to achieve that.

Absorption using liquid desiccants

Dehydration using liquid desiccants involves absorption of water from the gas stream in a counter-current fashion, using certain liquids that have a high affinity for water, i.e, are hygroscopic in nature. For this purpose, glycols are commonly used due to their high hygroscopicity, low vapour pressure, high boiling point, and low solubility in natural gas.

Mono-ethylene glycol, also known simply as ethylene glycol (MEG), di-ethylene glycol (DEG), tri-ethylene glycol (TEG), and tetra-ethylene glycol (TREG) are all used as desiccants. TEG is the most commonly used by far due to its superior dew-point depression (about 15°C - 49°C [6]), operating cost, and operation reliability [7].

Glycol dehydrators also have some disadvantages, however. Highly concentrated glycol solutions become viscous at low temperatures, which can cause issues with pumping. They can also be contaminated by suspended matter like dirt and iron oxide, which can create problems during recirculation. Even though heavier paraffin hydrocarbons present in natural gas are not very soluble in TEG, aromatic hydrocarbons are. These may be absorbed during the dehydration process and circulated to the reboiler, where they may be released into the atmosphere. This poses an environmental and safety hazard. These aromatic compounds are mainly benzene, toluene, ethylbenzene, and o-xylene, which are together classed as BTEX compounds [6]. Degradation due to prolonged/repeated exposure to high temperatures can also cause glycols to degrade. This can reduce the efficiency of the

dehydration process as well as clog the flow due to resultant foaming. This is something our study aims to look into.

Adsorption using solid desiccants

Solid desiccant dehydrators can be used to remove water vapour from the gas via adsorption. As the name suggests, this does not involve a chemical reaction and is solely a surface phenomenon that is affected by the operating temperature and pressure. Compared to liquid desiccants, solids can achieve higher dew point depressions, making them ideal for low quantity operations. They also do not suffer from some of the drawbacks of liquids like corrosion and foaming, and are less sensitive to changes in flow rate, gas temperature, and pressure fluctuations [7].

Three types of solid desiccants are commonly used for commercial gas dehydration: Alumina-based adsorbents, Silica-based adsorbents, and molecular sieves [8] [9].

1. Alumina-based adsorbents - made from either bauxite or derived from gels and crystalline minerals, they are the cheapest. However, they have their drawbacks. They can adsorb hydrocarbons, which can lead to the loss of useful components in the gas. They also require larger towers, which can raise the capital cost.

2. Molecular sieves - made of synthetic zeolites, they are more resistant to fouling and are characterized by uniform pore dimensions. However, they are also the most expensive.

3. Silica-based adsorbents - made of pure activated silica gel, they have higher adsorption capacity and are easier to regenerate at low temperatures. Additionally, they can also adsorb pentane and higher hydrocarbons, which can be useful for hydrocarbon recovery. However, they can get shattered if liquid water comes into contact.

2.4 Glycol Dehydration using TEG

A glycol dehydration unit at a natural gas processing site can be separated into two major parts: an absorption column where glycol absorbs water from the gas stream and a regeneration column where lean glycol is regenerated. Typically, there is also a flash separator to evaporate low-boiling hydrocarbons from the glycol that gets absorbed during dehydration, before it is sent for regeneration. In addition, there is a stripping column or a different method for enhancing the purity of regenerated glycol, and a system for removing BTEX compounds. Figure 2.5 represents a TEG

dehydration unit for natural gas, employing an additional gas stripping column for enhancing glycol concentration.

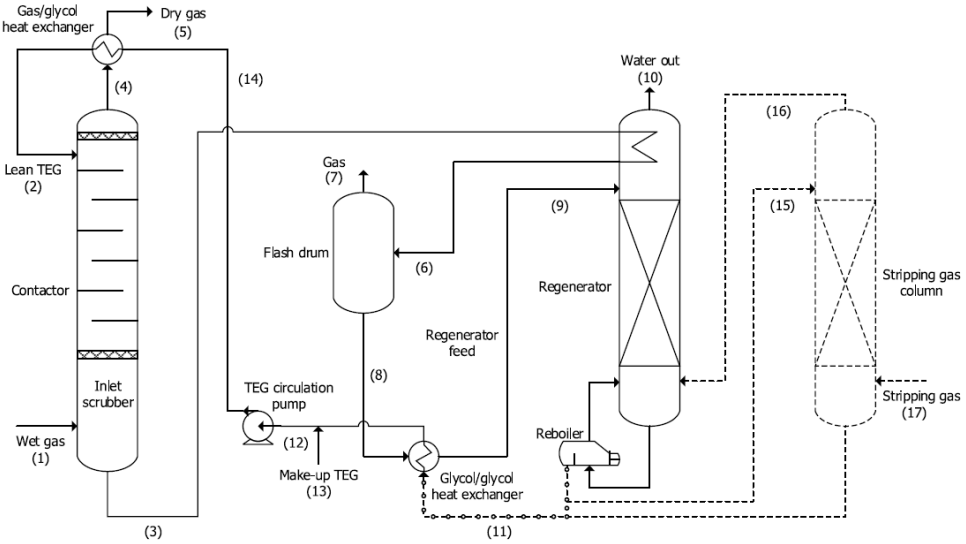

Figure 2.5: Depiction of a TEG dehydration unit with a gas stripping column. [10]

2.4.1 Absorption

Wet gas is sent into the absorption column from the bottom while dry TEG flows from the top, either through a packing material or trays, establishing a counter-current flow [11]. The column typically operates at temperatures between 20-60 °C and at high pressures, between 40-80 bar [12]. TEG-wet gas flow rate ratio is generally around 1:40 by mass [13]. Dry gas leaves the absorption column from the top can be used to cool down the stream of lean glycol coming into the column through a heat exchanger. The water-rich TEG leaves from the bottom and towards the top of the regeneration column, known as the vapour overhead, where it is used as a reflux cooling medium [14]. It is then sent to a flash drum separator-condenser to remove some of the absorbed hydrocarbons. Reducing the pressure allows lower-boiling hydrocarbons and methane to vaporize from the flash drum [15]. Finally, the glycol is heated by the stream of lean glycol exiting the regenerator via a glycol-glycol heat exchanger before being sent to the regenerator column.

2.4.2 Regeneration

In the regeneration column, water is removed from the glycol by either distillation at around 204 °C and atmospheric pressure, or by using a stripping gas. A reboiler is typically used in the case of a distillation column. Lean TEG of purity close to 99

wt% is obtained using distillation [6]. A stripping gas can also be sent directly into the regenerator to enhance the purity of TEG obtained, or an additional system can be used for the same purpose. In addition to water, the vapour leaving through the top of the regenerator also contains some aromatic hydrocarbons, including BTEX components. The lean TEG exits the column from the bottom and is cooled down first by the rich-TEG stream via the glycol-glycol heat exchanger, followed by the dry gas stream going out of the absorption column via a gas-glycol heat exchanger. It is then sent back into the absorber and thus completes the cycle [10]. Circulation rate of TEG is typically 2-5 gal/lbs of water removed (17-42 l/kg of water) [6].

2.4.3 Controlling BTEX emissions

There are three main ways to mitigate BTEX emissions from a dehydration unit.

Condensers

The overhead vent stream from the top of the regenerator can be condensed to collect BTEX compounds that are evaporated with the water. The condenser can be either water cooled, air cooled, a combination of water and air cooled system, or glycol cooled (using the water-rich glycol before it goes into the flash separator).

Incinerators

Incinerators are used when it is economically not feasible to recover BTEX compounds as a liquid. It is, however, a bit challenging to combust the overhead vent stream from the regenerator due to high water content. Catalytic combustion is also sometimes used for this reason, and to ensure up to at least 99% combustion of flammable compounds.

Recycle

In some cases, the water and hydrocarbons in the regenerator vent stream can be sent to the crude oil product or produced water disposal system by using a blower or low-pressure compressor [6].

2.4.4 Enhancing glycol concentration

Standard regeneration of TEG is performed at 204 °C and atmospheric pressure, which gives us about 98.7-99 % purity [6]. At higher temperatures, thermal degradation of TEG becomes an issue. Therefore, other methods to obtain higher purity TEG are used, and they all operate by reducing the effective partial pressure of water in the glycol reboiler's vapour space. While using a stripping gas is a common method, other patented methods are also available.

DRIZO

This method uses a stripping medium that is a mixture consisting of hydrocarbons heavier than C5. This can be obtained from external sources or internally from the hydrocarbons that were absorbed by TEG during dehydration (including BTEX components) and separated as liquid from the regenerator overhead condenser. Water is removed from this mixture using a 3-phase separator. The hydrocarbon mixture/stripping medium is then vaporised and superheated before being sent to the glycol stripping column. A simplified process flow diagram is shown in the Figure 2.6.

This method can achieve TEG purity above 99.99%. Additionally, using an internal source for stripping medium ensures there are no additional hydrocarbon emissions from the glycol regenerator even when using high stripping gas rates. The mixture of hydrocarbons and water forms a heterogeneous azeotrope at the condenser atop the regeneration column. This means the temperature for condensation is independent of the stripping rate. Since hydrocarbons absorbed by TEG are used for stripping medium, DRIZO also takes care of BTEX emissions in addition to providing very high TEG purity. [6]

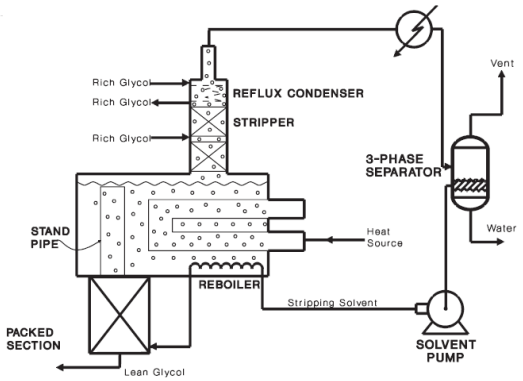

Figure 2.6: Simplified process flow diagram of DRIZO [6]

COLDFINGER

This method replaces the use of a stripping medium in favour of a condensing tube bundle ("cold finger"). This is inserted into a surge tank and uses water-rich glycol coming from the contactor as coolant. The surge tank operates at the reboiler temperature (204 °C), and the vapour phase in this space is water-rich, typically more than 50 wt% . This water condenses in contact with the tube bundle and is collected in a trough placed underneath, which is then removed from the surge tank. This makes the TEG at the bottom to lose water continuously to achieve equilibrium with the vapour phase, and becomes lean by the time it leaves through

the surge-tank outlet. Concentrations of TEG between 99.2-99.5 wt% have been reported using this method [6]. A simplified process flow diagram is shown in the Figure 2.7.

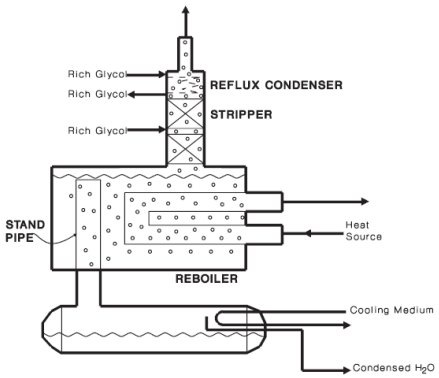

Figure 2.7: Simplified process flow diagram of COLDFINGER [6]

Stripping Gas

This is the most common way to improve the purity of TEG. Typically, dehydrated natural gas is used as the stripping gas itself. In some cases, nitrogen gas is used, which can obtain a TEG purity of more than 99.9 %. This is usually done by sending nitrogen directly into the reboiler or in a separate stripping column for better results. A simplified process flow diagram is shown in Figure 2.8.

On most offshore installations, the nitrogen gas for stripping purposes is obtained from the atmosphere by using a method known as alkaline membrane separation. However, the purity of nitrogen gas obtained is not 100 %, and some trace amount of oxygen is present. This can react with the TEG in the stripping column and cause degradation. [6]

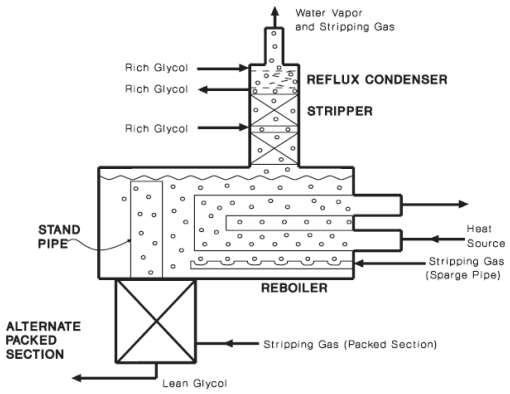

Figure 2.8: Simplified process flow diagram of stripping gas [6]

2.5 Glycol Degradation

It is known that glycols degrade over time when exposed to high temperatures in the reboiler. This is typically accompanied by a change in colour from colourless to yellow or yellowish-brown. The opacity also increases from completely transparent to sometimes almost opaque in highly degraded samples. As a result of degradation, the absorption capacity of glycols can also be reduced. This can result in a decline in the performance of the dehydration unit, as well as fouling and corrosion in the pipe system due to the formation of hydrates. There is little information available regarding the reaction and products of glycol degradation. Oxidative degradation, also known as thermal oxidative degradation, is when glycol breaks down into other compounds at high temperatures in the presence of either oxygen or oxidizing agents. Glycols can also degrade at high temperatures in the absence of oxygen. The degradation rate and products are different in this case compared to oxidative degradation [16].

2.5.1 Oxidative Degradation

While there are very few studies explaining the reaction mechanism, some studies have been done on different glycols. MEG is the simplest glycol, which is reported to break down into organic acids like formic acid, oxalic acid, acetic acid, and glycolic acid when kept heated at 100 °C for up to 12 weeks. [17]. Figure 2.9 shows the proposed oxidation pathway by which different organic acids are formed from MEG. The amount of acidic components formed depends on how long MEG is exposed to heat, as well as the temperature itself. These products are expected to form due to the oxidation of alcohol groups present in MEG. Additionally, the formation of CO_2 has also been reported.

In glycols like DEG and TREG, formation of MEG and other smaller glycols is also reported to occur, along with other compounds. DEG is reported to break down into formic acid, along with MEG, formaldehyde, diethylene glycol formate, water, and 1,3-dioxyolane [16].

Degradation of TEG is known to occur through oxidation reaction of the ether groups to form peroxide radicals, which then break down into smaller compounds, such as smaller glycols like MEG, DEG, ethers, esters, organic acids, and aldehydes. This happens at temperatures reportedly as low as 70 °C, and degradation increases with increasing temperature. However, the formation of acids increases only marginally beyond 100 °C, whereas the formation of other products like DEG, MEG, and aldehydes keeps increasing with temperature up to at least 150 °C. Formation of all of the degradation products does increase with an increase in the amount of oxygen present, reported from 1% to 24%. These degradation experiments on TEG were conducted for 2 weeks [16]. Formation of either MEG or DEG

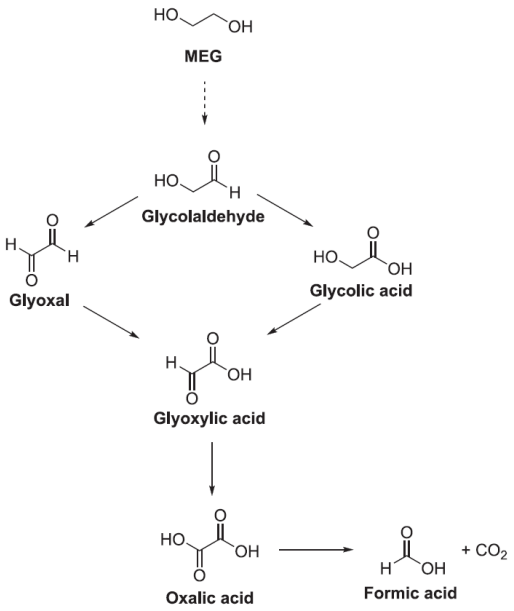

Figure 2.9: Proposed pathway for formation of acids from MEG via oxidation. [16]

depends on which side of the groups reacts. Once DEG is formed, it can get further oxidized to form MEG [18]. Figure 2.10 shows the pathway by which DEG is formed from TEG, and figure 2.11 shows the formation of MEG from either TEG or DEG.

