Degradation of polydimethylsiloxane in simulated industrial process environments

Oscar Nyman

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The Laboratory of Molecular Science and Engineering
Faculty of Science and Engineering
Åbo Akademi University
Supervisor: Docent Patrik Eklund

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ABSTRACT

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Author: Oscar Nyman

Supervisor: Docent Patrik Eklund

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Polydimethylsiloxane (PDMS) is commonly used in the Kraft process as an anti-foaming agent, which is added during the pulp-washing stage, where the pulp is separated from the black liquor. Crude tall oil (CTO) is later obtained from the process as a by-product and it can be further distilled or upgraded into renewable diesel or other products. However, traces of PDMS have been detected in the CTO and its distillation fractions. This has caused problems in the oil refineries, especially in the hydrotreatment processes, where it causes catalyst poisoning and solid deposits. The purpose of this work was therefore to investigate the fate of PDMS in industrial conditions, such as elevated temperatures and in different fatty acid-based matrices. Experimental work was carried out at Åbo Akademi University, where heating of PDMS in fatty acid-based matrices was carried out in sealed pressure tubes placed in a sand bath on a hot plate equipped with a magnetic stirrer. The effect of an adsorbent and the degradation of PDMS in bio-oil 1 at a slightly larger scale and higher temperature was also tested using an autoclave. The degradation rate of PDMS was analysed using HP-SEC, and the degradation products were analysed using NMR, GC-MS, and GC-FID. The fastest degradation of PDMS was observed in the bio-oil 4 matrix, followed by the bio-oil 1 matrix. Somewhat slower degradation was observed in bio-oil 3 and the least degradation in bio-oil 2. The degradation products were found to be cyclosiloxanes ranging from D3–D8, which subsequently suggested the degradation mechanism to be in the form of well-known back-biting reactions seen in the thermal degradation of pure PDMS. Based on results from an experiment and from the composition of the matrices, the catalytic component and driving force behind the degradation of PDMS was suggested to be the fatty and/or resin acids in the matrices.

Keywords: Polydimethylsiloxane, PDMS, degradation, hydrotreatment, biorefining

ABBREVIATIONS

CTO	Crude tall oil
DMSD	Dimethylsilanediol
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography mass spectrometry
GC-FID	Gas chromatography flame ionization detection
GLC	Gas-liquid chromatography
GPC	Gel permeation chromatography
HP-SEC	High pressure size-exclusion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
NMR	Nuclear magnetic resonance spectroscopy
MW	Molecular weight
PDMS	Polydimethylsiloxane
TGA	Thermogravimetric analysis
TOP	Tall oil pitch
TVA	Thermal volatilisation analysis

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1 INTRODUCTION

Silicon (Si) is the 14th element in the periodic table and the second most abundant element on earth after oxygen. It is a very valuable element with properties similar to those of carbon.[1] The tetravalent element rarely occurs in nature in its elemental state but rather in different forms of silicate minerals such as quarts, sand and glass. The term "silicone" is a misnomer as it was originally believed to be related to the ketone group. The name stuck and is sometimes used as a generic name for all monomeric and organosilicon compounds. In a more restricted sense, silicones, or polysiloxanes, are organosilicon polymers containing alternating silicon and oxygen atoms with organic groups bound to the silicon, typically methyl groups (Figure 1).[1–3]

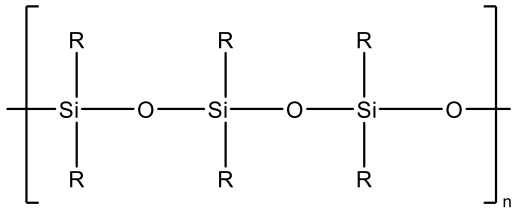


Figure 1. General structure of polysiloxanes, where R is an organic group.

The strong and flexible bonds in the Si-O repeating siloxane structure in combination with organic moieties give rise to unique properties, such as low temperature sensitivity, making silicone-based products functionable over a wide temperature range compared to other organic polymer materials with carbon-based structures.[3,4] These properties allow the use of silicones in many different fields such as aerospace (very low and high temperatures), building industries, electronics (insulation) and even in biological applications such as health care due to its excellent biocompatibility. The length and rotational freedom of the Si-O bond also allows for low energy configurations at interfaces, leading to low surface tension values. This has led to the use of silicones as a hydrophobic building block for surfactants.[4]

Because of the hydrophobic properties of silicones and since they are generally not soluble in water, they are used as an antifoaming agent in industrial applications. The silicone floats on top of water as an oily liquid, breaking the contact points between the bubble and water. This breaks the bubbles and prevents the formation of foam.[4] Polydimethylsiloxane-based (PDMS) oils are the most widely used antifoams in industrial settings. Although PDMS can be an effective antifoaming agent in itself, it is often modified with microscopic hydrophobically treated silica particles in order to increase efficiency. The fluid polymer carries the silica particles to the foam air-water interface where they break the liquid films. [4,5]

One example of industrial uses of PDMS is in the pulp and paper industry, specifically the Kraft process, which is the most dominant pulping process. The Kraft process produces stronger pulp compared to other methods and allows for high chemical recovery, greatly reducing costs.[6,7] In this process, the wood is impregnated with an alkaline liquor (white liquor) consisting of NaOH and Na_2S, dissolving the wood at high temperatures in a digester. Here, the cellulose fibres are liberated by dissolving the lignin that binds the fibres together, and esters from fatty acids, resin acids and sterols in the wood start to degrade in reactions that generate surface-active molecules.[8,9] This liquid stream of spent pulping chemicals and dissolved wood is called weak black liquor, which is separated from the pulp by washing. The surface-active molecules generate large amounts of foam during the pulp-washing stage and relatively high molecular weight (MW) PDMS-based oils are therefore added to the stream as antifoaming agents, as the foam would otherwise cause problems such as reduced washing efficiency and spilling from overflow.[7,9] After the washing, the weak black liquor is allowed to settle, and (non-volatile) tall oil soap, which has a lower density than the black liquor, settles as the top layer and is skimmed off and collected as a by-product.[6] The liquor is then evaporated in the Kraft recovery system, where other volatile extractives are recovered, while the remaining "heavy black liquor" is burned in a recovery boiler to recover energy and inorganic materials. If the tall oil soap is not collected, the efficiency of the recovery boiler decreases, and sulphur emissions start to increase.[6–8]

Crude tall oil (CTO) is produced by liberating the fatty acids and rosin (resin acids) in the tall oil soap by addition of heat and sulfuric acid (H_2SO_4), with an average yield of 30–50 kg/ton of pulp. The CTO is distilled and fractioned, yielding light oil, fatty acids, rosin and pitch residue, also known as tall oil pitch (TOP). This CTO and its fractions are used for chemical purposes in various industrial applications such as in oils, asphalt, paints, printing ink etc.[8] It has also been shown to be a viable and cheaper alternative to biomaterials such as vegetable oil in the oil refining industry. As the removal of tall oil is beneficial to the Kraft process and as industries strive to reduce the use of fossil fuel, utilizing CTO in biorefineries and converting it to fuel is highly beneficial.[6]

However, significant traces of silicon compounds from the PDMS antifoaming agents have been detected in the CTO in the form of cyclic oligomers or high MW PDMS. These compounds have been causing problems such as undesired solid deposits and catalyst poisoning in refining processes, particularly hydrotreatment, where cyclosiloxanes are adsorbed on the catalyst surface.[10,11] In this work, PDMS degradation phenomena in selected bio-oils will be investigated in simulated industrial process environments in order to gain further knowledge of its stability and degradation products.

2 THEORY

2.1 Silicones

2.1.1 Chemical properties

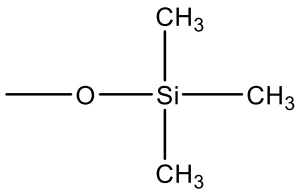
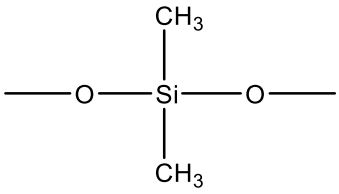
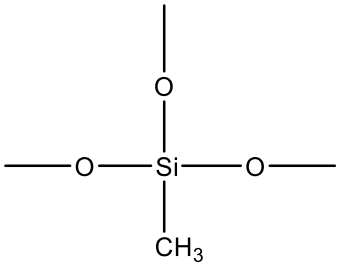
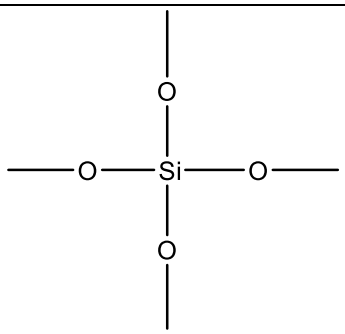
Unlike the carbon-oxygen double bond (C=O), the silicon-oxygen double bond (Si=O) is unstable. The silicones therefore tend to form single bonds (Si-O-Si), which makes them capable of forming polymeric compounds with oxygen, while carbon instead tends to form single molecules with oxygen. This gives rise to the different behaviours between the two, the silicone backbone builds up with oxygen, while carbon-based compounds are degraded by oxygen to form carbon dioxide.[2] The silicon-oxygen bond in combination with the lack of double bonds in the backbone of the structure also leads to chemical inertness, meaning it cannot be attacked by ions or radicals such as ozone (O_3). Silicones also have great thermal stability, which can be attributed to the strong Si-O bond with a bond energy of 106.0 kcal/mole, much higher than the 84.9 kcal/mole for a carbon-carbon bond. Another contributing factor is the fact that silicon is less electronegative than carbon, resulting in bonds with carbon and oxygen that are partly ionic. The polarity in these bonds allows for greater freedom of motion and flexibility within the molecule, giving silicone its unusual thermal properties and low surface tension values from low energy configurations.[3,4]

2.1.2 Structure and terminology

The silicon in polysiloxanes can be bonded with up to three organic groups, with the remaining valences satisfied by oxygen. These groups, containing silicon, oxygen and organic groups are referred to as siloxane units in the polymer. Both the complex ion SiO_4^-, which is the structural unit that forms silica and silicates, and the organosilicon compound R_4Si with four organic groups do not form polymeric compounds.[2]

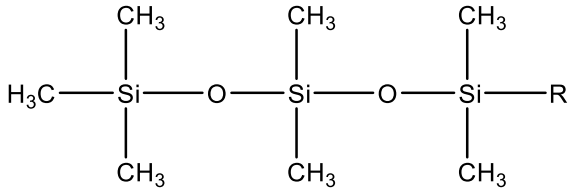
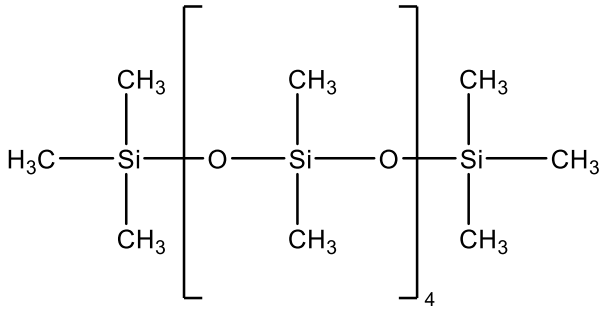
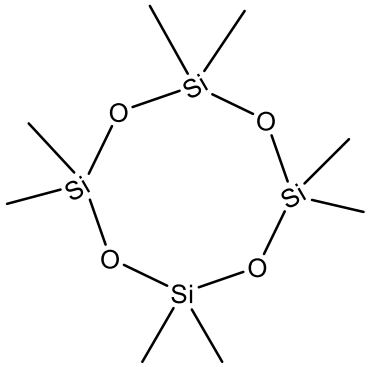
As silicones in industrial application are often polymeric, a chemical shorthand or the silicone backbone has been developed for simplicity's sake, making it possible to name even the more complicated polymers rapidly and clearly (Table 1).

Table 1. Siloxane unit nomenclature.

Description	Unit structure
An "M" siloxane unit is monosubstituted, meaning one oxygen atom is bonded to the silicon atom.	
A "D" unit is disubstituted	
A "T" unit is trisubstituted	
A "Q" unit is tetrasubstituted	

If organofunctional groups are introduced, an "*" is added. "M*" units are thus monosubstituted with organofunctionality (Table 2).[2,4]

Table 2. Examples of siloxanes.

Unit name	Unit structure
MDM*	
MD_4M	
D_4	

2.2 PDMS degradation

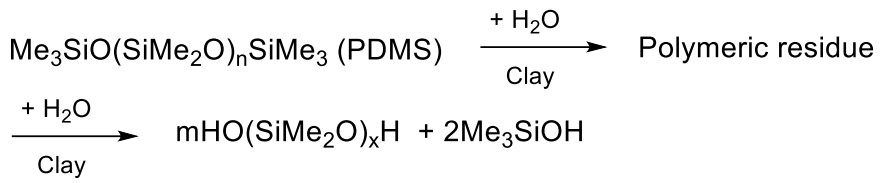
2.2.1 Environmental degradation

High MW PDMS from industrial and domestic applications, such as oils, antifoaming agents, shampoos, detergents, and polishes, can enter the environment in different ways, e.g. from heat transfer fluids spillage in outdoor applications, or more commonly via the wastewater in the sewage system. The water insoluble PDMS has a high adsorption coefficient and adsorbs to the sewage particles, and if not treated and removed properly, the PDMS will end up in the sludge. The sludge is disposed by either incineration, soil amendment or by landfilling. The two latter options result in PDMS being transferred from

an aqueous environment to a non-aqueous environment where degradation can take place.[12–14]

Degradation studies of PDMS in soil have been carried out in laboratories using ^{14}C-labelled dimethyl units in the PDMS. Two studies conducted by Buch and Ingebrigtson (1979) and Lehmann et al. (1998) showed that the moisture content and clay content of the soil affected the hydrolysis rates of the PDMS. PDMS was shown to exhibit significantly less rearrangement in moist or wet soil and degrade more rapidly in dry soil. PDMS migration both upwards and downwards was also noted. PDMS located several inches below the surface in wet soil can migrate to the dry surface soil where it degrades via clay-catalysed rearrangement.[15,16] Several other studies also indicate that the degradation products are influenced by clay-catalysed processes.[12,15,17] The study by Buch and Ingebrigtson noted a loss of approximately 80% of the PDMS via volatilisation in the form of cyclic species with some trimethylsiloxy end-blocked linear species, while the remaining 10–20% consisted of polar solvent soluble siloxanols. Later studies, however, only found silanols. This was explained by the high concentration of PDMS used in Buch and Ingebrigtson's method (1%). The main breakdown product has later been determined to be dimethylsilanediol (DMSD). DMSD is then either biodegraded or evaporated into the atmosphere where it is further degraded by OH-radicals in the presence of sunlight.[12,13] A later study by Lehmann et al. (2000) noted similar results in natural environments compared to the ones in laboratories, with a more rapid degradation in lower moisture during the hot and dry months.[14]

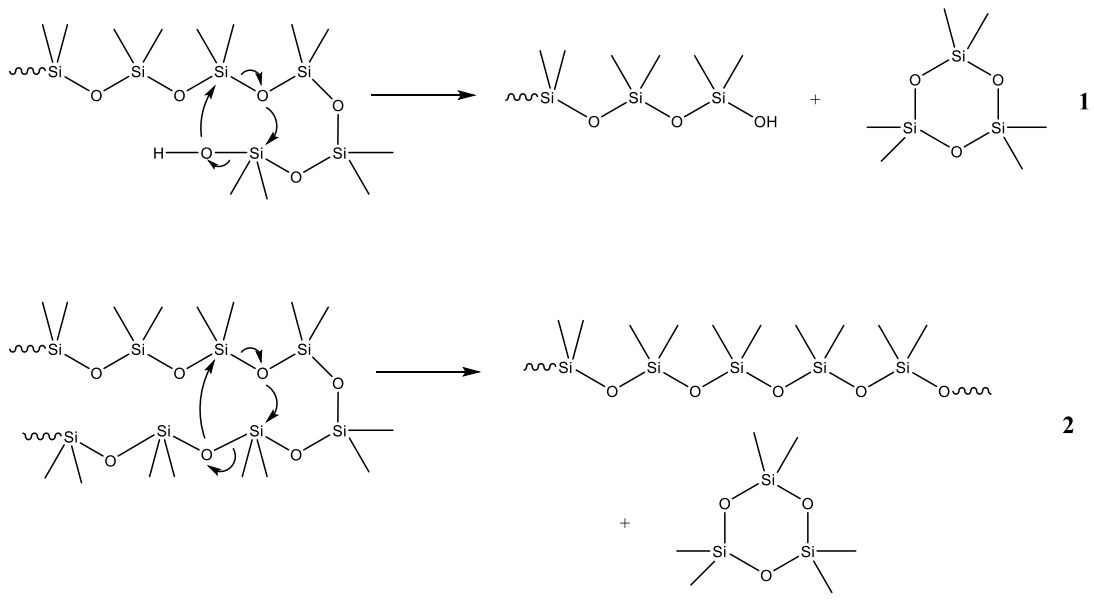
Xu. et al. (1998) observed varying catalytic effectiveness of Ca-saturated clays using HPLC/GPC analysis, where the most effective clays shifted the peaks to longer retention times faster. The researchers found that, on the one hand, Ca-kaolinite, Ca-beidellite and Ca-nontronite were the most effective in catalysing PDMS degradation, whereas gibbsite ($Al(OH)_3$) and goethite(α-FeOOH) were significantly less effective. On the other hand, the former mentioned mineral clays have much higher surface areas than the oxides (gibbsite and geothite), and after normalizing the results to the specific surface areas, it was found that on a surface-area basis, gibbsite and kaolinite are the most effective, demonstrating the critical role of clay surface area. However, surface area is not the only factor influencing the degradation rates, as clays with similar surface areas induced different degradation rates. The role of surface properties such as Brønsted and Lewis acidities are therefore stressed. Lewis acid sites are suggested to catalyse hydrolytic degradation of PDMS by coordinating the otherwise methyl group-shielded Si-O bonds in the backbone of polymer, exposing and weakening them for attack by water. In this study the main breakdown products were found to be silanols. The hydrolytic degradation of PDMS, forming these silanols such as DMSD can be seen in Scheme 1.[17]