The formation of organic acids happens due to the degradation of MEG, which can be considered as secondary degradation products. In addition, CO_2 is also formed along with some other carbon-containing gaseous products that have not been identified so far. A possibility of polymerization of glycols and formation of longer glycols like tetraethylene glycol and pentaethylene glycol is also speculated [16].

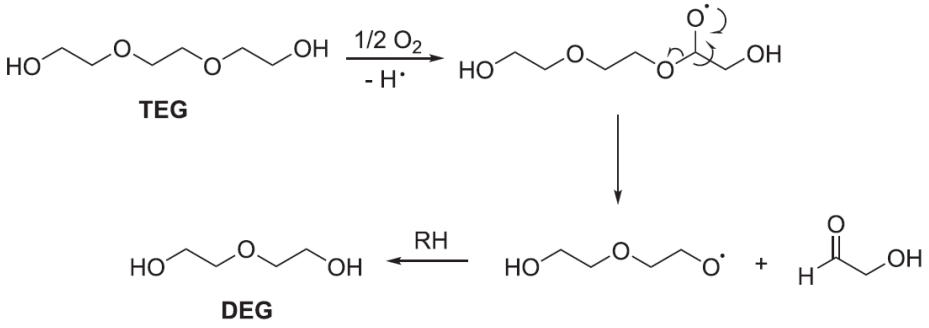

Figure 2.10: Proposed pathway for formation of DEG from TEG. [16]

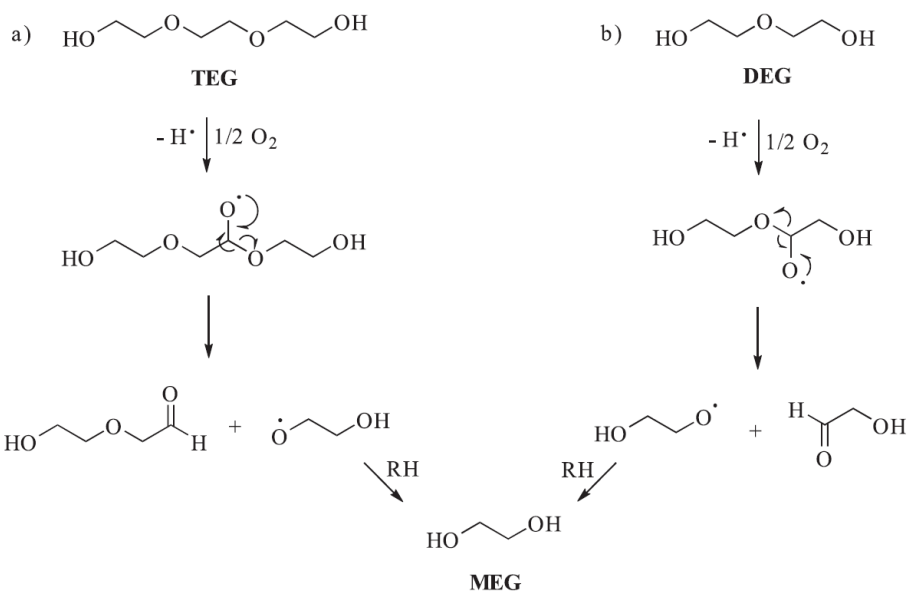

Figure 2.11: Proposed pathway for formation of acids from MEG via oxidation. [16]

2.5.2 Thermal Degradation

Glycols are also known to decompose in the absence of oxygen when exposed to high temperatures. Although little is known regarding the chemical process, it has been seen that a change in colour is associated with degradation without oxygen, just like in the presence of oxygen. The glycol goes from colourless to a shade of light yellow, dark yellow, or even dark brown. TEG is known to break down into MEG and DEG, via a radical splitting mechanism [19] as shown in figure 2.12. However, the formation of MEG is reported to occur only when water is added to a TEG sample, whereas DEG is known to form regardless. Organic acids are not reported in either case. The degradation rate is also reported to be much slower as compared to oxidative degradation and can take up to 7-8 weeks to get around 10% loss of TEG, at 220 °C [20]. Finally, some gaseous products are suspected to be formed but have not been analysed so far. Unfortunately, that is the extent of the literature available on the degradation of TEG in the absence of oxygen.

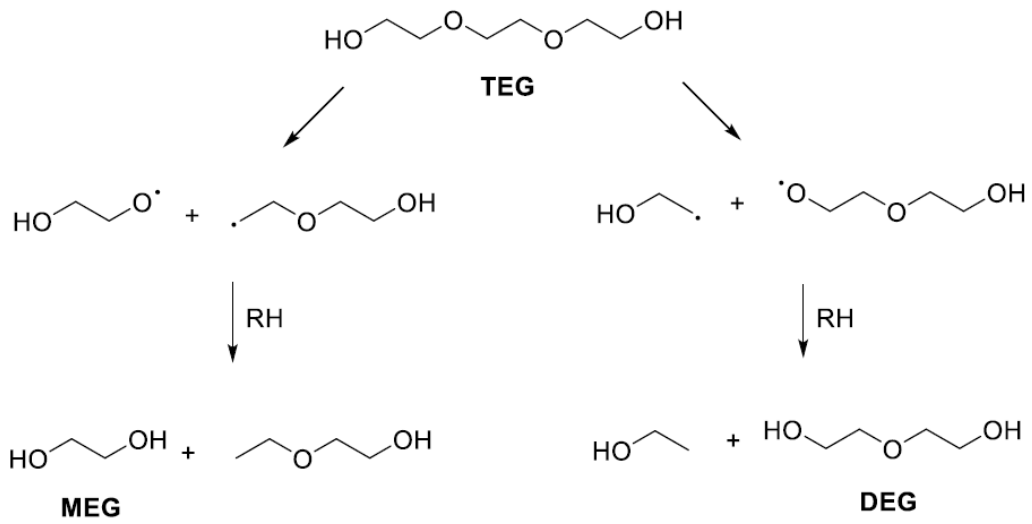

Figure 2.12: Proposed radical fragmentation of TEG during thermal degradation [20]

2.6 Analytical tools to monitor degradation

Degradation of glycols can be monitored by either quantifying the loss of glycol or by measuring the degradation products. This requires the selection of appropriate analytical methods. The most basic indicator of degradation in glycols is colour. Pure glycols are typically colourless. As they become more degraded, the colour turns into yellow or yellowish brown. Highly degraded samples are often opaque, dark brown, or even black. This has been studied on MEG [21]. In some studies on oxidative degradation of MEG, ion chromatography has been used to measure organic acids [17] [22]. Measuring the pH of the glycol solution to monitor degradation has been proposed as a method due to the formation of organic acids. This has been tested for oxidative degradation of MEG and DEG [23], however, no correlation has been established with degradation. High-performance liquid chromatography coupled with UV detection (HPLC-UV) and heat-stable salt analysis have also been used to monitor organic acids formed during oxidative degradation of TEG [16].

In addition to quantifying acidic components, measuring the formation of smaller glycols like MEG and DEG is important in the case of thermal degradation of TEG, especially in the absence of oxygen, where organic acids are not known to form [20]. For this case, gas chromatography coupled with flame ionization detection (GC-FID) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy has been shown to work [20].

Chapter 3

Analytical Methods

3.1 Gas chromatography coupled with flame ionization detection (GC-FID)

In gas chromatography, the analyte is transported in a gaseous state through the column by a gaseous mobile phase, known as the carrier gas. A volatile liquid or gaseous sample is injected into a heated port through a silicone rubber septum, where it rapidly evaporates because the injection block is maintained at a high temperature (injection temperature), as shown in the Figure 3.1.

The vapor is moved through the column by the carrier gas (H_2, He, or N_2). Analytes are separated and eluted at different times because they differ in volatility and how strongly they interact with the stationary phase inside the column. Each compound retention time (the time it takes to travel through the column and reach the detector) is unique under a given set of conditions, allowing them to be individually detected and quantified by the FID.

The analytes then flow through the detector, and the signal is displayed on the computer. The temperature of the detector is higher than that of the column to keep the analytes in the gaseous state. Moreover, the column must be hot enough to provide sufficient vapour pressure for the elution of the analytes in a reasonable time [24].

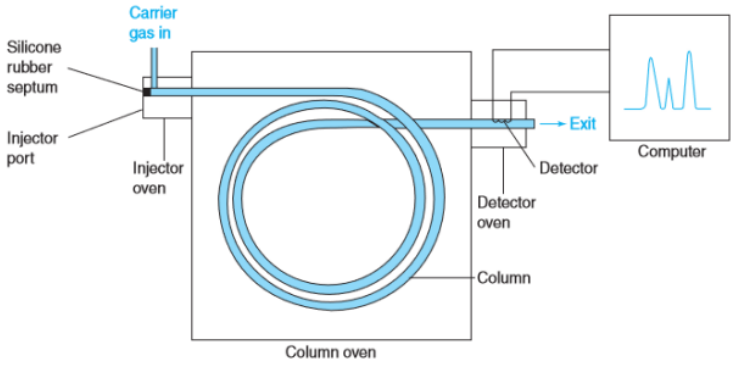

Figure 3.1: Schematic representation of a gas chromatograph. [24]

The flame ionization detector (FID) is widely used in gas chromatography for identifying and quantifying organic compounds, as shown in the Figure 3.2. After a sample is separated in the gas chromatographic column, the eluate enters the FID, where it is burned after being mixed with hydrogen and air. Organic compounds in the eluate are ionized in the flame, producing charged ions and electrons. These ions are collected by an electrode, generating an electrical current that is directly proportional to the amount of carbon in the sample. That flow of current generates the signal used to quantify the components of the mixture being analyzed.[24]

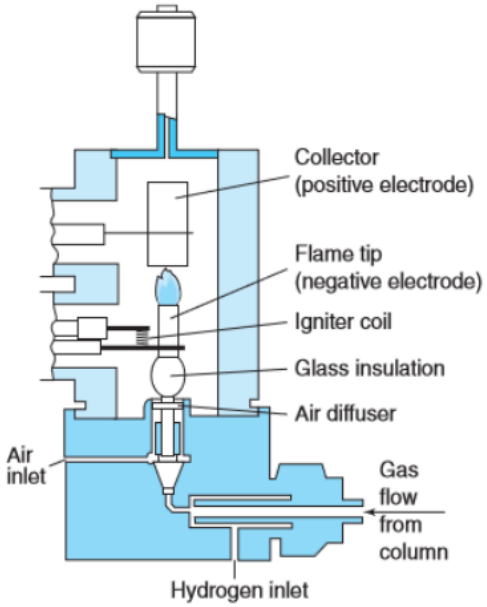

Figure 3.2: Flame ionization detector. [24]

3.2 Gas chromatography mass spectrometry (GC-MS)

Gas Chromatography is an analytical technique used to separate volatile components within a mixture. In a typical GC setup, as shown in the Figure 3.3, a small quantity of a sample is injected into a heated inlet where it is vaporized. An inert carrier gas (H_2, He, or N_2) transports the vaporized sample through a capillary column coated with a stationary phase. As the mixture travels through the column, each component interacts differently with the stationary phase depending on its chemical properties, such as boiling point and polarity. These interactions cause the compounds to elute (exit the column) at different times, known as retention times, allowing the mixture to be separated into its individual components.

Once the individual compounds have been separated in the gas chromatograph, they enter the mass spectrometer, where they are hit with a beam of high-energy electrons. This causes the molecules to break apart into smaller pieces, or fragments. These fragments are ionized, meaning they carry a charge, and the instrument measures their mass-to-charge ratio (m/z). Since most fragments carry a single positive charge, this ratio often corresponds directly to their actual molecular weight.

These ions then reach the detector, which turns their signal into an electrical output. One of the most common types of detectors is the electron multiplier,

which boosts the signal enough for even tiny amounts of substances to be detected. The data collected by the detector is typically displayed as a mass spectrum, where each peak corresponds to a specific ion. The position of the peak along the x-axis indicates the m/z value, while the height (or area) of the peak reflects the relative abundance of that ion [25].

In general, GC separates complex mixtures into individual components based on their physical and chemical properties, while MS provides detailed molecular and structural information about each component. Together, they enable both qualitative (identification) and quantitative (concentration) analysis of compounds.

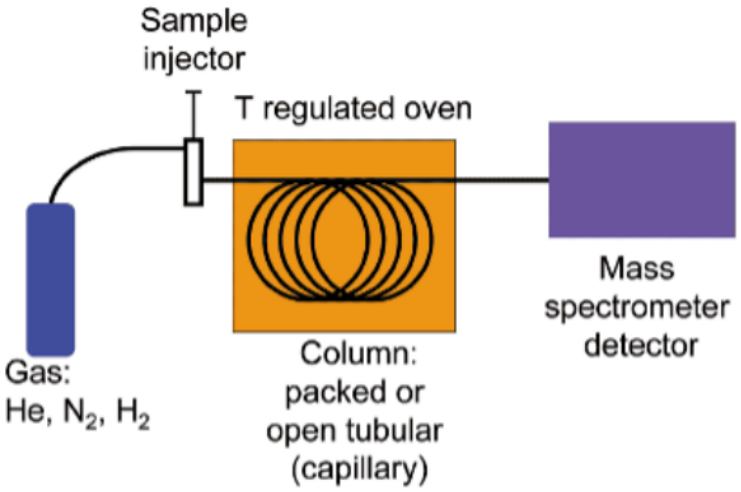

Figure 3.3: Schematic representation of a GC-MS. [26]

3.3 Raman spectroscopy

Raman spectroscopy operates on the basic principles of spectroscopy; it uses light to detect different molecular species within a tested sample. It is based on the inelastic scattering of light when a monochromatic laser beam interacts with a sample. When a photon strikes a molecule, it can excite the molecule into a higher vibrational energy state. As the molecule relaxes and re-emits the photon, the wavelength of the scattered light changes. This shift in wavelength corresponds to the energy difference between specific vibrational modes of the molecule.

Each peak in the resulting Raman spectrum represents a unique vibrational mode, typically associated with certain chemical bonds or functional groups. The position of each peak reflects the vibrational energy, while the intensity of the peak indicates the amount of scattering occurring at that mode, which can be correlated to the concentration of the corresponding molecular species. [27].

3.4 Fourier-transform infrared spectroscopy (FTIR)

In a Fourier transform spectrometer, the sample is usually placed between the interferometer and the detector as shown in the Figure3.4. The beam splitter sends the light in two directions at right angles, and then the two beams recombine to create the interferogram. Then, the sample absorbs the wavelengths characteristic to its spectrum, and the specific wavelengths are subtracted from the interferogram. The sampling interval for the interferogram is controlled by passing a monochromatic visible laser beam through the interferometer along with the polychromatic infrared light [24].

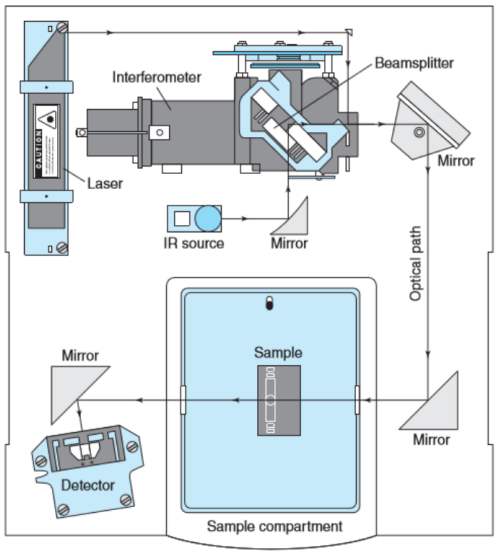

Figure 3.4: Schematic representation of a FTIR spectrometer. [24]

3.5 Karl Fischer Titration

Karl Fischer titration is a widely used analytical technique for accurately determining the water content in various substances, especially organic solvents, as shown in the Figure3.5. The method can measure both dissolved and suspended water with high accuracy in a broad concentration range, from 100% down to 0.01% [28].

The method is based on the chemical reaction of water with iodine and sulfur dioxide in the presence of a base, typically in a methanolic solution [29]. The key components used in the titration include a titrant, solvent, and water standard. Additionally, a standard solution is used regularly to determine the titer (the exact amount of titrant needed to react with a known amount of water), ensuring accuracy over time.