Scheme 1. PDMS degradation in contact with clay minerals, where n > 100; m <n – 3x; with x = 1 – 3.[17]

2.2.2 Thermal degradation

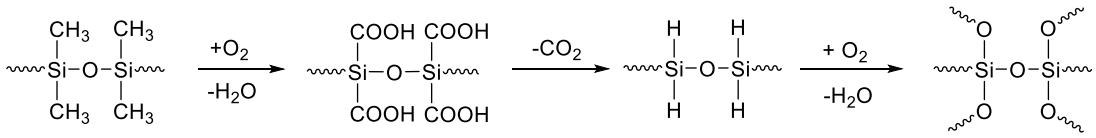
The thermal degradation of PDMS has been studied extensively for over 70 years.[18] It is generally accepted that PDMS degrades primarily via internal, chain "back-biting" reactions (Scheme 2), yielding cyclic siloxane oligomers with D_3 as the most abundant product and decreasing amounts of D_4 to D_6.[19–23] The back-biting reactions can occur in two different forms. One being the hydroxyl chain end attacking the backbone of the polymer, producing cyclic oligomers varying in size depending on the attack point. In the other mechanism, the polymer chain folds back on itself in a cyclic transition step where a rearrangement occurs, forming a new Si-O bond and subsequently a cyclic siloxane oligomer. This transition state can be formed anywhere in the polymer chain and take place indefinitely until the structure is too short to cyclise and/or when evaporation of the shortened chain components is more favourable. This mechanism produces a cold-ring fraction of cyclic oligomers with ring sizes of D_7 or greater in addition to the primary degradation products.[23–25]



Scheme 2. Backbiting mechanism with hydroxyl chain end (1) and via folding within the polymer chain (2).

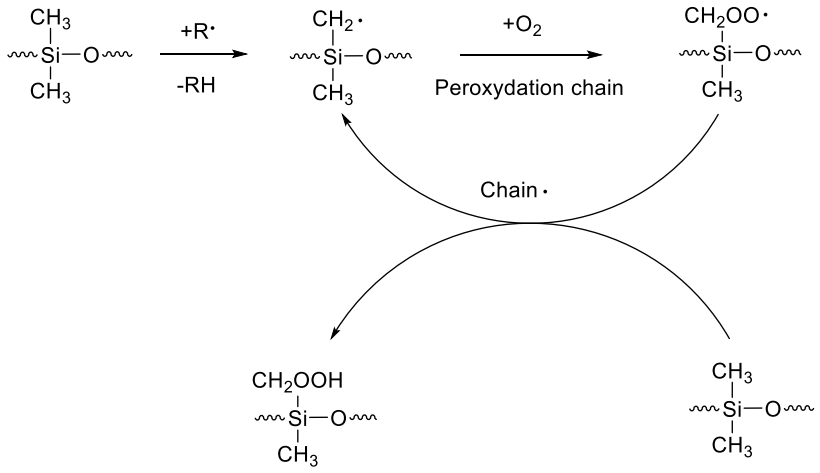
The degradation of PDMS differed in vacuum from inert atmospheres. A Thermogravimetric Analysis (TGA) of PDMS under a flow of helium determined an onset non-oxidative thermal degradation temperature of 418 °C and a maximum temperature of 524 °C at which the maximum rate of mass loss occurs. A Thermal Volatilisation Analysis (TVA) conducted in the same study showed an onset degradation temperature of about 310 °C and a maximum volatile evolution rate at 487 °C in vacuum. The differences in the degradation temperatures were speculated to stem from the fact that the TVA is conducted under vacuum, but a catalytic effect on the surface of the borosilicate glass TVA pyrolysis vessel was also hypothesised.[23] Similar results were noted by Grassie and Macfarlane in 1978. Their TVA indicated a non-oxidate thermal degradation temperature of PDMS starting at about 300 °C with a maximum volatile evolution at 443 °C.[22]

The thermal degradation of PDMS also yields different results when in contact with air and when in inert atmospheres. In a TGA conducted by Camino et al., comparing the thermal degradation in air and in nitrogen, it was found that there are at least two stages of degradation in the oxidative degradation. The first stage starts at about 290 °C (T^1_{max}= 339 °C), much lower than in nitrogen with a T_{max} of 514°C. The second stage starts at about 400 °C (T^2_{max}= 445 °C). The first step can be explained by a catalytic effect from the oxygen, resulting in an earlier weight loss from the depolymerisation to cyclic oligomers. The volatilisation is then slowed down before the second step. This is explained by condensed phase oxidation of PDMS, resulting in tight crosslinking of the polymer with an increased thermal stability (Scheme 3). At 400 °C the crosslinked structure starts to break down.[25] These results are comparable with the TG analysis earlier mentioned that noted a maximum weight loss at 524 °C for degradation in an inert atmosphere.



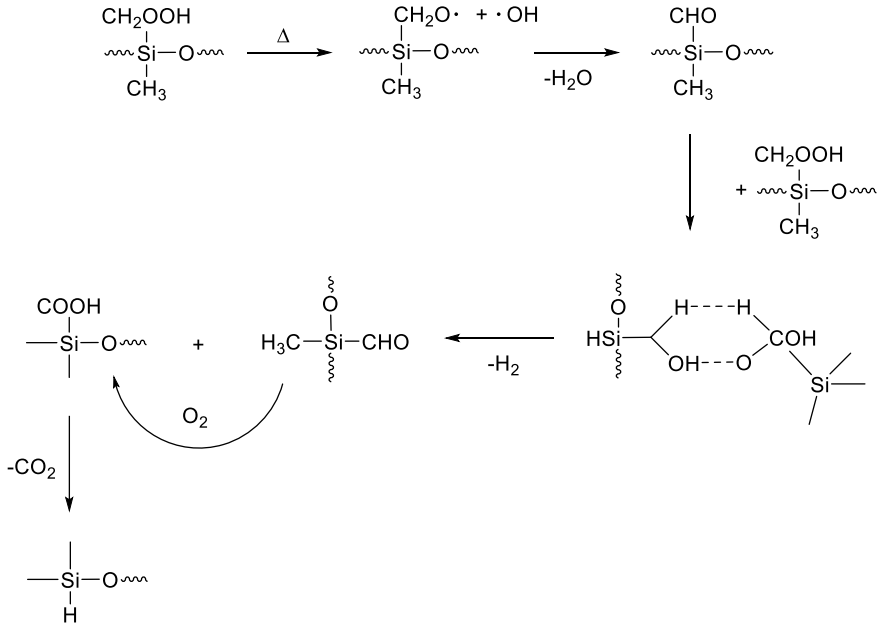
Scheme 3. Crosslinking reaction proposed by Camino et. al.[25]

The degradation of PDMS caused by oxidation most likely proceeds through a peroxidation reaction caused by free radicals R•, yielding primary hydroperoxides (Scheme 4).



Scheme 4. Peroxydation mechanism of PDMS.[25]

These hydroperoxides then decompose, releasing hydrogen (Scheme 5).



Scheme 5. Breakdown of primary hydroperoxides.[25]

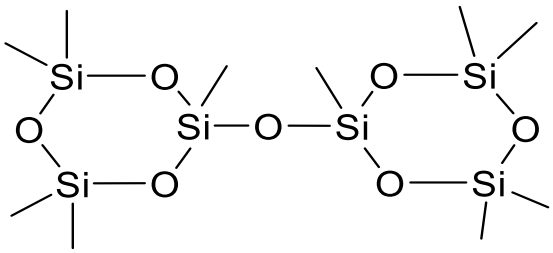
Because this has been studied for so many years, the thermal degradation behaviour of PDMS is well understood, but one must remember that these reaction models are based on simplified laboratory studies. Antifoaming agents in industrial applications for example are often only based on PDMS and may contain other fillers and impurities. In real processes the

conditions might be much different, and the degradation may be catalysed or otherwise influenced by other factors.