Figure 3.5: Schematic representation of Karl Fischer titration equipment.[30]

Chapter 4

Problem Formulation and Project Delineation

The thermal breakdown of TEG not only reduces its dehydration capacity but also leads to the accumulation of acidic and polymeric compounds, causing corrosion, scaling, and fouling within the gas dehydration system. These issues result in increased operational costs, unplanned maintenance, and higher environmental risks due to the disposal of spent glycol. Additionally, thermal degradation can lead to the formation of volatile organic compounds (VOCs), which pose further environmental and regulatory challenges. Understanding the degradation process is therefore critical to minimizing VOC emissions and ensuring compliance with environmental standards.

Degraded TEG and its by-products can significantly impact the performance of gas dehydration units by fouling heat exchangers, reducing heat transfer efficiency, and necessitating frequent system shutdowns for cleaning. Corrosive degradation products may damage key equipment such as pumps, reboilers, and pipeline infrastructure, ultimately leading to equipment failure and higher repair costs. Moreover, the presence of flammable and toxic degradation products also introduces significant safety risks, especially in high-pressure natural gas processing environments.

While previous studies have identified some degradation products, critical knowledge gaps remain in understanding the complete reaction mechanisms, product formation under varying thermal conditions, and the role of oxygen and moisture in accelerating the degradation process. Comprehensive characterization of these products often requires the use of multiple, advanced analytical techniques, as no single method can provide a complete picture.

A detailed investigation into TEG thermal degradation is essential to address these questions. This includes analysing degradation behaviour at elevated temperatures, identifying by-products, quantifying their formation, and evaluating

how different key variables such as temperature, moisture content, and exposure time influence these outcomes. Insights gained from such a study can directly contribute to improving operational practices, such as:

- Optimized regenerator temperature control and improved re-boiler design to extend the lifespan of TEG.
- Development of chemical inhibitors or stabilizers to reduce by-product formation.
- Improved selection of materials for corrosion resistance.
- Reduced operational cost, lower maintenance frequency, and reduced TEG consumption.
- Enhanced compliance with environmental and safety standards in natural gas processing.

This study aims to address these challenges by investigating the thermal degradation of TEG under oxygen-free conditions. To achieve this, TEG is exposed to temperatures close to those of operating conditions in a regenerator column at a TEG dehydration unit. The additional effect of water on degradation will also be tested. To characterize the degradation products, analytical tools, including Gas Chromatography with Flame Ionization Detection (GC-FID), Gas Chromatography-Mass Spectrometry (GC-MS), and Raman spectroscopy, will be employed.

Ultimately, an in-depth understanding of TEG thermal degradation is key to optimizing costs, ensuring operational safety, and enhancing the sustainability of gas processing operations.

Chapter 5

Materials and Experimental Methods

5.1 Chemicals

The chemicals that were used for this work, including the ones used for analytical measurements, are reported in the Table 5.1. All solutions were prepared volumetrically. All chemicals were purchased from Sigma-Aldrich (SIAL) and VWR Chemicals. The chemicals noted with (IS) were used as internal standards for gas chromatography.

Table 5.1: Overview of chemicals used in this work.

Chemical Name (Abbreviation)	Supplier	CAS Number	Purity (%)
Triethylene glycol (TEG)	SIAL	112-27-6	$\geq$99
Diethylene glycol (DEG)	SIAL	111-46-6	$\geq$99
Monoethylene glycol (MEG)	VWR	107-21-1	$\geq$99
Methanol (MeOH)	VWR	67-56-1	$\geq$99
1-Propanol (IS)	VWR	71-23-8	$\geq$99
*BSTFA + TMCS (IS)	SIAL	25561-30-2	$\geq$ 98.5 (excluding TMCS)

*Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane

The physical and chemical properties of the components that were used in this project for the thermal degradation experiments are reported in Table 5.2. All information was taken from the manufacturer's specification sheet [31],[32],[33].

Table 5.2: Physical and chemical properties for TEG, DEG, and MEG.

Property	Unit / Description	TEG	DEG	MEG
Product number	–	8.08245	32160	24041
Physical state	–	Liquid	Liquid	Liquid
Color	–	Colorless	Colorless	Colorless
Boiling point	°C	286.5	245	198
Density	g/L	1130 at 15 °C	1116 at 20 °C	1115 at 20 °C
Molecular weight	g/mol	150.17	106.12	62.07
Water (Karl Fischer)	%	≤ 0.30	≤ 0.10	≤ 0.10
Flash point	°C	166	138	116
Autoignition temperature	°C	347	372	410

5.2 Thermally Degradation Experiments of TEG

To investigate the thermal degradation behavior of triethylene glycol (TEG) and understand the key- factors influencing its breakdown into diethylene glycol (DEG) and monoethylene glycol (MEG), two separate experimental campaigns were conducted.

The first campaign focused on studying how TEG degrades into DEG and MEG at different temperatures. The goal was to evaluate how temperature alone influences the rate of degradation. The second campaign focused on investigating the effect of water as an impurity at a specific temperature to understand how the presence of water affects the degradation of TEG into DEG and MEG under controlled thermal conditions.

Both sets of experiments were conducted under oxygen-free environments to eliminate the possibility of oxidative reactions. The following section provides detailed information on each experimental campaign.

5.2.1 Experimental Campaign 1

Thermal degradation experiments were conducted at three different temperature conditions, 180 °C, 200 °C, and 220°C, using high-pressure glass tubes with an outer diameter of 2.5 cm and a capacity of 25 mL, sealed with PTFE end plugs. For each temperature condition, three tubes were separately prepared by adding 15 mL of triethylene glycol (approximately 17 grams by weight) per tube, making a total of nine tubes.

Before adding TEG, the tubes were purged with nitrogen to eliminate oxygen and prevent oxidative reactions, ensuring the experiments were performed under oxygen-free conditions. After adding TEG, the tubes were purged again with nitrogen, sealed, and placed in the ovens at the designated temperatures of 180 °C, 200 °C, and 220°C for a duration of five weeks. Every week, the tubes were removed

from each oven, and small drops were extracted from each tube using precision pipettes for analysis. After sampling, the tubes were again purged with nitrogen, resealed, and placed back in the ovens.

In addition, each tube was weighed before and after the experiment to monitor any mass loss over time. This sampling and monitoring process was repeated weekly for five weeks. A schematic representation of the experimental procedure is provided in the Figure 5.1 for clearer visualization. The details of experimental campaign 1 for TEG are provided in the Table 5.3.

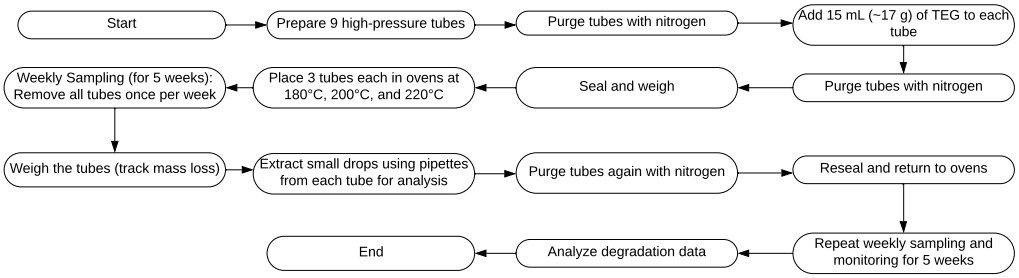

Figure 5.1: Flowchart illustrating the experimental procedure for Campaign 1.

Sample Description	Temp (°C)	Volume(mL)	# of Weeks	Total Tubes
TEG	180	15	5	3
TEG	200	15	5	3
TEG	220	15	5	3

Table 5.3: Summary of Experimental Campaign 1

5.2.2 Experimental Campaign 2

To investigate the effect of water on the thermal degradation of triethylene glycol (TEG), a controlled experiment was conducted at a constant temperature of 200 °C. High-pressure glass tubes with a capacity of 15 mL were used, each filled with 10 mL of a TEG-based solution prepared using demineralized water.

Two sets of solutions were prepared, one containing 5 wt% water in TEG and the other containing 15 wt% water in TEG. Before the addition of the TEG-based solutions, the tubes were purged with nitrogen to eliminate oxygen and prevent oxidative degradation, ensuring that all experiments were conducted in the absence of oxygen. After the solutions were added, the tubes were purged again with nitrogen, then sealed and placed in an oven at 200 °C for a total duration of five weeks.

To maintain the actual water contents in the tubes throughout the experiment, each sample was stored in a separate, individually sealed tube that was opened only at the time of analysis. Once a tube was opened for sampling, it was not reused to prevent changes in water content throughout the experimental period. To ensure accuracy and reproducibility, two tubes were taken out from the oven for each water concentration at every weekly interval. The remaining tubes were left in the oven until their scheduled sampling for subsequent weeks (weeks 2, 3, 4, and 5).

Samples were extracted using precision pipettes, and each tube was weighed before and after the experiment to monitor any mass loss. This sampling and monitoring process was repeated weekly over a period of five weeks, enabling a systematic evaluation of TEG degradation at both 5 wt% and 15 wt% water concentrations. A schematic representation of the experimental procedure is provided in the Figure 5.2 for clearer visualization. The details of experimental campaign 2 for both concentrations are provided in the Table 5.4.

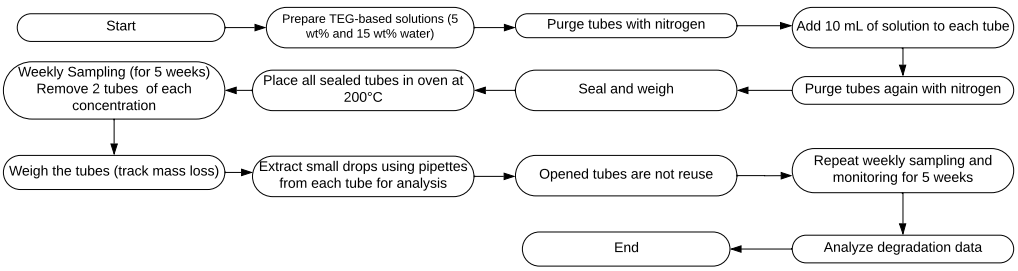

Figure 5.2: Flowchart illustrating the experimental procedure for Campaign 2.

Sample Description	Temp (°C)	Tubes per Week	# of Weeks	Total Tubes
TEG + 5 wt% water (10mL)	200	2	5	10
TEG + 15 wt% water (10mL)	200	2	5	10

Table 5.4: Summary of Experimental Campaign 2

5.3 Experimental Analysis of Thermally Degraded TEG

This section explains how thermally degraded trimethylene glycol (TEG) samples were analyzed in the lab. Each technique required its own set of preparation steps, careful calibration, and specific procedures to ensure accurate and consistent results.

5.3.1 Gas chromatography coupled with flame ionization detection (GC-FID)

GC-FID was the analytical tool used for both quantification and qualification of TEG and its degradation products, particularly low molecular weight glycols such as monoethylene glycol (MEG) and diethylene glycol (DEG). In order to smooth the potential error of the gas chromatography measurements, every sample of unknown concentration was analyzed in triplicate, and the average value was taken.

The GC was separately calibrated for each of the two concentrations for high molecular weight glycol triethylene glycol (TEG) from 0.5 to 10 g/L and for low molecular weight glycols such as monoethylene glycol (MEG) and diethylene glycol (DEG) from 0.005 to 0.1 g/L. In this regard, Nicolai Kruse Nielsen, laboratory technician, provided invaluable assistance with the calibration of the GC-FID for the quantification of MEG, DEG, and TEG, as well as with the preparation of standard solutions for GC-FID analysis.

The calibration of the gas chromatograph refers to a procedure that is performed prior to the quantitation of samples with unknown concentrations. That typically includes measurement of samples with a known concentration and using the GC response of those in order to compare to the response of the samples to be analyzed. The samples with the known analyte concentrations are the standard solutions and that is how they will be referred to from here onwards. Details about the preparation of the standard solutions are available in Appendix A.

The accuracy of the calibration largely depends on how precisely the standard solutions are prepared and how consistently the measurement conditions are maintained. To ensure this, high-precision volumetric flasks (Class A) with an accuracy ranging from ±0.01 mL to ±0.1 mL, depending on the flask size (100 mL to 200 mL) were used. For smaller volumes, precision pipettes were used specifically, the Gilson Microman M100 (10–100 μL) and M1000 (100–1000 μL) equipped with positive displacement tips to accurately handle small liquid samples used in this project.

To prepare the samples, 45 μL of degraded TEG was put into a 10 mL tube and mixed with 5 mL of internal standard solution. After shaking the vial, 1 ml was put in a standard screw-thread autosampler vial and was ready for injection.

A PerkinElmer Clarus 690 gas chromatograph equipped with an FID detector was used to analyze the samples. The samples were injected through a split injector maintained at 200 °C. Separation was performed on an Elite-BAC-1 Advantage capillary column (30 m length, 0.32 mm inner diameter, Cat. nr. N9315071). The temperature program of the oven was set as follows:

- Initial temperature: 100 °C, hold for 0 minutes
- Ramp rate: 25 °C/min up to 200 °C

- Final temperature: 200 °C, hold for 3 minutes

A split ratio of 75 was used, and the carrier gas flow rate was maintained at 1.2 mL/min. To ensure accurate quantification, glycol concentrations were kept below 10 g/L by diluting samples in methanol before analysis. This prevents detector saturation and maintains measurements within the detector's linear response range, where the signal is directly proportional to concentration.

Calibration curves were prepared using standard solutions of known concentrations of (MEG, DEG, and TEG), and the results were validated based on calibration curves and reproducibility across replicate runs. A calibration curve for high molecular weight glycol triethylene glycol (TEG) and low molecular weight glycols such as monoethylene glycol (MEG) and diethylene glycol (DEG) was made as shown in the Figure 5.4,5.5, 5.6 respectively.

The x-axis represents the ratio between the analyte concentration and the IS concentration. In contrast, the y-axis represents the ratio between the peak area of the analyte and the IS. Each level of the line represents triplicate injections of the standard solutions. Linearity is displayed by the value of the coefficient of determination R^2, the closer it is to 1, the higher the linearity.

Retention times, the linear calibration range and R^2 values for TEG, DEG and MEG is given in the Table 5.5.An example of a GC-FID result is reported in the Figure5.3, in which the response in form of peaks is shown for glycols as the analyte and 1-Propanol as the IS.

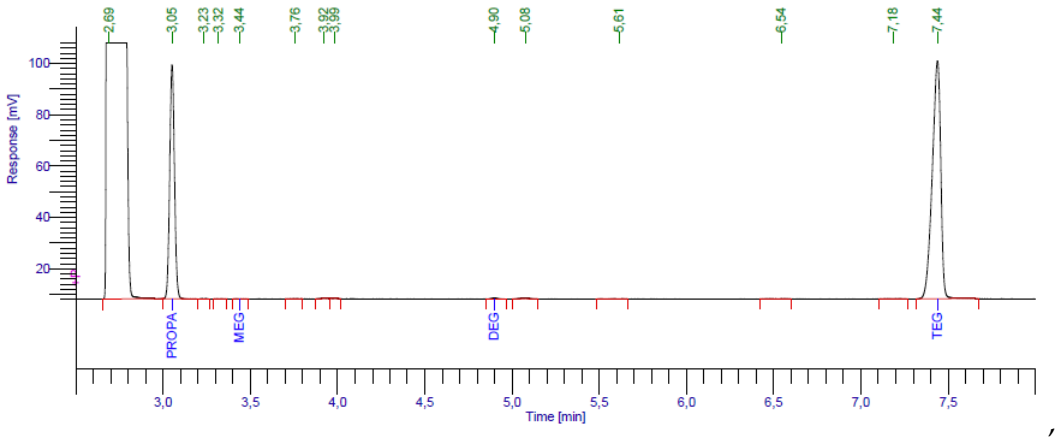

Figure 5.3: Gas chromatograph response example

Chemical	Retention Time [min]	Linear Calibration Range [g/L]	R^2	IS Conc.[g/L]
TEG	7.438	0.5–10	0.9954	2.5
DEG	4.894	0.005–0.1	0.9937	0.025
MEG	3.438	0.005–0.1	0.9933	0.025

Table 5.5: Retention time, linear calibration range, and R^2 values for TEG, DEG, and MEG analyzed by GC-FID.