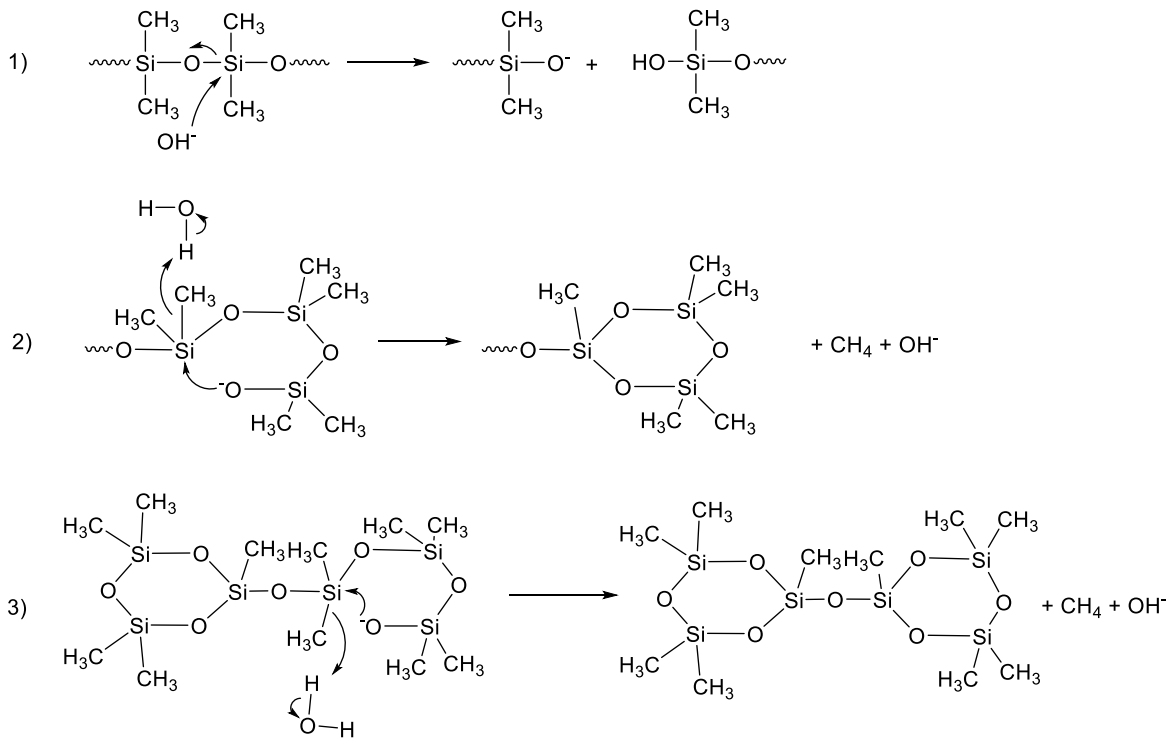
2.2.3 Degradation in alkaline and acidic conditions

Ducom et al. investigated PDMS degradation in aqueous solutions of HNO_3, HCl, NaOH, $Ca(OH)_2$ and demineralised water. PDMS exhibited maximal degradation at the highest concentrations, i.e., in the most alkaline and acidic conditions. However, the degradation levels were not the same for all solutions. In alkaline conditions, $Ca(OH)_2$ induced more degradation compared to NaOH, regardless of pH value. This suggests that the nature of the cations is significant in the degradation mechanism. The apparent catalytic behaviour of the Ca^{2+}-ion is consistent with the studies of catalysed PDMS degradation by clay minerals discussed in chapter 2.2.1. Much like in the studies on environmental degradation, water soluble hydrolysis products were observed to form in the $Ca(OH)_2$ solution. These products were assumed to be siloxanols or silanols. Regarding the acidic conditions, both HNO_3 and HCl induced similar degradation levels.[26] The study, however, only analysed the total amount of silicon released the PDMS into an aqueous phase, and the degradation products and mechanism could therefore not be concluded.

The thermal degradation in presence of alkaline impurities, often found in polymerisation catalysts for example, have also been studied. A TVA of a PDMS sample mixed with 5 weight-% of KOH demonstrated the threshold degradation temperature of PDMS to be lowered by as much as 250 °C. Degradation products started to form at as low temperatures as 187 °C. An Infrared (IR) spectroscopy determined these products to be predominantly methane, suggesting a catalytic cleavage of Si-C bonds by KOH. Overall, the degradation products are the same as with regular thermal degradation; a mixture of cyclic oligomers with predominating and steadily decreasing amounts of D_3, D_4, etc. However, in a Gas-Liquid Chromatography (GLC) of PDMS that had been heated for 1.5 hours at 300 °C with 5 weight-% of KOH, trace amounts of minor products in addition to the cyclic oligomers were detected. The most abundant of these products was determined to be the following structure (X):



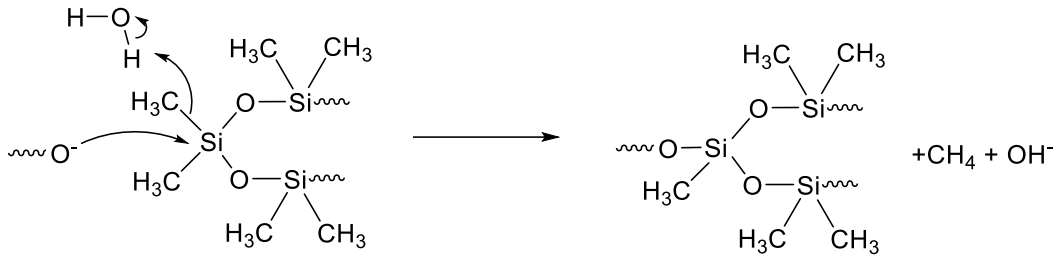
The proposed formation of X (Scheme 6) involves the formation of a siloxy ion (step 1). An intramolecular reaction of this ion would then result in a cyclisation with a subsequent formation of methane (step 2). A similar reaction with another siloxy ion then liberates compound X from the polymer chain (step 3). These reactions would explain the formation of methane. Since the regular cyclic oligomers are still formed, this must be a separate reaction. It is suggested that the negatively charged hydroxyl ions from KOH is driving the back-biting reactions from Scheme 2, thus destabilising the polymer.[22]



Scheme 6. Proposed formation of compound X.

An oxidative thermal degradation was also investigated in this study. The same crosslinking behaviour as in the study by Camino et al. (mentioned in 2.2.2) was observed and the

mechanism of its formation is suggested to be an intermolecular reaction with a siloxy ion, similar to the mechanism for the formation of X (Scheme 7).[22]



Scheme 7. Crosslinking mechanism involving a siloxy ion.

2.2.4 Characterisation of silicones and their degradation products

The thermal degradation of polysiloxanes can be studied by TG analysis. TGA measures the onset of weight loss or the amount of weight lost in the polymer at a fixed temperature. This is a quantitative analysis, meaning it does not give information of the type of degradation products that are volatilised.[9] As earlier noted in chapter 2.2.2, whether or not the atmosphere is inert will also result in highly different results.

For high MW polysiloxanes, high pressure size-exclusion chromatography (HP-SEC), also known as gel permeation chromatography (GPC), is a useful analytical method. It separates molecules based on size, providing molecular weight averages and size distribution information of the polymer.[9] This information makes it possible to investigate the distribution and amount of degradation products of fully or partially degraded polymers, as for example seen in this HP-SEC chromatogram (Figure 2), where the degradation of PDMS, which has been loaded onto different clay types, can be observed. The numbers indicate average molecular size of PDMS in the form of siloxane units.[17]

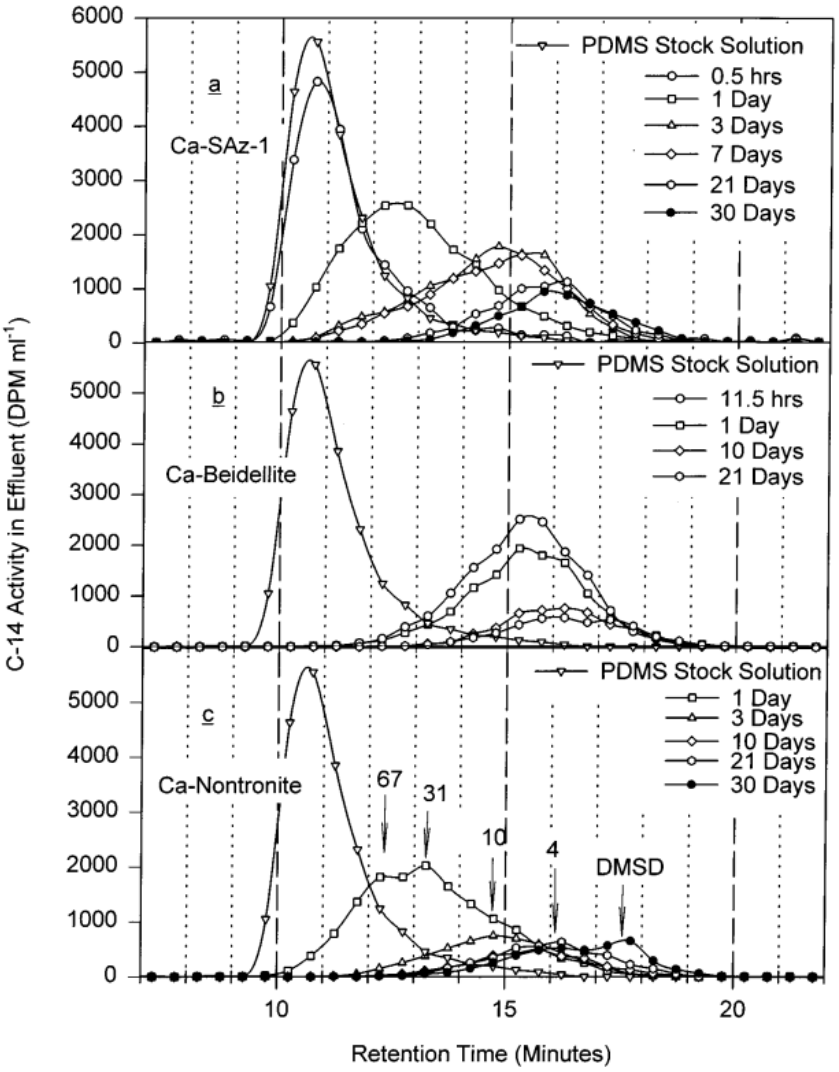


Figure 2. HP-SEC chromatogram of PDMS residue after incubation with different clay minerals (smectites).[17]