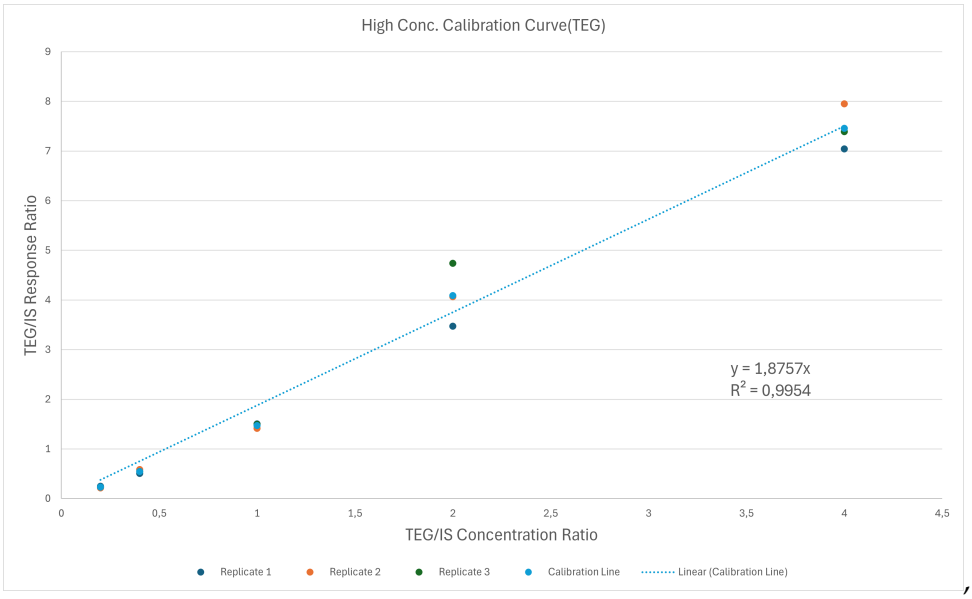

Figure 5.4: High concentration calibration curve (TEG)

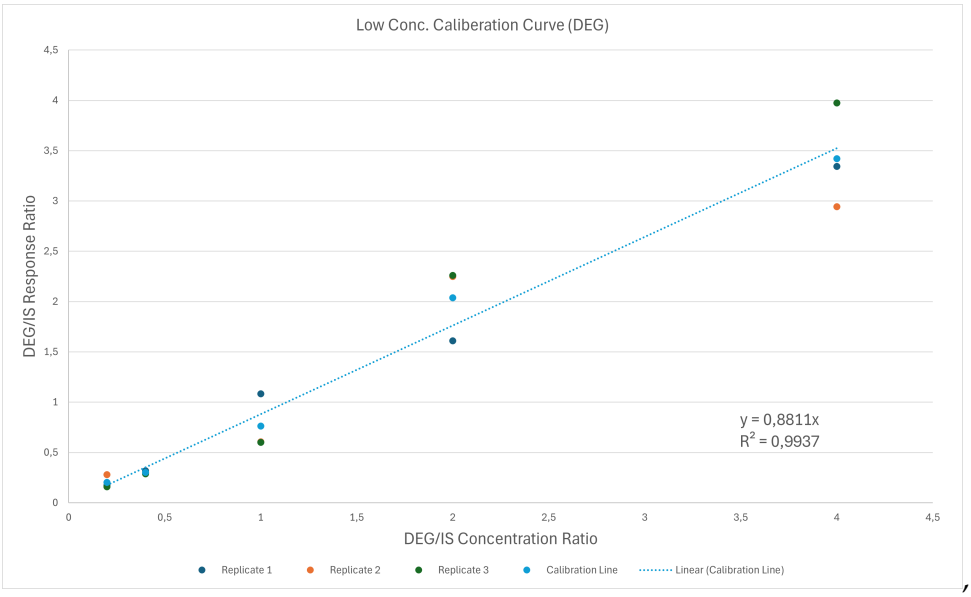

Figure 5.5: Low concentration calibration curve (DEG)

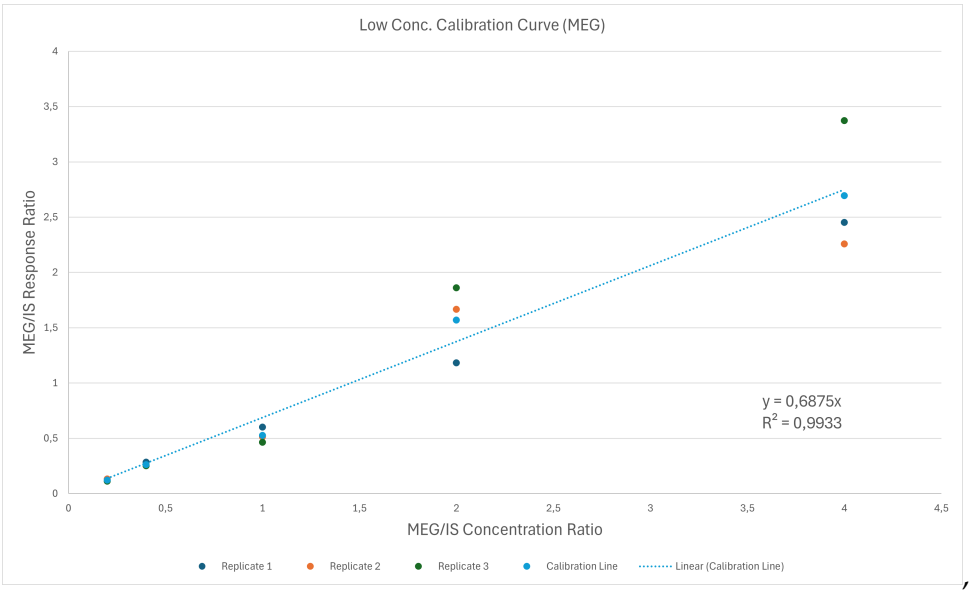

Figure 5.6: Low concentration calibration curve (MEG)

5.3.2 Gas chromatography mass spectrometry (GC-MS)

GC-MS was used as a qualitative method to confirm the presence of TEG and associated degraded by-products (MEG and DEG). While GC-MS provides high specificity through mass spectral analysis, it was not used for quantification in

our case. The column in the GC connected to the MS detector at our lab is apolar and is suitable for a broader range of chemicals. This required an additional derivatization step before samples could be run in the GC-MS, as discussed below. This additional step, along with the properties of the GC column, added a layer of uncertainty and error in the results. For this reason, GC-MS was not used for quantification. Instead, it played a supportive role in confirming the presence of expected molecular fragments in the degraded samples.

Standard solutions in small amounts (1mL) of pure TEG, DEG, and MEG (not dissolved in any solvent) were taken for GC-MS analysis(served as a reference) and can be seen in the Figure 5.7. In a chromatogram, the x-axis shows the retention time, which tells us how long each chemical compound takes to come out of the column. Each compound has its own unique retention time can be found in the Table 5.6, so we can use this as a reference to identify degraded glycols. The y-axis shows the signal strength from the detector. The higher the peak, the more of that compound is present in the sample.

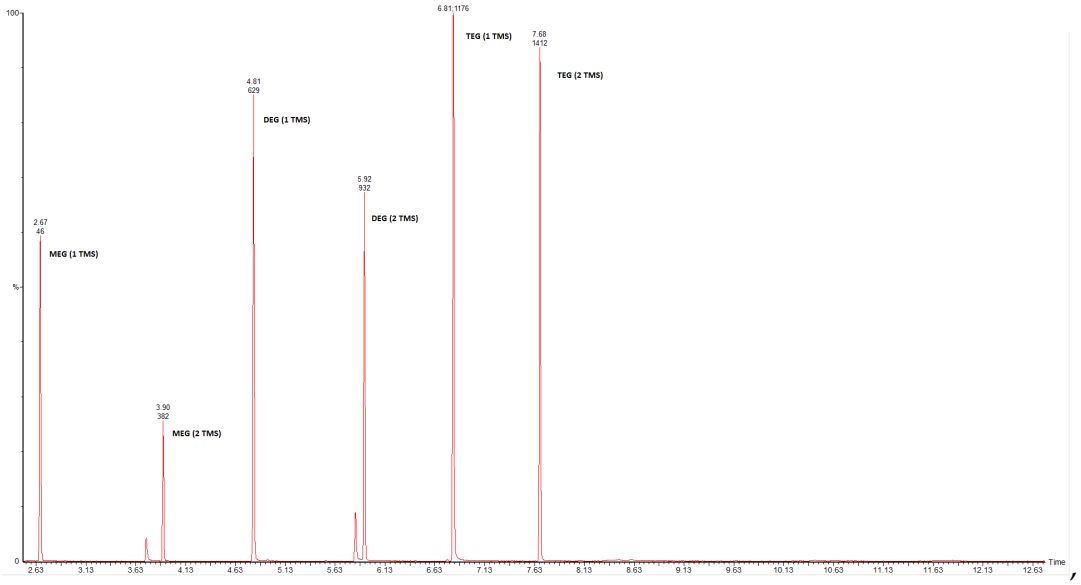

Figure 5.7: GC-MS chromatogram showing references of TMS-derivatized monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) with their retention times.

Chemical	TMS Form	Retention Time [min]	Derivatization
MEG	1-TMS	2.67	1 OH group
MEG	2-TMS	3.90	Both OH groups
DEG	1-TMS	4.81	1 OH group
DEG	2-TMS	5.92	Both OH groups
TEG	1-TMS	6.81	1 OH group
TEG	2-TMS	7.68	Both OH groups

Table 5.6: Retention times and descriptions of 1-TMS and 2-TMS derivatives of MEG, DEG, and TEG observed in GC analysis.

The standard solutions and thermally degraded TEG samples had to undergo a derivatization process to improve their affinity towards the GC column so that they separate well. For derivatization of each sample, 200 μL of BSTFA with 1% TMCS (Product#15238) was added. The tube was sealed and gently heated at 75 °C for 30 minutes. Once the reaction was complete, any leftover BSTFA was removed by slowly evaporating it under a stream of nitrogen gas. The sample was then redissolved in 1.5 ml of iso-octane and transferred around 1 mL of the sample into a clean vial, ready for GC-MS analysis.

In gas chromatography (GC), typically the goal of derivatization is to convert substances into more volatile and thermally stable compounds, making them suitable for the long and hot journey through a capillary column, which ensures good separation and more reliable results. MEG, DEG, and TEG each have two hydroxyl (–OH) groups. During derivatization for analysis, these OH groups are replaced with trimethylsilyl (TMS) groups to increase volatility.

A PerkinElmer Gas Chromatography(Clarus 580)-Mass Spectrometry(Clarus SQ 8 S) instrument was used to analyze the samples. The samples were injected through a split injector maintained at 200 °C. Separation was performed on an Elite-5 silica capillary column (30 m length, 0.25 mm inner diameter, Cat # N9316076). The temperature program of the oven was set as follows:

- Initial temperature: 65 °C, hold for 1 minute
- Ramp rate: 20 °C/min up to 200 °C
- Final temperature: 200 °C, hold for 5 minutes

A split ratio of 50 was used, and the carrier gas flow rate was maintained at 50 mL/min.

5.3.3 Raman spectroscopy

Raman spectroscopy was explored to confirm the presence of TEG and associated degraded by-products (MEG and DEG). For a clear and accurate quantitative anal-

ysis of the concentration of each species present, it is essential to use standard solutions with known concentrations. By analyzing the Raman spectra of these standards, the characteristic Raman shifts of each species, such as TEG, DEG, and MEG can be identified. These shifts serve as reference points for detecting and measuring changes in concentration within actual degraded samples. The standard solutions prepared for this purpose, as suggested by Professor Sergey Kucheryavskiy, containing known concentrations of TEG, DEG, and MEG, are detailed in the Table 5.7.

The interpolation and interpretation of the Raman spectra, both for standard solutions and actual measurements were done by Professor Sergey Kucheryavskiy, using Generalised Least Squares (GLS) [34] on the data obtained from the spectra, and then using simple linear regression to match it with the reference values given in the Table 5.7. The outcome from this calibration can be seen in the Figure 5.8. It is clear that there is some variation in predicted values compared to their reference values, which gives us an idea of our lower limit of quantification.

An in-house Raman setup was used to collect spectra. The setup included a MarqMetrix All-In-One Raman system connected to a computer. It is a portable device with a probe attached by a cable to take measurements.

The system runs on MarqMetrix AIO software, which also provides a user interface. Through this interface, settings could be adjusted, like the laser power and brightness. The laser power was set to 200 mW, and the brightness was adjusted as needed to make sure the peaks in the spectrum were clear and easy to see. The results are shown on the screen as a graph, with peak intensity plotted against the Raman shift in $^{-1}$.

Mixture no.	TEG (mol%)	DEG (mol%)	MEG (mol%)
1	100	0	0
2	90	10	0
3	80	20	0
4	90	0	10
5	80	10	10
6	70	20	10
7	80	0	20
8	70	10	20
9	60	20	20

Table 5.7: Synthetic mixtures used for calibrating Raman spectroscopy

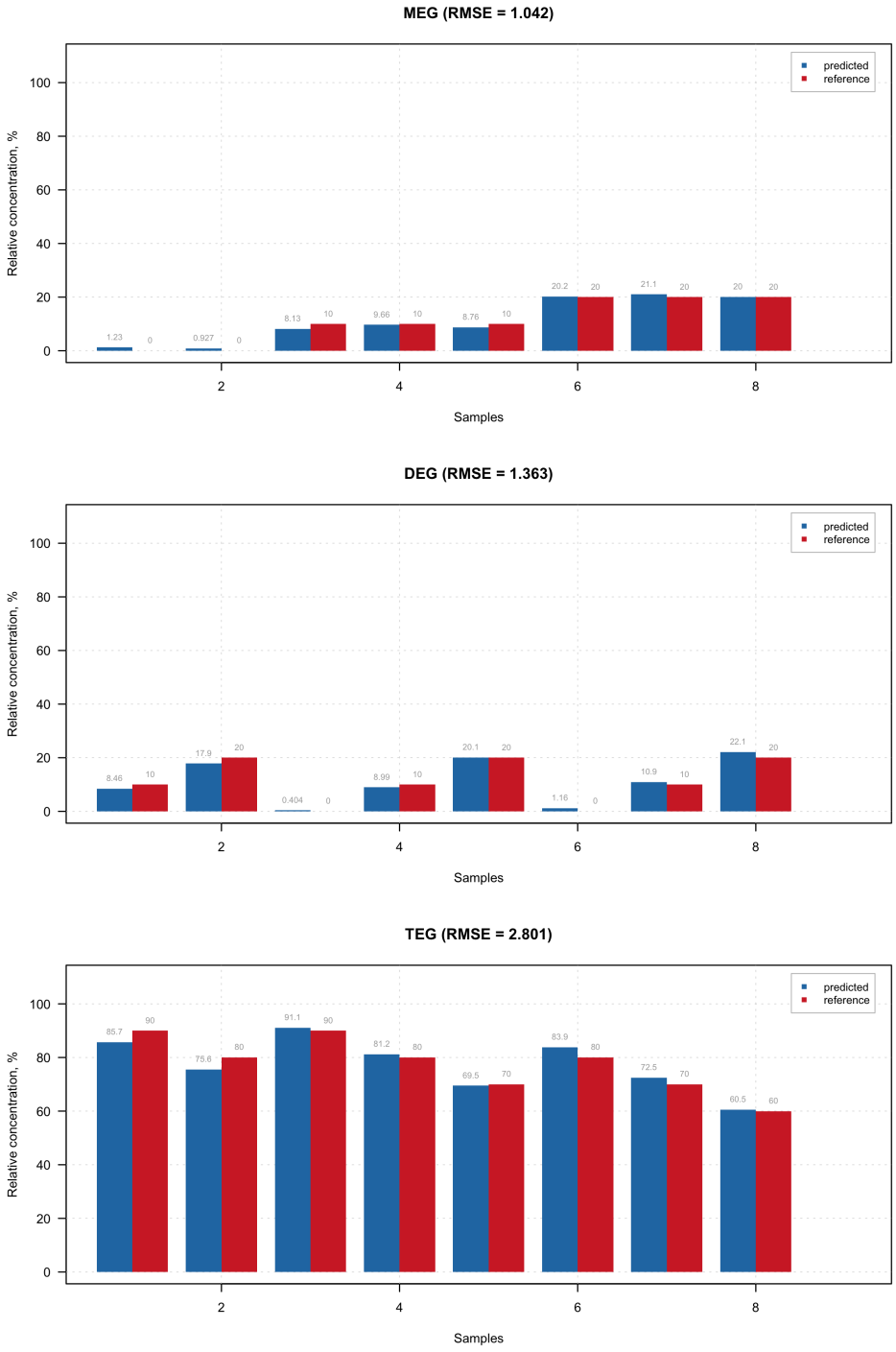

Figure 5.8: Predicted and reference values of glycols obtained from synthetic mixtures.

5.3.4 Karl Fischer Titration

Karl Fischer titration was used to accurately measure the water content in triethylene glycol (TEG) samples before and after thermal degradation.

Karl Fischer titration was performed using the 870 KF Titrino plus in combination with the 860 KF Thermoprep oven, employing the volumetric method. To evaluate the system, approximately 0.5 g of a 1% water standard, prepared in Karl Fischer solvent, was accurately weighed and sealed in a vial with a cap. The vial was then placed in the preheated Thermoprep oven. Once the system indicated that conditions were stable and ready (Conditions OK), the titration was initiated. During the titration process, a curve was generated in real time and upon completion, the result was automatically displayed on the instrument screen.

Chapter 6

Results and Discussions

6.1 Initial Observations

6.1.1 Colour

It is evident that glycol changes colour at high temperatures. However, this change is not necessarily indicative of degradation. In this study, the colour of some samples progressively darkened during the experiment shifting from yellow to dark yellow and eventually to a pronounced amber, as shown in the Figures 6.2, 6.3 and 6.4. In contrast, other samples showed minimal colour change under the same conditions. For comparison, the original colour of the TEG before the experiment can be seen in Figure 6.1.The colour change of thermally degraded TEG samples containing water contents can be seen in the Figures6.5, 6.6, 6.7, 6.8

Although colour change has been associated with degradation in glycol solutions, the thermally degraded TEG samples in this study displayed a dark yellow colour even with minimal degradation. This makes it difficult to determine the exact cause of the colour change.

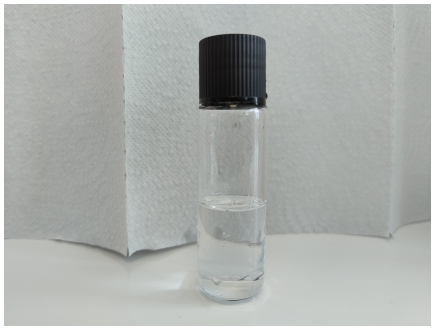

Figure 6.1: Initial colour of TEG before experiment

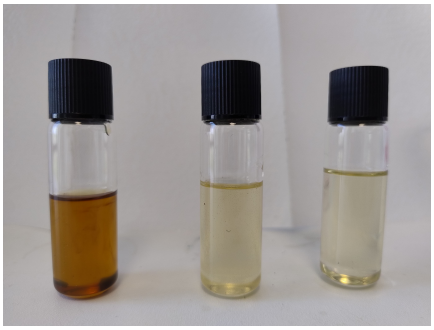

Figure 6.2: Thermally degraded TEG samples at 180 °C

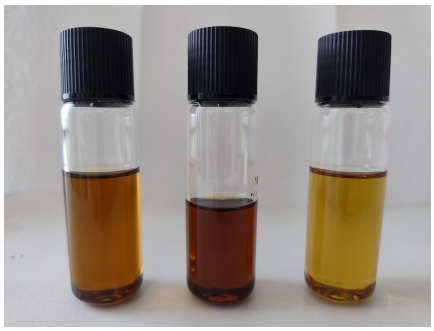

Figure 6.3: Thermally degraded TEG samples at 200 °C

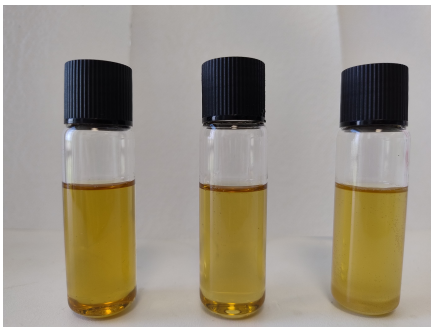

Figure 6.4: Thermally degraded TEG samples at 220 °C

Figure 6.5: Thermally degraded TEG samples A with 5 wt% water contents

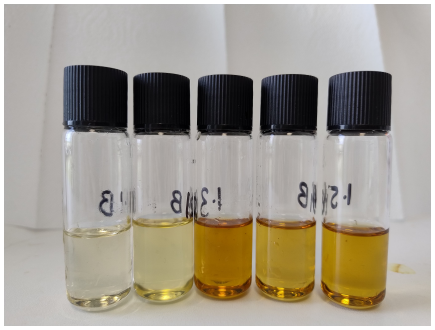

Figure 6.6: Thermally degraded TEG samples B with 5 wt% water contents

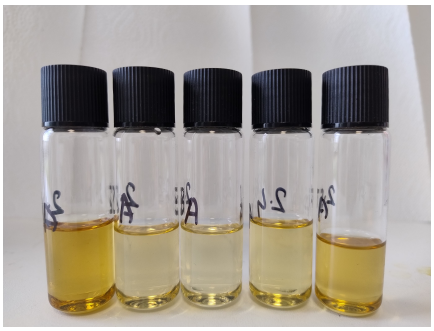

Figure 6.7: Thermally degraded TEG samples A with 15 wt% water contents

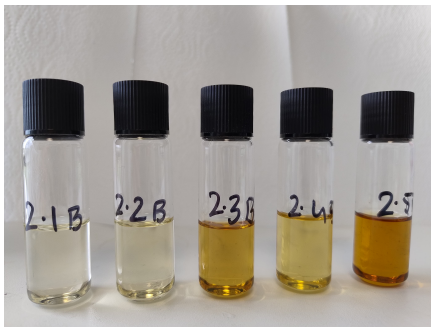

Figure 6.8: Thermally degraded TEG samples B with 15 wt% water contents

6.1.2 Odour

While preparing sample dilutions for analysis, a noticeable smell was detected from some degraded samples. It likely came from unknown compounds formed during the breakdown of TEG or may be associated with the acids. To investigate the presence of acidic components, FT-IR spectroscopy was employed, but no distinct peaks were detected. However, it was also suspected that the rubber from the tube caps may have started to degrade at the high temperatures used can be seen in the Figure 6.9, which could have added to the odour.

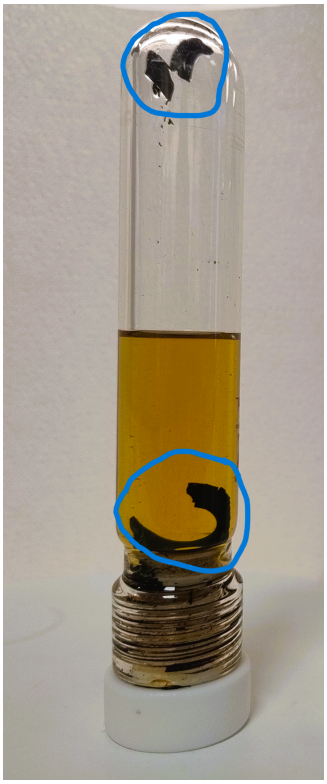

Figure 6.9: Detached rubber fragments of tube cap

6.2 GC-FID Results

This section presents the GC-FID results obtained from the two experimental campaigns conducted to evaluate the thermal degradation behavior of triethylene glycol (TEG) and the formation of its degradation products, monoethylene glycol (MEG) and diethylene glycol (DEG). The experiments were carried out over five weeks under oxygen-free conditions, with systematic sampling and analysis performed weekly. A summary of both experimental campaigns is provided in the Table 6.1 for quick reference.

Parameter	Campaign 1	Campaign 2
Objective	Study thermal degradation of TEG at different temperatures	Investigate the effect of water contents on TEG degradation
Temperature Conditions	180 °C, 200 °C, 220 °C	Constant at 200 °C
Water Content	0 wt%	5 wt% and 15 wt%
Atmosphere	Oxygen-free conditions	Oxygen-free conditions
Sampling Frequency	Weekly over 5 weeks	Weekly over 5 weeks

Table 6.1: Summary of Experimental Campaign 1 and 2

6.2.1 Effect of temperature on the formation of DEG and MEG, and degradation of TEG over time

When evaluating the influence of temperature on the formation of diethylene glycol (DEG) and monoethylene glycol (MEG) as well as the behavior of triethylene glycol (TEG) over a five-week period, clear trends were observed as shown in the Figures 6.10, 6.11 and 6.12 respectively.

DEG concentrations steadily increased over time at all three temperatures, with the effect of temperature being quite pronounced. By week 5, DEG concentration reached around 11.7 mg/g at 220 °C, compared to 8.8 mg/g at 200 °C and 5.9 mg/g at 180 °C. This trend clearly indicates that higher temperatures promote the formation of DEG. However, MEG follows a different trend. Its concentration peaked at 200 °C, reaching around 3.6 mg/g by week 5, while lower formation was observed at 180 °C (about 2.3 mg/g). Interestingly, MEG levels decreased at the highest temperature of 220 °C, ending at around 2.7 mg/g. This reduction may result due to vapourization, as MEG has a boiling point of 198 °C [33], leading to limited accumulation at higher temperatures.

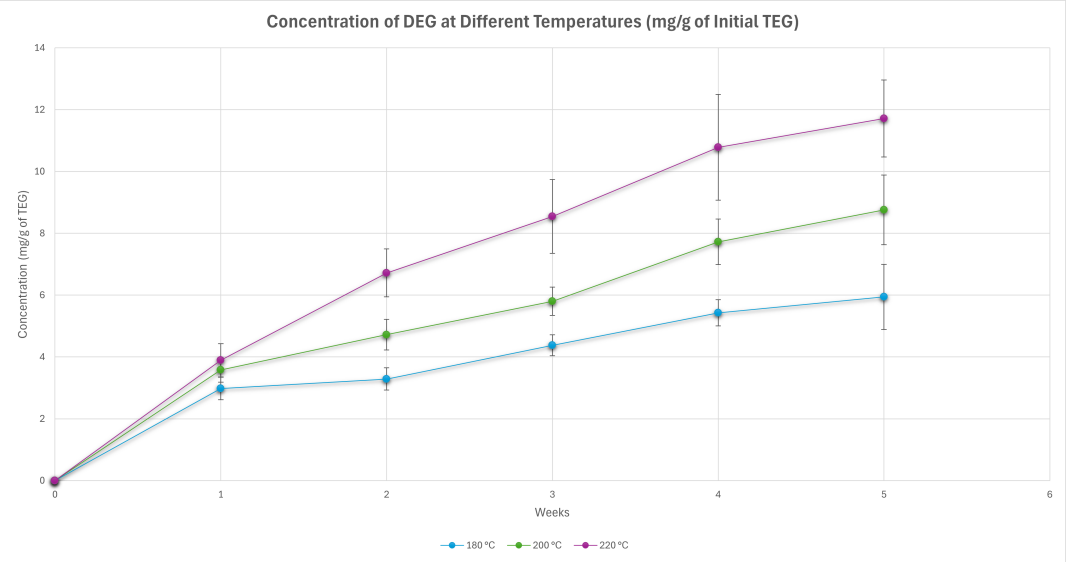

Figure 6.10: Formation of DEG in thermal degradation experiments of TEG at different temperatures.

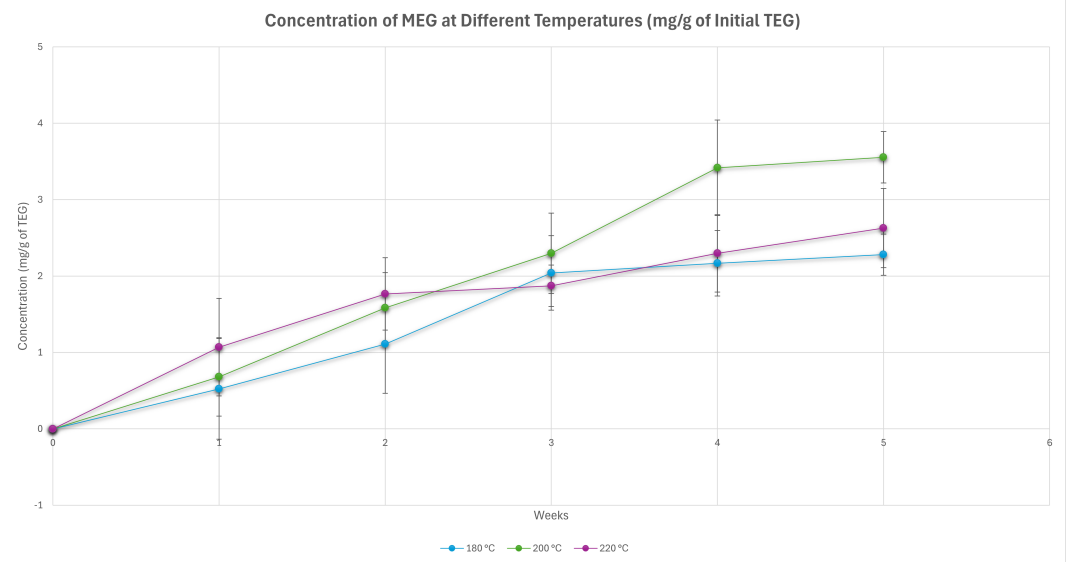

Figure 6.11: Formation of MEG in thermal degradation experiments of TEG at different temperatures.

In contrast, the relative amount of TEG over time remains nearly constant at 180 °C and 200 °C, with only minor variations observed by week 5, indicating minimal impact under these conditions. At 220 °C, a slight increase to around 104% was observed in the first week, possibly due to measurement variation, followed by a gradual decline to about 97% by week 5. This suggests that TEG remains

mostly unchanged at lower temperatures, but it may slowly decrease when exposed to higher temperatures for a longer time. Overall, higher temperatures promote DEG formation, MEG forms at moderate temperatures, and TEG shows only slight changes, mainly at the highest temperature.

The summarized trends in DEG and MEG formation, as well as the behaviour of TEG at different temperatures are presented in the Table 6.2 .

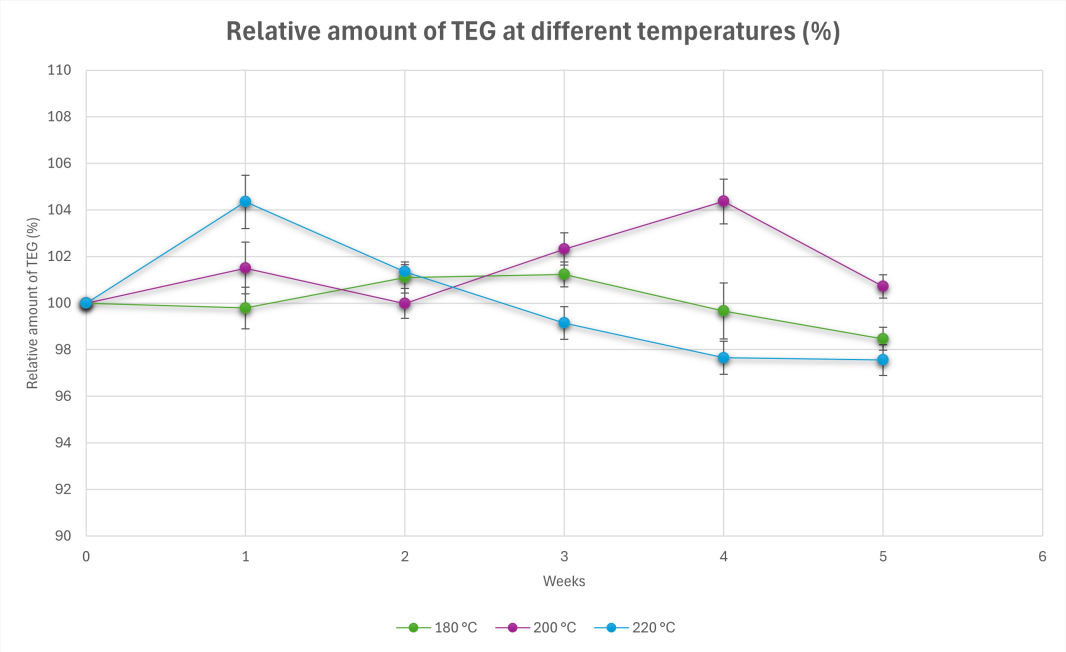

Figure 6.12: Thermal degradation of TEG at different temperatures.