Inductively coupled plasma optical emission spectrometry (ICP-OES) is often used to determine total Si amount in samples. The method is very precise, Ducom et al. for example achieved a detection limit of 0.0014 mg/l in their study of PDMS hydrolysis in controlled aqueous solutions.[26] Furthermore, by coupling the ICP with mass spectrometry (MS) instead of OES, an even higher detection limit can be achieved.[11]

Nuclear magnetic resonance spectroscopy (NMR) is widely used method for the identification of molecules in analytical chemistry. The ^{1}H-NMR method is the most common NMR method used to identify silicones. The protons on the methyl groups bonded to silica have a very specific and low chemical shift located between 0 and 0,5 ppm, seen in Figure 3. Therefore, the interference with signals of other functional groups within this range is minimal, allowing for a highly specific analysis. Furthermore, it also allows for the

detection of different chain lengths and chain-end groups.[27,28] The method can be complemented with the quite insensitive ^{29}Si-NMR, ^{13}C-NMR methods, but for a slightly more precise analysis, quantitative NMR (qNMR) can be employed for a more quantitative analysis of PDMS, even in complex matrices.[27]

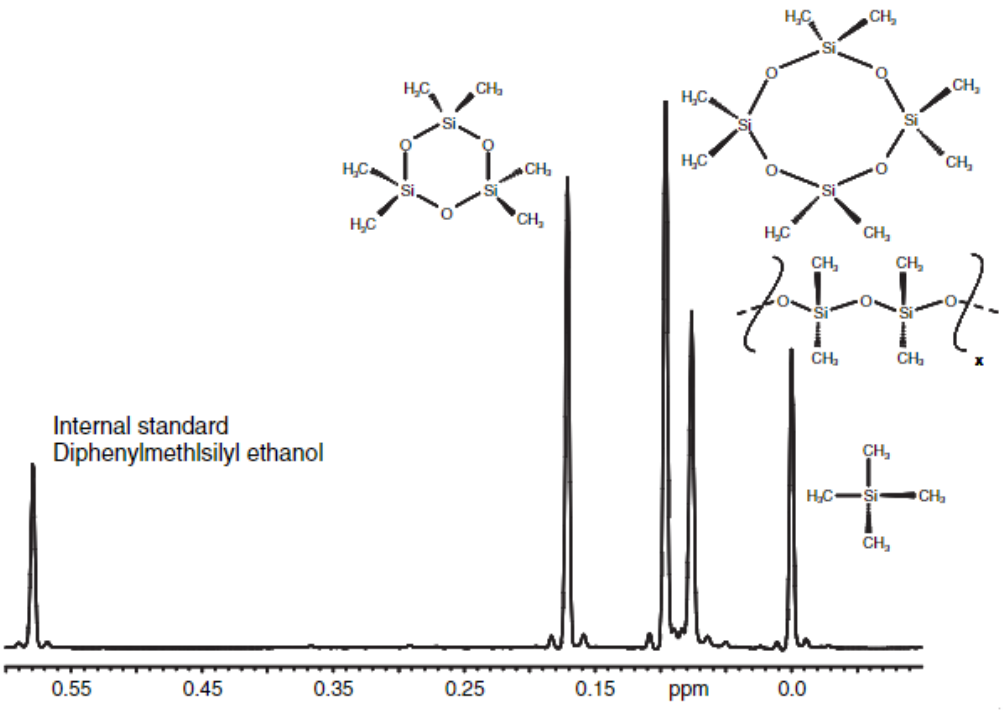


Figure 3. Example of 1H-NMR spectrum of different silicone types.[27]

Table 3. Typical ^{29}Si NMR chemical shifts.[9]

Unit structure	Unit type	Chemical Shift
$Me_3SiO_{1/2}$	M	+7 ppm
$Me_2SiO_{2/2}$	D	-22 ppm
$MeSiO_{3/2}$	T	-66 ppm
$SiO_{4/2}$	Q	-110 ppm
$HOMe_2SiO_{1/2}$	M^{OH}	-10 ppm

Gas chromatography (GC) is a separation technique suitable for smaller oligomers that can be volatilised. When coupled with mass spectrometry (GC-MS), the degradation products

can be separated by their retention times and then identified based on their mass. Another detector that can be deployed is a flame ionization detector (GC-FID). The FID measures the ionisation current from ions that are formed by burning gaseous organic substances in an oxyhydrogen flame surrounded by a high electric field.[29]

Fourier transform infrared spectroscopy (FTIR) is another method commonly used to identify smaller oligomers. IR provides an adsorption spectrum of infrared frequencies that can be ascribed to the bond between the silicon and other atoms or molecules. These spectra can be compared to a reference spectrum, providing information of the molecular structure of smaller siloxanes for example.[30] An example of FTIR analysis of PDMS can be seen in a study by Kaali et al. (2010), where the degradation of PDMS exposed to *in vivo* biofilms was investigated. The FTIR results can be seen in Figure 4. The strongest peak at 787 cm^{-1} corresponds to Si–C stretching vibration, the peak between 1008 cm^{-1} and 1078 cm^{-1} corresponds to Si–O–Si stretching vibration, and bending and rocking vibrations of $Si–CH_3$ can be observed at 1258 cm^{-1} and 864 cm^{-1}, respectively. A peak between 3200 cm^{-1} and 3600 cm^{-1} corresponding to Si–OH bond vibrations had also formed in sample (b), which indicated a hydrolysis of PDMS.[31] However, due to overlapping peaks, this method might not be suitable for the analysis of complex matrices, and the silicone must therefore be separated beforehand.

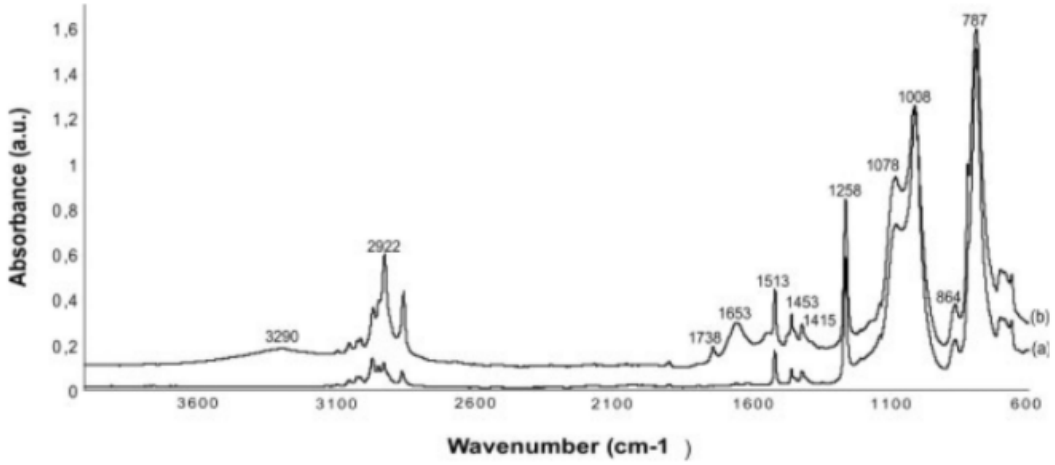


Figure 4. FTIR results of an unexposed reference (a) and an *in vivo* used (b) PDMS tracheostomy tube.[31]

2.3 Biorefining

2.3.1 Kraft pulping

Biorefining is the process of producing material, chemicals products and/or energy from biomass and waste. The traditional papermaking industry has gone from simply making paper to utilizing side streams and waste in biorefining processes.