Temperature	DEG (mg/g at Week 5)	MEG (mg/g at Week 5)	TEG (% at Week 5)
180 °C	∼5.9	∼2.3	(∼98%)
200 °C	∼8.8	∼3.6 (Peak)	(∼99%)
220 °C	∼11.7 (Peak)	∼2.7	(∼97%)

Table 6.2: Summary of DEG and MEG formation and TEG behaviour at different temperatures after 5 weeks.

6.2.2 Effect of water on the formation of DEG and MEG, and degradation of TEG over time at specific temperature

To investigate the effect of water content on the thermal degradation of triethylene glycol (TEG), a five-week experiment was conducted at 200 °C, focusing on the formation of degradation products diethylene glycol (DEG) and monoethylene glycol

(MEG), as well as the behavior of TEG itself. Throughout this duration, DEG and MEG concentrations increased progressively under all three tested conditions: no water, 5 wt% water, and 15 wt% water. This degradation rate significantly accelerated in the presence of water, particularly after week 3.

As shown in the Figures 6.13 and 6.14, by week 5, the 15 wt% water samples yielded the highest concentrations of both degradation products, around 12 mg/g DEG and 5.1 mg/g MEG. In comparison, the 5 wt% water samples showed concentration levels around 10.5 mg/g DEG and 3.9 mg/g MEG, while the no-water samples resulted in the lowest concentrations, approximately 8.9 mg/g DEG and 3.5 mg/g MEG. These results suggest that water facilitates the breakdown of TEG and that higher water content leads to more degradation.

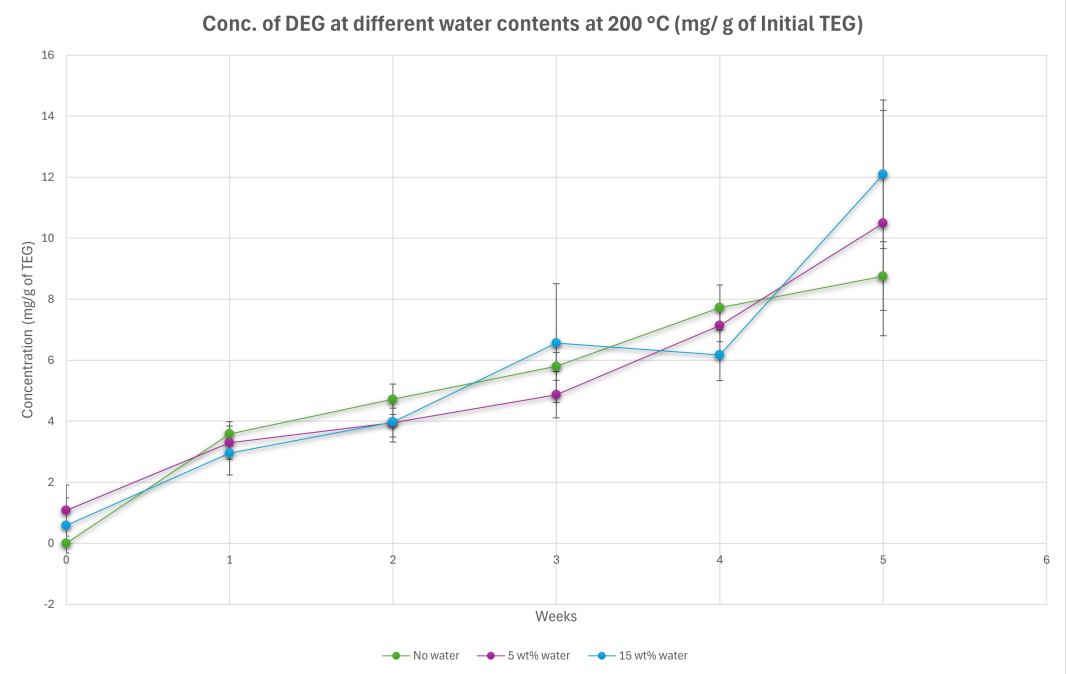

Figure 6.13: Formation of DEG in thermal degradation experiments of TEG at different water contents at 200 °C.

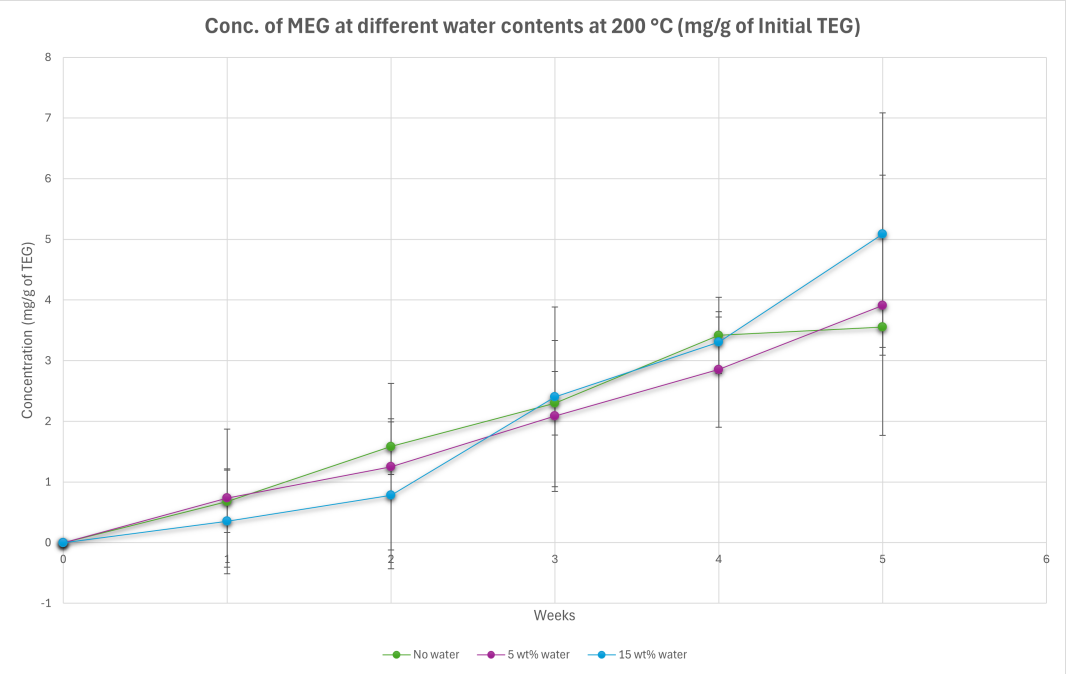

Figure 6.14: Formation of MEG in thermal degradation experiments of TEG at different water contents at 200 °C.

Interestingly, the relative amount of TEG remained nearly constant throughout the experiment across all conditions. According to Figure 6.15, a notable increase in TEG was observed during the first week in the water-containing samples, up to around 118% for 15 wt% water and 112% for 5 wt%, likely due to water vaporization that increased the concentration of TEG while the no-water sample remained around 102%. Following this initial rise, TEG levels in the water-containing samples gradually decreased, and by the end of the experiment, the TEG content remained the same or showed only slight changes compared to the initial value. This indicates that while water promotes the formation of degradation products, it does not lead to a significant reduction in the overall TEG concentration.

Although water is not generally expected to act as a solvent in radical reactions, it can facilitate the radical hydrogenation (RH) step by promoting proton transfer through the formation of hydroxyl OH• radicals. This could explain the increased concentrations of DEG and MEG observed in water containing experiments. The presence of water, especially at higher concentrations, may thus be accelerating the degradation process by influencing key reaction mechanisms including radical pathways and proton transfer steps [35] [36].

The summarized trends in DEG and MEG formation, as well as the behaviour of TEG at different water contents at fixed temperature, are presented in the Table 6.3

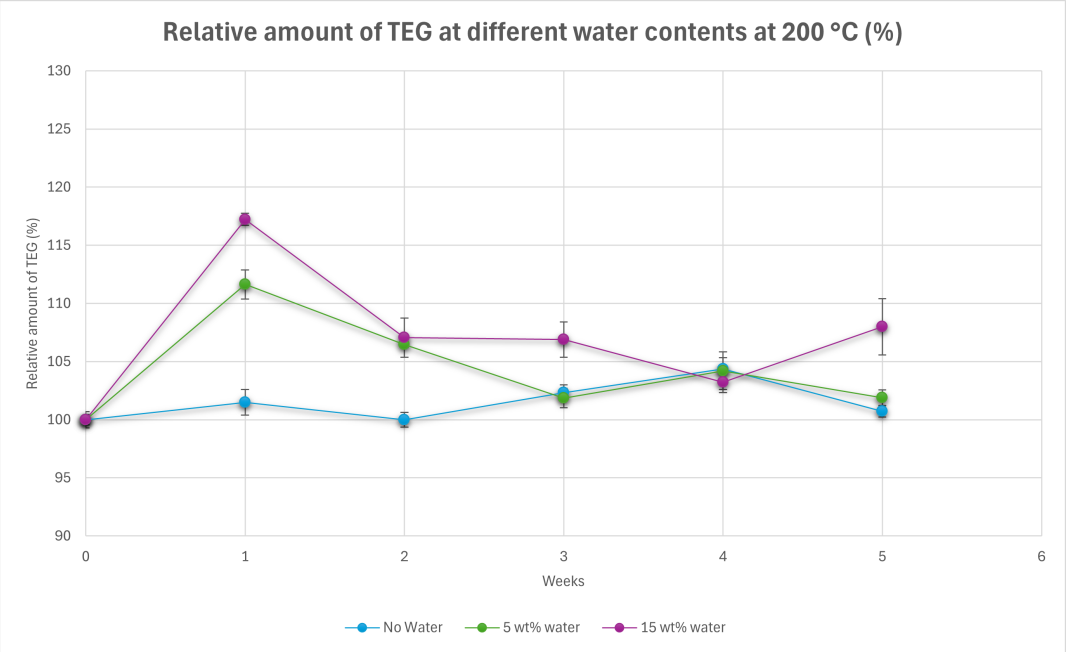

Figure 6.15: Thermal degradation of TEG at different water contents at 200 °C.

Water Content	DEG (mg/g at Week 5)	MEG (mg/g at Week 5)	TEG Behavior at Week 5
0 wt%	∼8.9	∼3.5	Negligible variation
5 wt%	∼10.5	∼3.9	Negligible variation
15 wt%	∼12.0	∼5.1	Negligible variation

Table 6.3: Summary of DEG, MEG formation, and TEG behaviour under different water contents at 200 °C after 5 weeks

6.3 GC-MS Results and Limitations

GC-MS was used as a qualitative tool, rather than for quantification, due to limitations related to column polarity and variability because of derivatization, as discussed in the section 5.3.2. Thus, it played a vital role in qualitatively confirming the thermal degradation of TEG and in identifying its breakdown products.

The Figure 6.16 displays an overlay of GC-MS chromatograms for thermally degraded TEG samples collected weekly over five weeks at 200 °C. A standard reference chromatogram of MEG, DEG, and TEG is included at the bottom for comparison. In these chromatograms, the x-axis represents retention time (in minutes), while the y-axis indicates relative abundance (percentage). The reference chromatogram shows well-separated peaks for the 1-TMS and 2-TMS derivatives

of MEG (at 2.67 and 3.90 min), DEG (4.81 and 5.92 min), and TEG (6.81 and 7.68 min), which served as benchmarks for identifying the corresponding compounds in the degraded samples.

In the weekly degraded samples, distinct peaks emerge that align with the retention times of DEG (2-TMS) around 6.10–6.16 min, TEG (1-TMS) around 7.06–7.09 min, and TEG (2-TMS) around 7.91–7.93 min. In the earliest stage, the peaks for DEG appeared at lower intensities but became more prominent as degradation progressed, particularly in Week 5. This trend confirms the thermal breakdown of TEG into smaller glycol units, with DEG being a major product. MEG peaks are visible in standard and not observed in the degraded samples due to their very low concentration. In summary, GC-MS confirmed the presence of TEG and its degradation product, DEG, throughout the study period, while not being used for precise quantification.

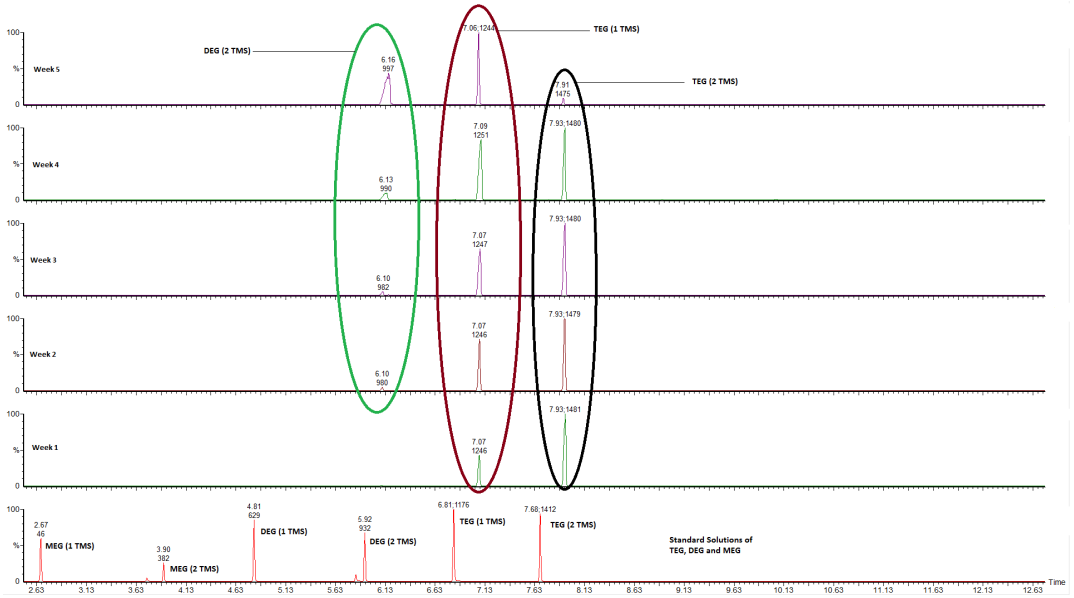

Figure 6.16: GC-MS chromatogram of degraded products with retention times compared to MEG, DEG, and TEG standards, showing thermal degradation of TEG at 200 °C over weeks 1–5.

Furthermore, the mass spectra obtained from the GC-MS analysis were compared with the mass spectra of a library database of known spectra. This comparison showed that the spectra from Weeks 1 through 5 closely matched library references, confirming the presence of TEG (1-TMS and 2-TMS) and DEG (2-TMS), as highlighted in the Figures 6.17, 6.18, 6.19. The library mass spectra of DEG (1-TMS), MEG (1-TMS), and MEG (2-TMS) can be seen in appendixA

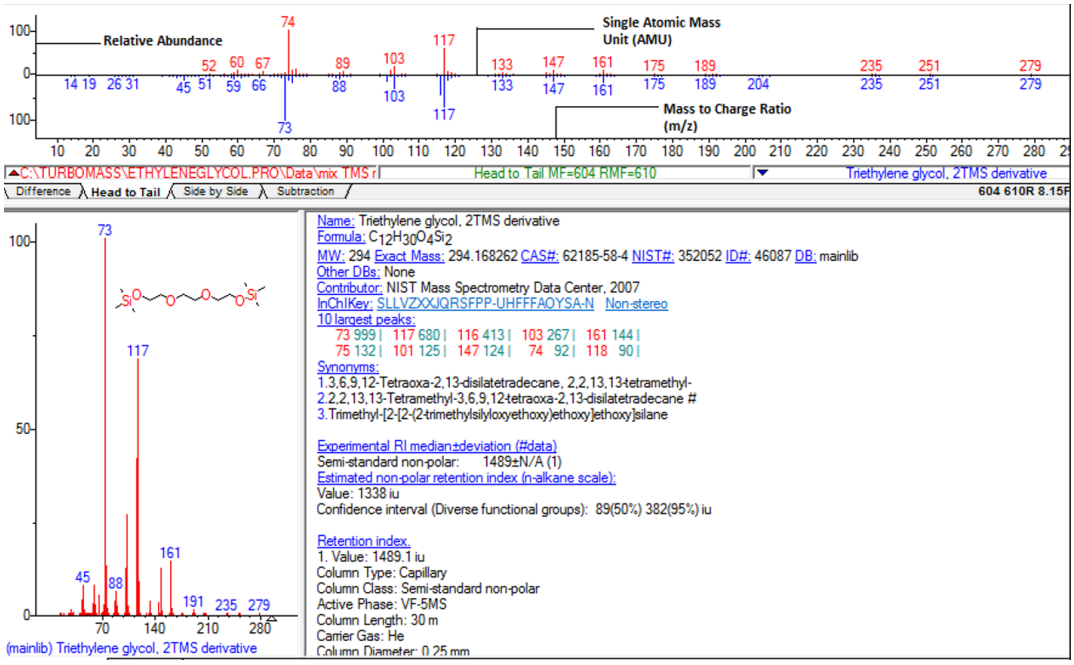

Figure 6.17: Mass spectra of TEG (2-TMS) with mass spectra of TEG (2-TMS) from a library database.