Pulping is the process by which biomass such as wood or other fibrous mass is converted into a pulp, which is a mass with liberated fibres. Pulp can be produced by chemical pulping, semichemical pulping, chemimechanical pulping and mechanical pulping, with chemical pulping being the most common method, accounting for 70% of worldwide production. The typical pulping wood feedstock contains 40–45% cellulose, 25–35% hemicellulose, 20–30% lignin and <5% extractives. The Kraft (sulphate) pulping process is the most common process, making up for 90% of chemical pulping methods. In Kraft pulping, white liquor (NaOH and Na_2S) is used to digest, or "cook" the wood chips. The spent cooking liquor, "black liquor" is separated from the pulp by washing and it is at this stage PDMS antifoaming agents are added.[9] The liquor is then concentrated to 65–80% solids content, consisting of about 30% lignin, 30% aliphatic carboxylic acids, 7% other organics and 22% inorganic compounds. Tall oil soap is formed from saponification reactions with the wood extractives in the alkaline conditions and sodium salts are formed from the free acids. The most common way to remove the tall oil soap is to let the black liquor settle in a soap tank, remove black liquor from the bottom and remove the soap from the top by skimming. The optimum for soap removal is at 28–32 weight-% dry solid content in the black liquor. At lower percentages, the liquor is too diluted for efficient soap removal and at higher percentages the viscosity prevents particles from rising.[32,33] CTO is produced by acidulation by H_2SO_4 at 93–97 °C in the following manner:

$2RCOONa + H_2SO_4 \rightarrow 2RCOOH + Na_2SO_4$

Transforming the fatty and resin soaps (salt) into acids.[33]

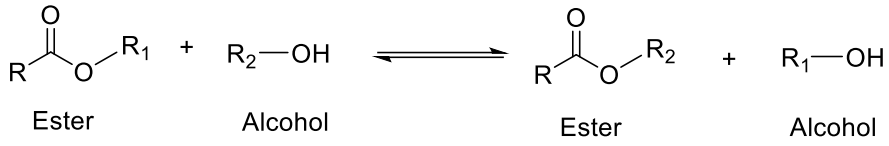
The CTO comprises an acidic fraction with typically 40–60% resin acids and 30–50% free fatty acids, and a neutral fraction with about 10–15% "unsaponifiables" that consists of hydrocarbons, sterols, fatty alcohols etc.[34,35] The CTO is normally distilled by vacuum distillation at 3–30 mbar and 170–290 °C , yielding fatty acids (20–40%), light oil (10–15%), resin acids (25–35%) and pitch residue (20–30%).[8,32] The pitch residue, also known as tall oil pitch (TOP), and light oil are often burned, while the other components are utilized in

the industry for several purposes such as detergents, drilling fluids, fungicides, lubricants etc.[33]

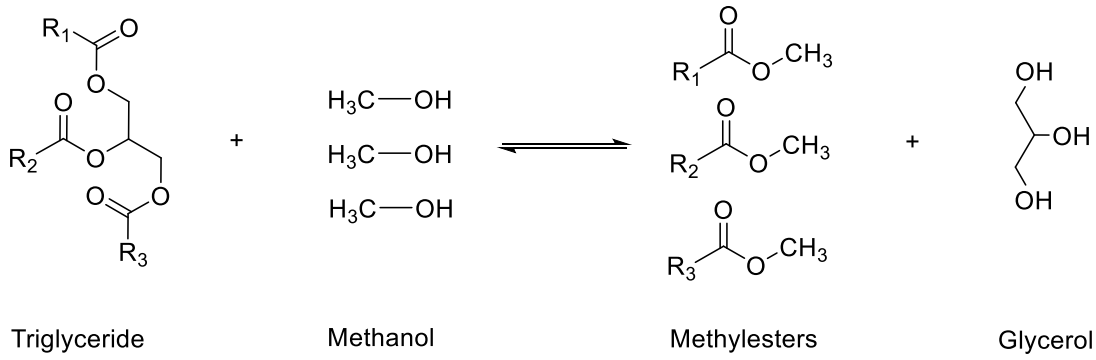
2.3.2 Production of biodiesel from tall oil

The tall oil fatty acids (TOFA) recovered from the Kraft process can be further upgraded into valuable chemicals such as lubricants and biodiesel. The term biodiesel most often refers to long-chain fatty acid (m)ethyl esters (FAME) derived from renewable sources, traditionally vegetable oils and animal fats but also tall oil.[34,36]

There are several different ways to produce biodiesel, the most common one being transesterification. Transesterification is a reaction where a short-chain alcohol reacts with a fat, such as triglyceride or oil, producing a mixture of fatty esters and glycerol (Scheme 8 and Scheme 9). A 3:1 stoichiometric ratio of alcohol and triglyceride is needed for a complete transesterification; however, the reaction is reversible, therefore an excess of the alcohol is used in order to shift the equilibrium towards the products. The alcohol is often methanol or ethanol due to their availability and low cost, but especially methanol is favoured because of its polarity, plus it has the shortest carbon chain and allows for quick reactions with the triglycerides in the presence of alkaline catalysts. The reaction is more often than not catalysed, either homogeneously or heterogeneously, with most commercial biofuels using a base-catalysed homogeneous method. This method requires an anhydrous alcohol, otherwise the presence of water will lead to partial saponification, producing soap, which subsequently lowers the ester yield, deactivates catalysts, and causes problems at the ester and glycerol separation stage. The purity of the feedstock is also of importance, as free fatty acids (FFA) will also react with the base catalyst, causing saponification. "Lower grade" unrefined oils with high amounts of FFA therefore benefit from an acid-catalysed transesterification pre-treatment to lower FFA amounts, followed by a base-catalysed transesterification.[37–39] Both the base-catalysed and acid-catalysed reaction conditions are relatively mild, with temperatures generally around 60–65 °C for the base-catalysed transesterification and somewhat higher temperatures for the slower acid-catalysed transesterification.[40]



Scheme 8. Simplified transesterification reaction.



Scheme 9. Transesterification of triglyceride with methanol.

The catalysed transesterification methods suffer from problems such as problematic separation of products, need for feedstock with low FFA amounts, mixing problems etc.[38,41] Non-catalytic methods also exist. One example is the use of supercritical methanol. This method allows for high amounts of FFA, which is beneficial since tall oil fatty acids can be converted into biodiesel (FAME). However, the conditions are often quite extreme, with temperatures upwards 350 °C.[36]

2.3.3 Upgrading and purification of biodiesel

Biodiesel, or FAME, has a high oxygen content, making it incompatible with most engines as it damages seals in the fuel system and causes blockages and it must therefore be upgraded.[42] Hydrodeoxygenation (HDO) is a method of removing the oxygen from fatty acids and triglycerides, producing n-aliphatic hydrocarbons, usually ranging from n-C_{15} to n-C_{18} depending on the corresponding triglyceride. The method requires little investment as the method is already used in the traditional petroleum industry to remove impurities such as metals, sulphur and nitrogen from the petroleum-derived feedstock.[38,43] The resulting fuel is referred to as green diesel or renewable diesel, not to be confused with the oxygenated biodiesel, and can be used in regular diesel engines. Typical catalysts for hydrodeoxygenation are, for example, sulfided Ni-Mo or Co-Mo catalysts on porous

supports.[42,44–46] After hydrogenation, lighter components are separated from the mid-distillate using common fractionation methods.

The previously mentioned methods allow for the use of different kinds of feedstock, including TOP, although it must be pre-treated and purified from impurities such as solid particles and metals before hydrotreatment. In a previous study on the subject by Kenneth Arandia, it was shown that TOP comprises mainly steryl esters, fatty acids, sterols and resin acids.[47] It might also contain traces of metal cations such as Ca, Fe, P, Al, Si and others. If the purpose is to make renewable diesel, the TOP must be purified from these metal residues, otherwise problems such as catalyst poisoning will occur in the upgrading processes.[48] Other possible impurities such as glycerol, water, soap, residual catalyst, and excess alcohol also need to be removed. This is done either by wet or dry washing. Wet washing is the traditional method, where hot water is introduced to dissolve the impurities, but the addition of water leads to other problems such as the formation of soap and large volumes of wastewater. Dry washing, which is done by introducing an adsorbent in a liquid-solid adsorption process that removes these impurities could therefore be a better alternative.[49–51]

2.4 Objective

PDMS exhibits an onset degradation temperature in inert atmospheres at ~400 °C with known degradation products, but in oxidizing, alkaline or acidic conditions or if the degradation is otherwise catalysed, the onset degradation temperature can be lower than 300° and the resulting degradation products might be very different. The high temperatures, pressures, and feedstock-related conditions in the previously mentioned biorefining methods are therefore likely to induce a catalytic effect on the degradation on PDMS.

The objective of this thesis was therefore to achieve a better understanding of the fate of PDMS under industrially relevant conditions, such as possible degradation phenomena in selected conditions and bio-oil matrixes. Furthermore, the objective included an evaluation of a possible effect of an adsorbent on PDMS degradation in different matrixes.

The experimental work was to be carried out at Åbo Akademi University. The thermal stability was to be analysed by HP-SEC analysis and degradation products were to be analysed by ICP-OES, GC, GC-MS, and NMR.

3 EXPERIMENTAL

3.1 Experimental methods and instruments

3.1.1 Heating

The lower temperature experiments, with a maximum temperature at around 260 °C, were conducted in a simple sand bath placed on a magnetic stirrer with a hot plate (Figure 5). The plate was connected to a digital thermometer, which measured the temperature at the bottom of the sand bath and adjusted the temperature to the desired temperature. The samples were placed directly in the sand bath when the desired temperature had been reached and remained stable.

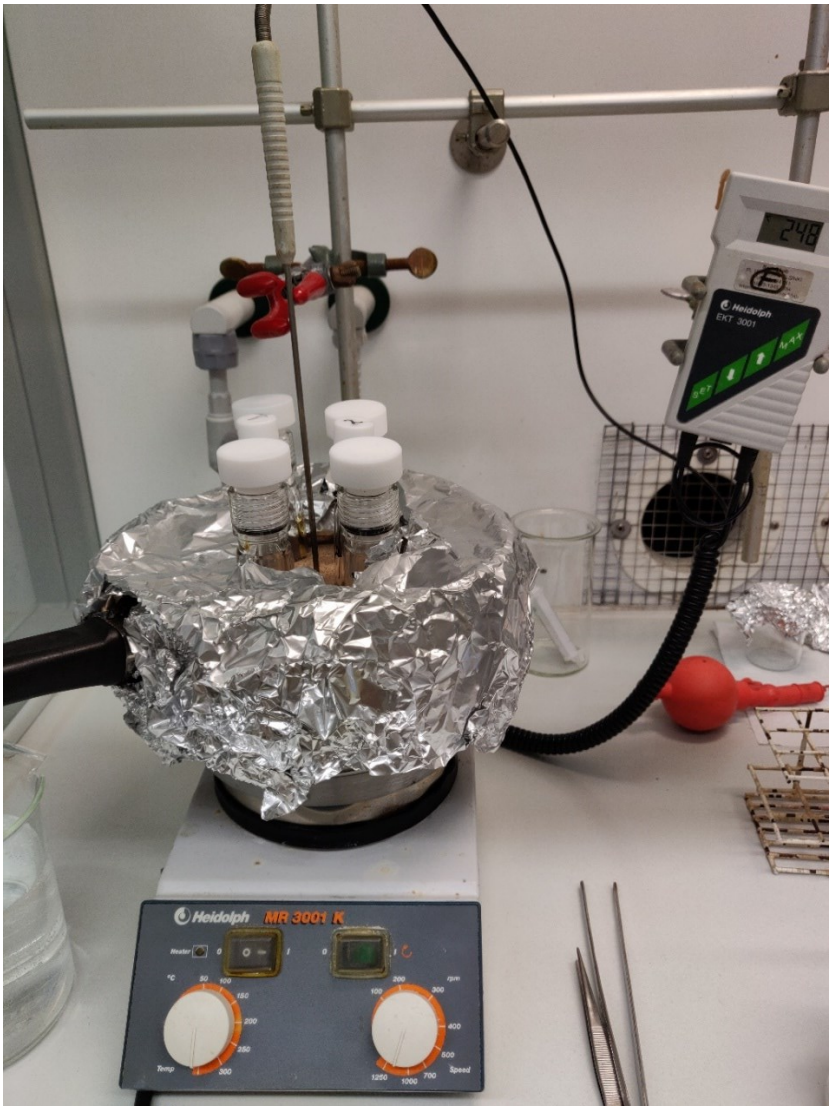


Figure 5. Sand bath heating setup.

The higher temperature experiments were conducted in an autoclave capable of reaching temperatures up to 300 °C (Figure 6). The reactor was connected to an argon tank, and through the inlet (1) the inert gas was led into the reactor. The gas could then be released through the outlet (4) to flush the reactor. Gas phase samples could be taken from the same outlet if coupled to a gas sampling mechanism/syringe. The pressure in the reactor could be read from the pressure gauge (6) but the reactor conditions were also measured with a pressure sensor (7) and temperature sensor (8), which were then observed on a separate display. The reactor was equipped with a curved turbine type stirrer/agitator (2). Samples were taken from the sample collector (3), which consisted of a valve that led the reaction mixture out from the reactor due to the overpressure inside the reactor. The heating was achieved by an electrical heating clamp (5), which was placed around the steel pressure reactor.

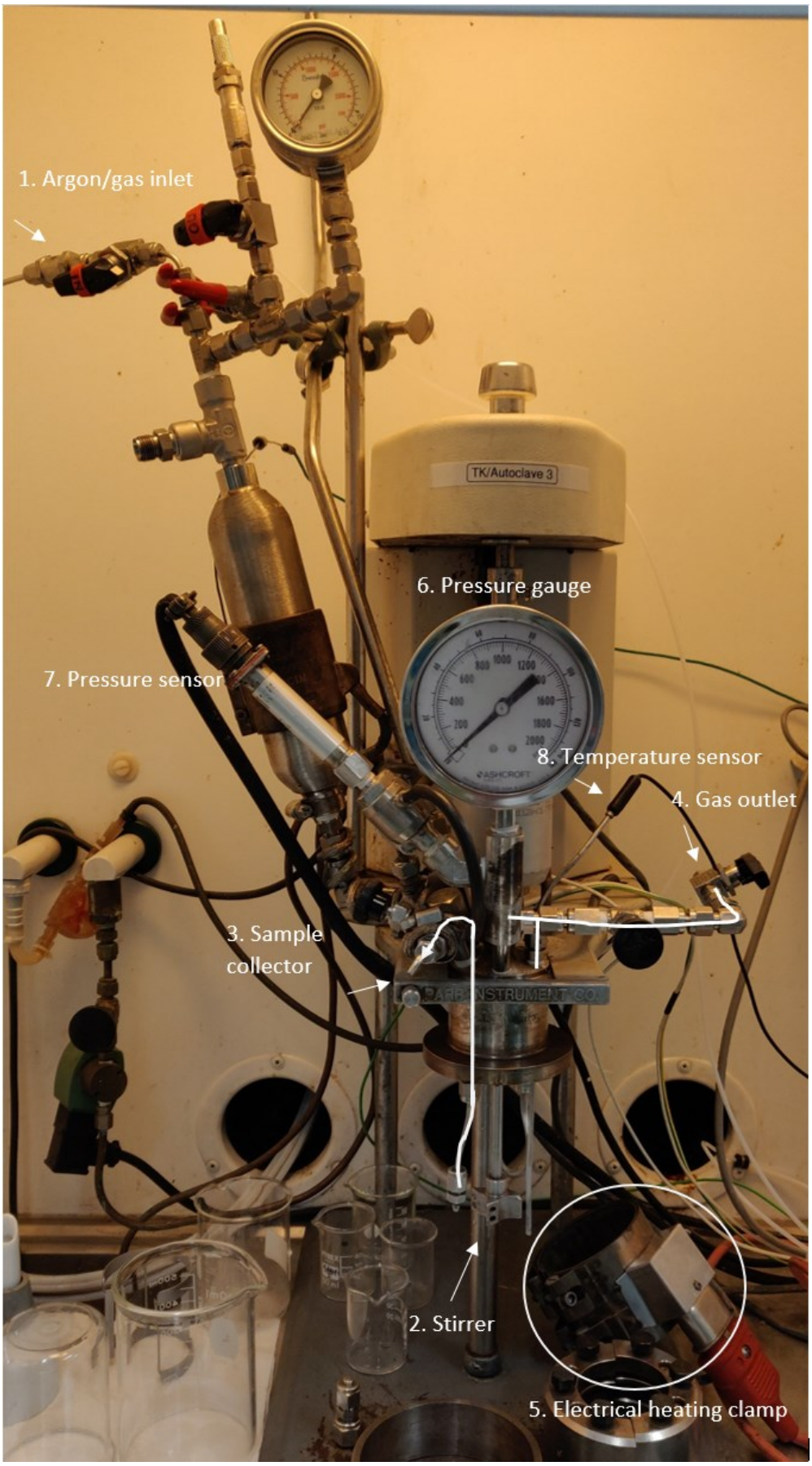


Figure 6. Autoclave setup (without reactor vessel/bomb).

3.1.2 Extraction

Samples from the experiments were extracted using a hexane and methanol extraction method described by Kennet Arandia in a previous study.[52] First, samples weighing 250 mg were prepared. Then, 4 ml methanol, 4 ml hexane and 100 µl 25%-ammonia solution was added to the samples. The samples were then vortexed for about 1 minute and later centrifuged for 5 minutes at 1500 rpm. The solution was allowed to settle and the top phase (hexane), containing PDMS and some components from the bio-oil matrix, is transferred to another tube using a pipette. Another 4 ml of hexane is added for a double extraction and the procedure was repeated. The solvent was then evaporated in an evaporator and the samples were further prepared for analysis.

3.1.3 Analysis methods and materials

A high MW silicone oil acquired from Sigma Aldrich, with a viscosity of 1000 cst, was used. The selected bio-oil samples and adsorbent were acquired from Finnish industrial companies.