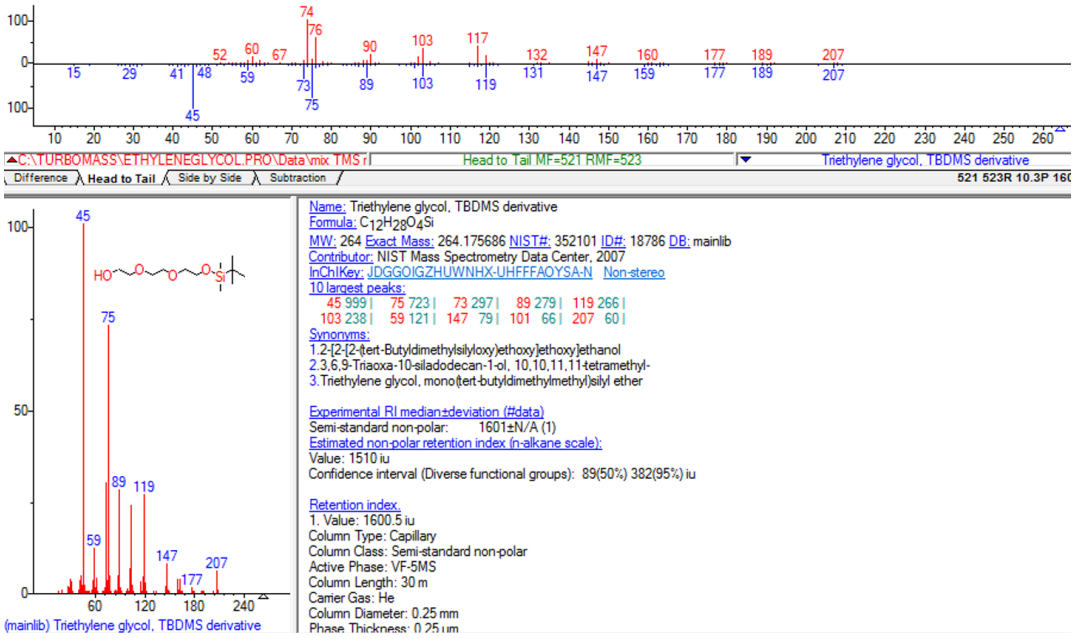

Figure 6.18: Mass spectra of TEG (1-TMS) with mass spectra of TEG (1-TMS) from a library database.

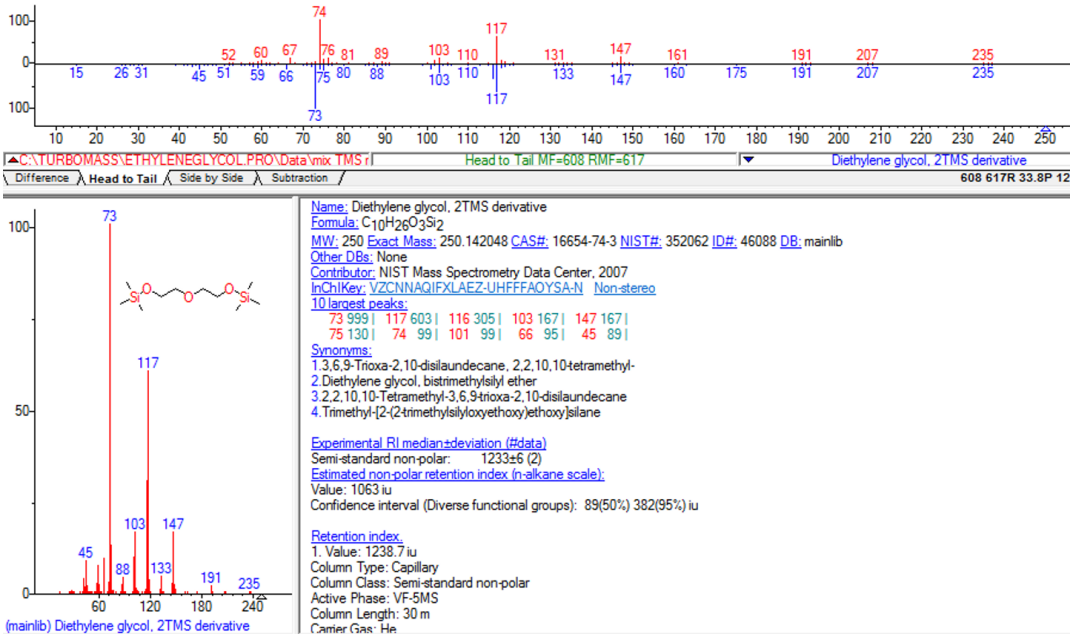

Figure 6.19: Mass spectra of DEG (2-TMS) with mass spectra of DEG (2-TMS) from a library database.

6.4 Raman Spectroscopy Results and Limitations

In order to quantify MEG, DEG, and TEG using Raman spectroscopy, synthetic mixtures of the glycols were initially prepared to determine whether their individual spectral features could be identified. This calibration step was essential to ensure accurate detection and quantification of these compounds in degraded samples. The preparation of standard solutions, selection of reference values, and the method used to interpolate spectral data are already discussed in section 5.3.3. The results of the calibration process are presented in Figure 6.20.

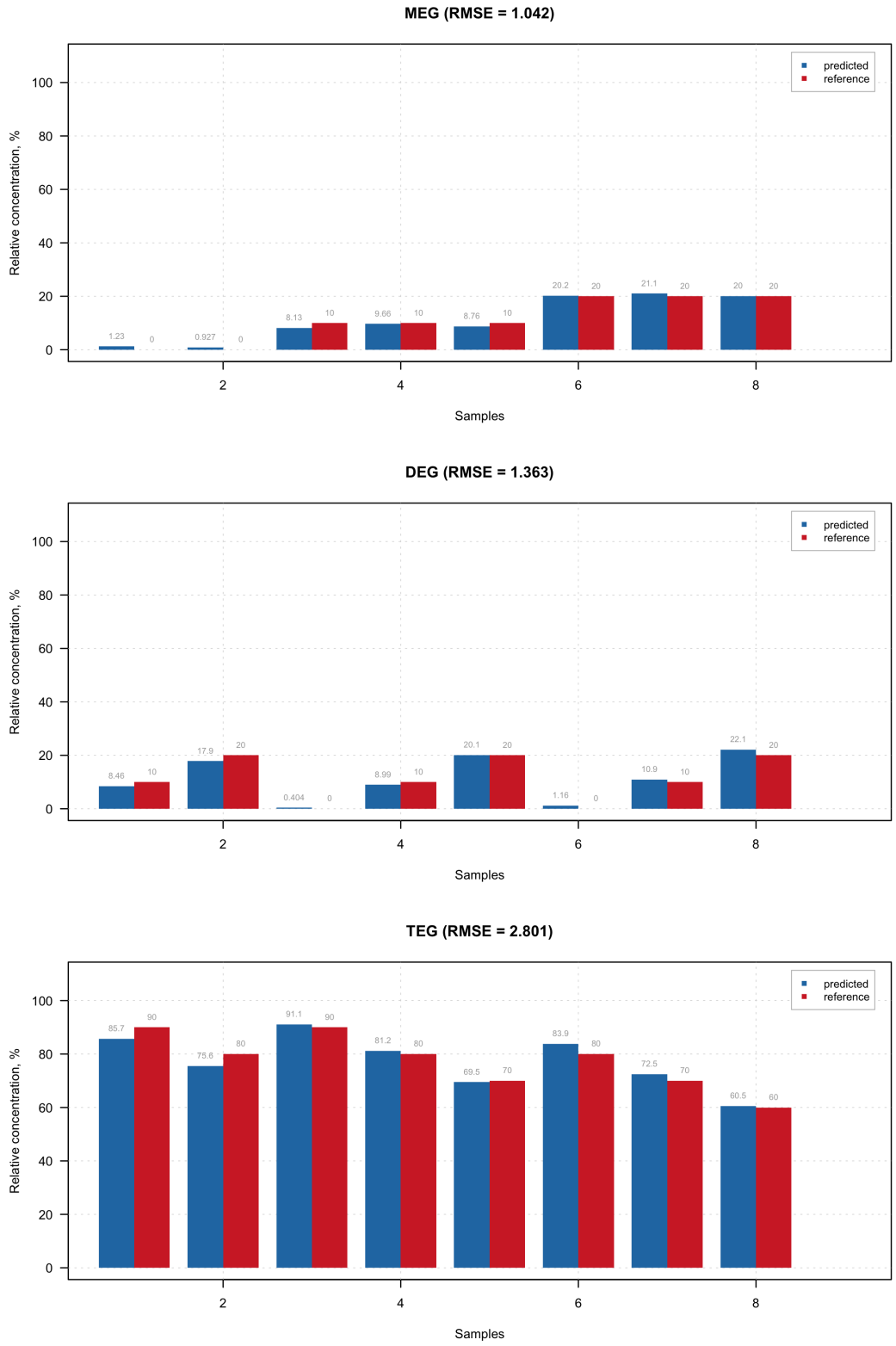

Figure 6.20: Predicted and reference values of glycols obtained from synthetic mixtures.

This calibration was subsequently applied to the analysis of our experimental samples. Unfortunately, the spectra for a lot of the samples, especially from later weeks, showed signs of oversaturation, seen in the Figure6.21. This issue is likely due to the change in color of degraded TEG, which can interfere with Raman signal detection. Although some spectra remained within measurable range and were analyzed, the concentrations of MEG and DEG detected were too low to be considered statistically significant. A similar observation was made regarding changes in TEG concentration. Figure 6.22 shows a visual representation of values obtained for MEG, DEG, and TEG from the analysed samples.

It is important to note that Raman spectroscopy presented certain limitations in this study. The dark color of the degraded TEG samples impacted the outcome of Raman measurements, as darker solutions tend to produce poor-quality spectra and do not yield a clear spectrum, which can obscure the peaks. This limitation made it difficult to detect degradation products. As a result, quantitative analysis of the degradation process using Raman spectroscopy was not feasible within the scope of this study.

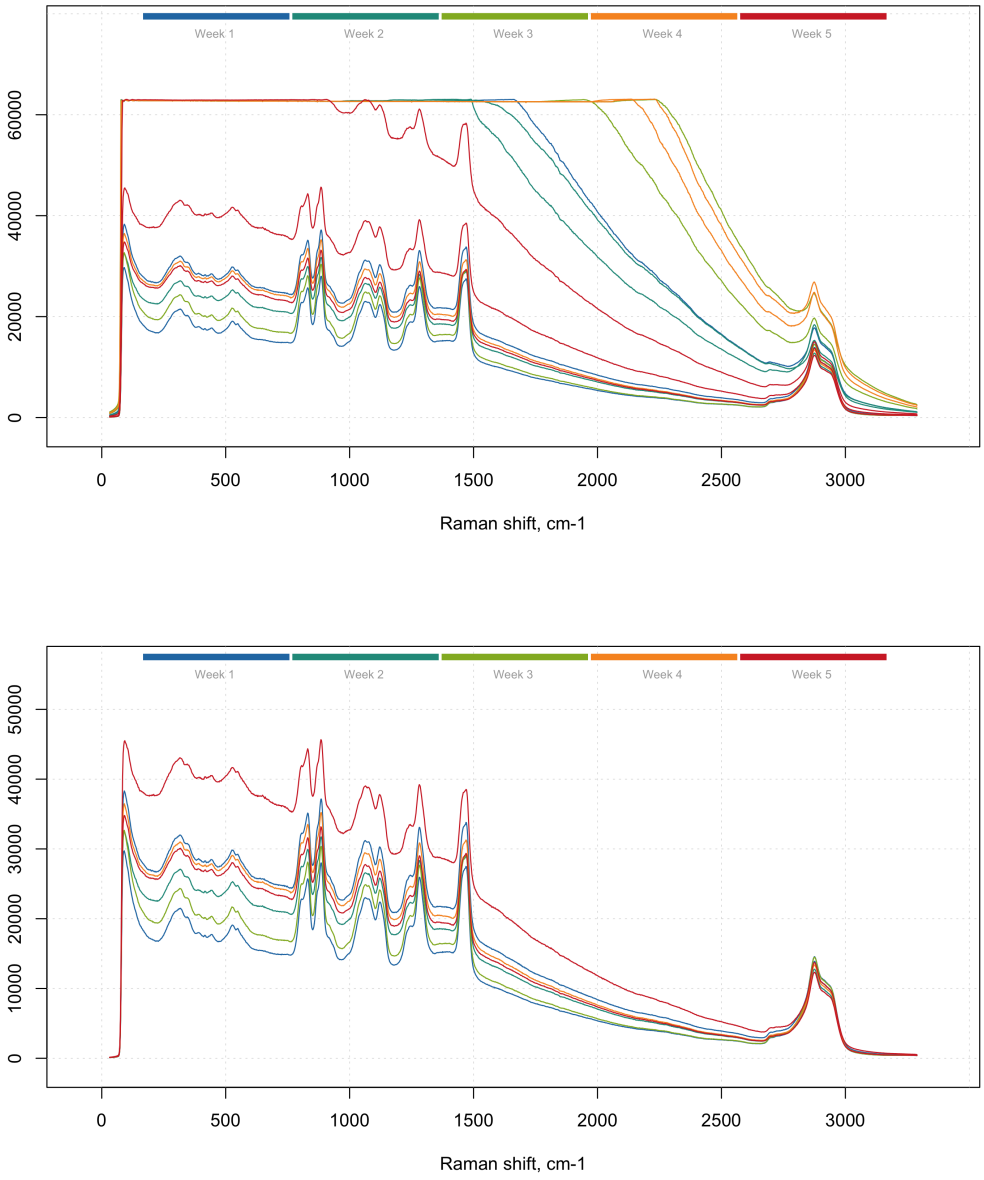

Figure 6.21: Spectra of thermally degraded samples (Raman shift plotted against intensity)

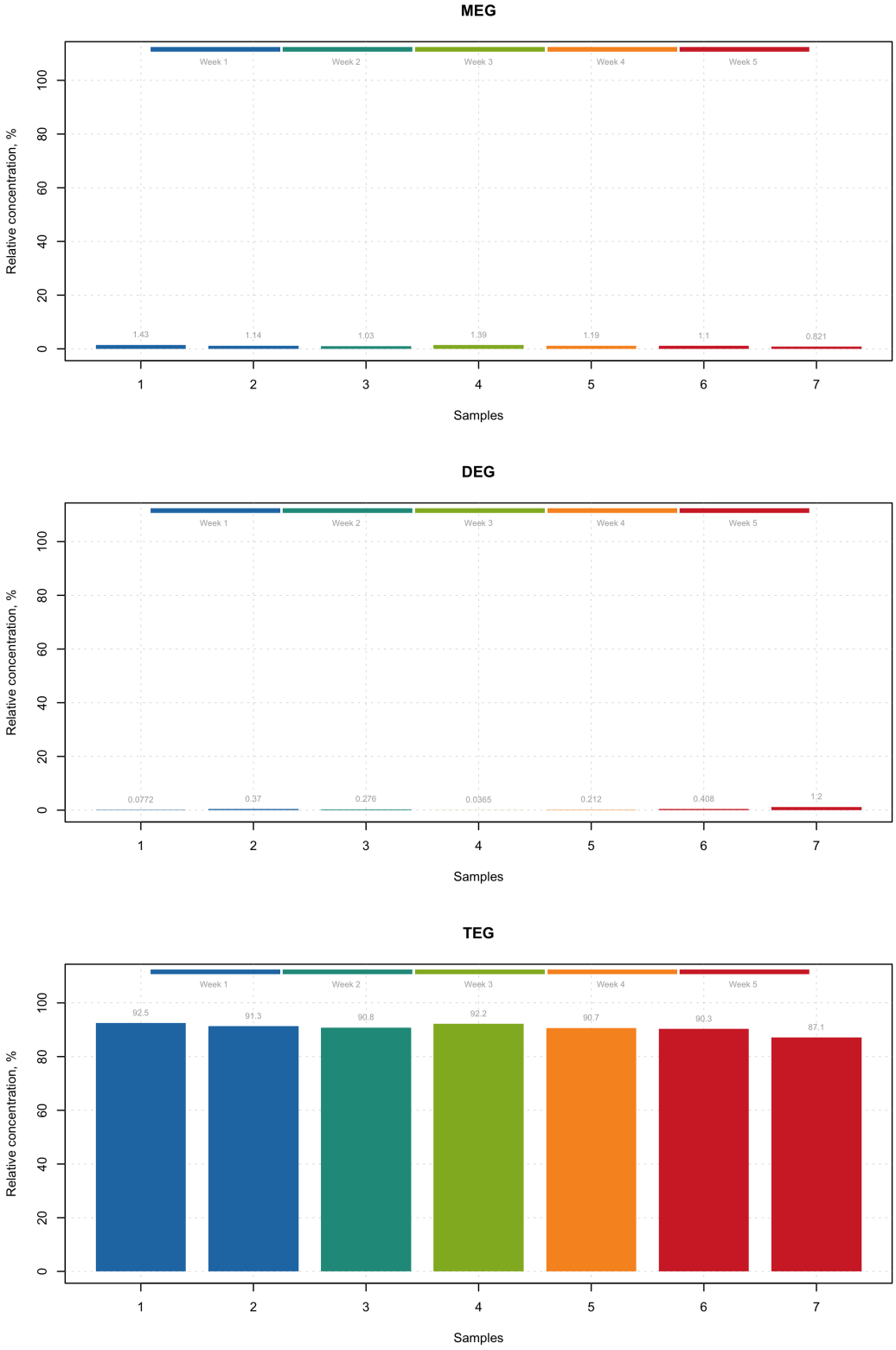

Figure 6.22: Predicted values of glycols in thermally degraded samples from experiment (by mol%).

6.5 Karl Fischer Titration Results

To evaluate the water content in thermally degraded TEG samples, the TEG was first analysed before the thermal degradation experiments and found to contain approximately 0.5 wt% water. After thermal degradation experiments, samples were randomly selected and tested using Karl Fischer titration. Degraded samples also showed water contents below 0.5 wt%, suggesting that no significant increase in moisture occurred.

6.6 Mass Balance

Samples from each experiment were weighed before being put into the oven. In case of experimental campaign 1, samples were weighed each week before opening the cap. The overall weight loss each week was negligible (around 1%). Since some sample was lost each week when it was extracted through a pipette for analysis, this weight loss is insignificant.

Samples from experimental campaign 2 were weighed after being taken out of the oven. The overall weight loss was around 2-3%, which might indicate that some water escaped due to leakage.

Chapter 7

Conclusion and Future work

7.1 Conclusion

The main objective of this study was to explore the thermal degradation of TEG in the absence of oxygen. Since there is limited information available in the literature, there are multiple aspects that can be targeted, like degradation rate, identification and quantification of degradation products, the effect of external parameters, and other components. A better understanding of the chemical properties of TEG would lead to possible improvements in the dehydration process, reducing cost and boosting efficiency while minimizing damage to the environment and equipment due to the formation of hydrates.

Formation of both MEG and DEG is confirmed by GC-FID during degradation of TEG in the absence of oxygen. DEG is the more prominent product at 180 °C, 200 °C, and 220 °C. Degradation increases with temperature, as higher amounts of DEG are detected consistently over the weeks at higher temperatures. MEG, however, forms the most at 200 °C, followed by 220 °C and 180 °C. This may be because MEG has a boiling point of 198 °C [33].

In earlier studies, MEG was not found in samples of TEG with no added water, although it has been detected in our case. However, this may possibly be due to trace amounts of water already present in the TEG stock or absorbed from the atmosphere during sample preparation. The presence of water affects the degradation rate, as slightly higher amounts of MEG and DEG are formed when water is added to TEG. The amount of DEG formed is still higher than MEG.

The overall amount of MEG and DEG formed is quite low, even after 5 weeks, amounting to around 1% by mass with respect to initial TEG, meaning degradation of TEG without oxygen takes significantly longer time. This can be seen in the degradation curves for TEG, which pretty much stay around 100%. In the case of samples with added water the amount of TEG goes up from initial value at week 1, due to water escaping the samples. Week 2 onwards, concentration of TEG

decreases due to degradation. MEG and DEG were successfully quantified despite being in very low concentrations. This demonstrates the strength of GC-FID as a tool to detect low-concentration compounds, especially glycols in this case.

Quantification using Raman spectroscopy could not be done either due to concentrations of MEG and DEG being lower than the limit of quantification during the initial weeks, and due to excessive colouration in later weeks. GC-MS, while being useful for qualitative analysis of components in our case, was not suitable for quantification due to the particular column used in our lab GC unit. MEG could not be detected in it due to its very low concentration, and hence could be derivatized effectively during sampling for GC-MS. Lastly, FT-IR was used to detect any organic acids formed, but nothing was found.

The colour of TEG does not seem to correlate with the degree of degradation. Some samples with a slight yellow tint had a similar amount of MEG and DEG as brown coloured ones.

7.2 Limitations and Future work

There were certain limitations related to the experimental setup itself. Firstly, the sealed glass tubes used in the experiment seemed to show some signs of burning on the caps and some leakage, although in case of samples without water the mass losses were not significant. The sampling process involved multiple steps of dilution with methanol and an internal standard, which may have introduced some human error.

While MEG and DEG are the known major degradation products, there may be some additional minor products like polymeric and gaseous compounds that would have escaped once the cap was opened. These could not be analysed in this study. Using a GC-MS system with a column that does not require derivatization in order to analyse samples could be a solution to this problem. This would also allow better quantification of MEG and DEG.

The scope of this study was limited by the long duration of each experiment, as degradation of TEG in the absence of oxygen is rather slow. With a limited number of pressure and temperature-resistant glass tubes available, degradation experiments for durations much longer than 5 weeks were deemed unfeasible.

Future work on this could be on finding other possible degradation products, especially gaseous compounds. A longer experimental study would be able to look into the degradation over a longer period of time. Since TEG during the dehydration process absorbs other components like hydrocarbons or trace amounts of scavengers like MEA-triazine, degradation studies involving these additional factors could provide better insight into degradation occurring at an actual dehydration unit.

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Appendix A

Appendix A

A.1 Calibration of GC-FID for Quantification of MEG, DEG, and TEG

To quantify Mono-ethylene glycol (MEG), Di-ethylene glycol (DEG), and Tri-ethylene glycol (TEG) using Gas Chromatography with Flame Ionization Detection (GC-FID), the following internal standard calibration method is applied.

1. Internal Standard (IS) Preparation

A stock internal standard solution is prepared by pipetting 1200 µL of Propanol-1 into a 200.00 mL volumetric flask, then diluting to the mark with methanol.

IS Concentration Calculation

$$\text{Propanol (g/L)} = \frac{1200 \times 10^{-6} \times 803}{0.200} = 4.818 \text{ g/L}$$

2. Stock Standard Solution

A stock solution of MEG, DEG, and TEG is prepared by pipetting 900 µL of each into a 100.00 mL volumetric flask and diluting with the IS solution to the mark.

Calculated Concentrations

- MEG: 9.99 g/L
- DEG: 10.08 g/L
- TEG: 9.90 g/L

3. Calibration Standards

Standards of various concentrations are prepared by diluting the stock solution with the IS solution. Two calibration ranges are used depending on the expected analyte concentration.

High Concentration Calibration (Propanol = 4.82 g/L)

Standard	Volume of Stock (mL)	MEG (g/L)	DEG (g/L)	TEG (g/L)
1	0.50	0.50	0.50	0.50
2	1.00	0.99	1.01	0.99
3	2.50	2.50	2.52	2.48
4	5.00	5.00	5.04	4.95
5	10.00	9.99	10.08	9.90

Table A.1: High concentration calibration standards.

Low Concentration Calibration (Propanol = 0.025 g/L)

Standard	Volume of Stock (mL)	MEG (g/L)	DEG (g/L)	TEG (g/L)
1	0.05	0.005	0.005	0.005
2	0.10	0.010	0.010	0.010
3	0.25	0.025	0.025	0.025
4	0.50	0.050	0.050	0.050
5	1.00	0.100	0.100	0.100

Table A.2: Low concentration calibration standards.

A.2 Mass Spectra of Glycols

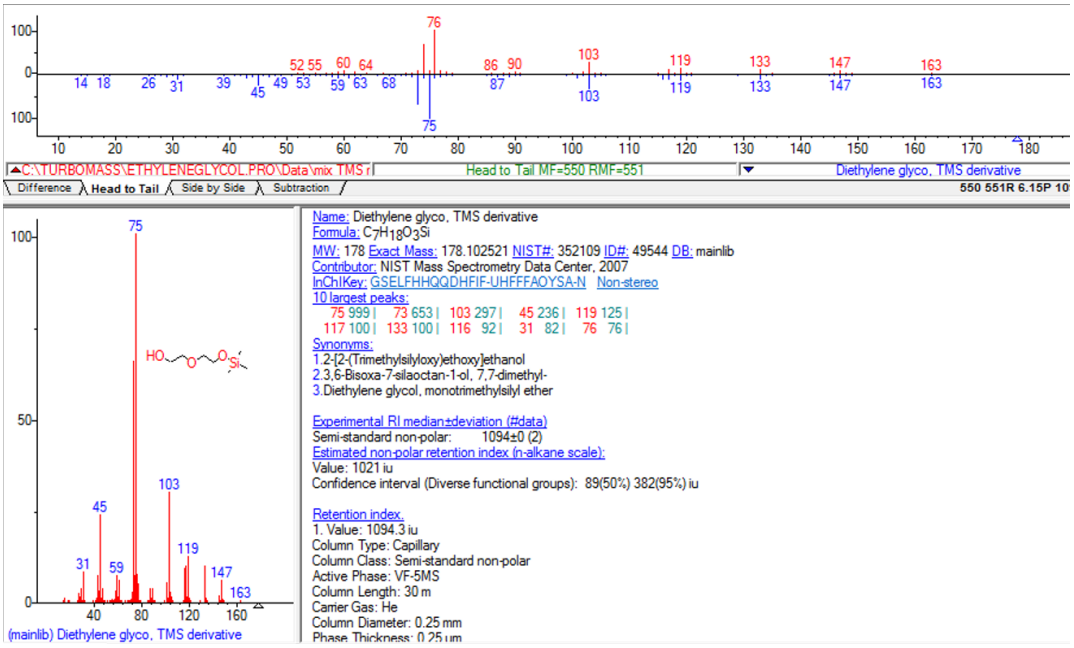

Figure A.1: Mass spectra of DEG (1-TMS) with mass spectra of DEG (1-TMS) from a library database.

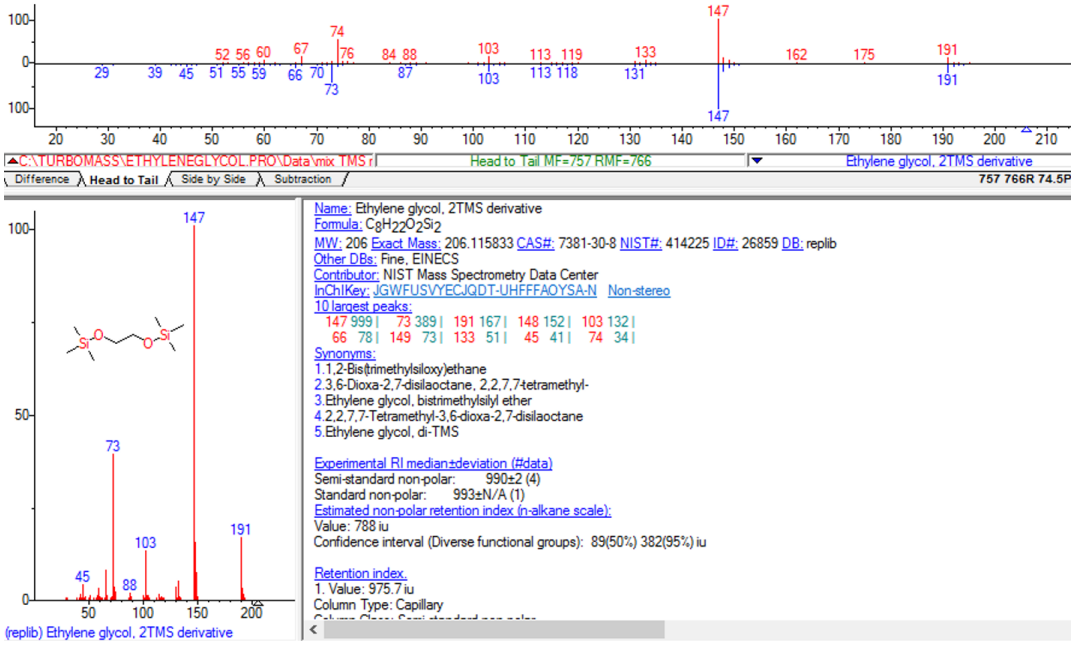

Figure A.2: Mass spectra of MEG (2-TMS) with mass spectra of MEG (2-TMS) from a library database.

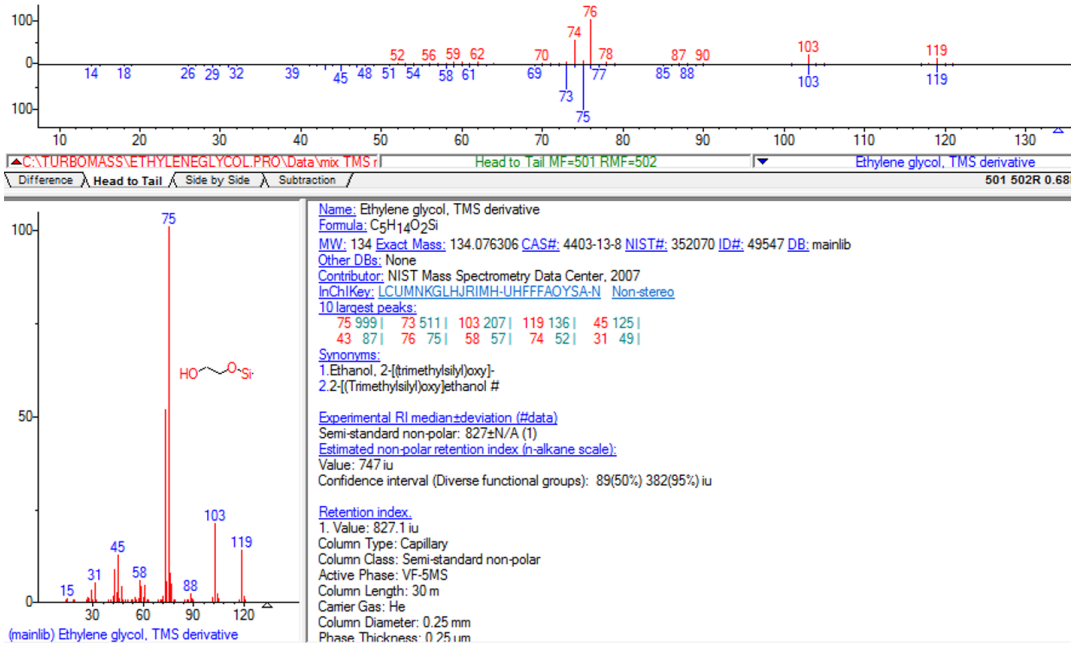

Figure A.3: Mass spectra of MEG (1-TMS) with mass spectra of MEG (1-TMS) from a library database.