HP-SEC analyses were performed on a Shimadzu LC-10AT liquid chromatograph with a Sedex 85 LT-ELSD (Low-Temperature Evaporative Light-Scattering Detector). The columns consisted of a Jordi Gel DVB 500Å 50 x 7.8 mm guard column and two Jordi Gel DVB 500Å 300 x 7.8 mm columns. A HPLC-grade THF eluent with 1% glacial acetic acid was used with the sensitivity value Gain 3. The injection volume was 50 µl with a flow rate of 0.8 ml/min. Before analysis, the samples were diluted to either 3 or 5 mg/ml in THF. From there, 1 ml of sample was transferred and filtered through 0.2 µm PTFE filters into HPLC/GC autosampler glass vials.

NMR analyses were conducted on two different instruments, both with Bruker 500 MHz actively shielded magnets and probes with automatic tuning and matching. The first instrument was equipped with a liquid nitrogen cooled Prodigy BBO CryoProbe and the other with a BB/1H Smartprobe. Samples were dissolved in deuterated chloroform and diluted to 25–50 mg/ml.

GC-MS analyses were run on an Agilent 6890 series GC coupled with a HP 5973 MS detector using an Agilent 19091Z-002 HP-1 methyl siloxane capillary column. Some samples were silylated using a silylation mixture consisting of pyridine, BSTFA and TMCS in the ratio 1:4:1. About 150 µl of this mixture is then added to the extract and gently shaken.

The sample were then placed in an oven for 45 minutes at 70 °C and vortexed after about 5 minutes of heating.

For short- and long column GC-FID analyses, Clarus 500 Gas Chromatograph and Autosystem XL gas chromatographs from Perkin Elmer were employed. The long column used was a HP-1 Agilent Narrowbore GC column with a length of 25 m and an internal diameter of 0.2 mm. The short column was an Agilent J&W Megabore GC column with a length of 6 m and an internal diameter of 0.53 mm.

3.2 Preliminary experiments

Preliminary experiments were conducted to achieve an insight into the degradation phenomena of PDMS at a broad level. The information obtained was then used to determine the relevant conditions for the main experiments.

3.2.1 Heating of pure PDMS

The first preliminary experiment that was conducted was a simple heating and later extraction of pure PDMS. This was done to see if there are any signs of degradation of PDMS at 250 °C, and to test the methanol-hexane extraction method described in 3.1.2. The experiment was carried out in a closed system consisting of two test tubes (A and B), which were placed in a simple autoclave flushed with nitrogen. An untreated sample C was also prepared for reference. The autoclave was placed in a sand bath that had been heated up to around 210 °C. Test tube A and C contained 250 mg of PDMS, and test tube B contained 250 mg of PDMS and about 1 weight-% of 85% phosphoric acid. After 20 minutes the temperature of the sand reached around 240 °C and was kept at this level for 3 hours. After these 3 hours the autoclave was removed and allowed to cool for about 15 minutes in room temperature and subsequently opened. The phosphoric acid had unfortunately not been in contact with the PDMS and was instead stuck on the side of the tube. The samples were first weighed, and as expected they showed no weight loss and thus no degradation and formation of volatile species. The PDMS was then extracted from the samples using the hexane and methanol extraction method. Weighing revealed that over 99% of the PDMS was extracted using the method.

3.2.2 Heating of PDMS in bio-oil 1 matrix

A second experiment was conducted to see if the degradation behaviour is different for PDMS in a bio-oil matrix at similar temperatures as the first experiment. Two mixtures A and B with 20% PDMS and 80% bio-oil 1 totalling 250 mg were prepared. Mixture A was heated in a sealed nitrogen flushed Ace glass pressure tube directly placed sand bath for 3 hours at temperatures between 250 °C and 260 °C. Mixture B was untreated for reference. Both mixtures were extracted using the hexane-methanol method. The hexane phases in A and B were evaporated and collected for preparation for HP-SEC analysis, where the mixtures were dissolved in 10 ml tetrahydrofuran (THF) and later diluted to 5 mg/ml. The solutions were then filtrated and analysed by HP-SEC. After this, another experiment in the same conditions was conducted for later NMR analysis.

3.2.3 Catalytic efficiency of bio-oil 1 on PDMS degradation

After getting the results of the second experiment, a third experiment was conducted; this time with 250 mg samples of 20% bio-oil 1 and 80% PDMS. This would potentially give more information on the catalytic ability of bio-oil 1 on PDMS degradation. Four samples were prepared. The First sample (A) was an untreated reference sample that was not heated. The three other samples (B, C and D) were flushed with nitrogen in Ace pressure tubes, sealed and placed in a sand bath at around 260 °C. Sample B was removed after 45 minutes, sample C at 83 minutes and lastly sample D after 3 hours of reaction time. After fractionation, the hexane phase was collected, evaporated, and later prepared for HP-SEC analysis by dilution with THF to a concentration of 3 mg/ml.

3.3 Thermal degradation of PDMS

3.3.1 Thermal degradation of PDMS in bio-oil 1 matrix with long residence time

Samples containing a 250 mg mixture of 20% PDMS and 80% bio-oil 1 were prepared in Ace glass pressure tubes, which were then flushed with nitrogen and sealed. The samples were placed in a sand bath at 250 °C for 3 hours under constant stirring with magnets. After 3 hours had passed the samples were cooled to room temperature in a water bath. Sample A was directly dissolved in THF for HP-SEC analysis and sample B was fractionated and dissolved in THF for HP-SEC analysis. All HP-SEC samples were diluted to 3 mg/ml in THF. Sample A and B were also analysed using short column GC. Samples C and D were

dissolved in chloroform for NMR analysis, where sample D was spiked with D3 and D4 cyclosiloxanes for comparison. Unheated reference samples containing the same amount of PDMS and bio-oil were made for both HP-SEC and NMR. Pure PDMS and bio-oil was also analysed for comparison.

3.3.2 Thermal degradation of PDMS in bio-oil 1 matrix with shorter residence time

Samples containing a 250 mg mixture of 20% PDMS and 80% bio-oil 1 were prepared in argon flushed and sealed Ace glass pressure tubes. The samples were then heated to 250 °C for 30, 60 and 90 minutes in a sand bath under constant stirring and subsequently fractionated with the hexane-methanol dissolution method. The samples were then placed in a vacuum oven at 40 °C for a couple of days and then diluted to 3 mg/ml in THF for HP-SEC analysis.

3.3.3 Thermal degradation of PDMS in bio-oil 2 matrix

In order to gain a better understanding of the catalysed degradation of PDMS, another similar matrix, bio-oil 2, was used instead of bio-oil 1. Samples containing 250 mg of 20% PDMS and 80% bio-oil 2 were prepared in argon flushed and sealed Ace glass pressure tubes. Sample A was untreated for reference and samples B, C and D were heated to 250 °C in a sand bath for 30, 60 and 90 minutes, respectively. After the reaction, the samples were cooled to room temperature in a water bath. All samples were then fractionated using the hexane-methanol dissolution method. Sample C was unfortunately destroyed during extraction and only samples A, B and D were collected for HP-SEC preparation. After evaporation of the hexane phase in a rotary evaporator the samples were placed in an oven at 40 °C at atmospheric pressure over the weekend to ensure that the hexane had fully evaporated. The samples were then diluted to 3 mg/ml in THF and analysed using HP-SEC. Solid particles were observed in the THF solution, and the samples were therefore placed in an ultrasonic bath for a few seconds to dissolve the solid material.

3.3.4 Thermal degradation of PDMS in bio-oil 3 matrix

The same experiment as in 3.3.3 was conducted again, only with the slight difference that bio-oil 3 was used instead of bio-oil 2. Samples A, B, C and D were placed in an oven at 40 °C at atmospheric pressure over the weekend to evaporate the hexane. The samples were

diluted to 3 mg/ml in THF and analysed using HP-SEC. Pure, untreated bio-oil 3 and heated bio-oil 3 was also analysed as a reference.

3.3.5 Thermal degradation of PDMS in bio-oil 4 matrix

Five samples containing 250 mg of 20% PDMS and 80% bio-oil 4 were prepared in Ace pressure tubes, which were flushed with argon and sealed. The first sample was not heated and used as a reference, while the other four were heated in a sand bath to 250 °C for 30, 60, 90 and 120 minutes respectively. The samples were then cooled down to room temperature in a water bath and later fractionated using the hexane-methanol dissolution method. All samples were placed in a vacuum oven at 40 °C overnight and later diluted to 3 mg/ml in THF and prepared for HP-SEC analysis.

3.3.6 Thermal degradation of PDMS in bio-oil 1 matrix in an autoclave

A 50 ml mixture of roughly 20% PDMS and 80% bio-oil 1 was weighed up and transferred to an autoclave reactor. The autoclave was flushed and later filled with argon to an overpressure of 10 psi (~0.7 Bar). The overpressure is needed in order to take samples from the autoclave during the experiment. The heating was then turned on and a stirring speed of 850 rpm was applied to ensure proper mixing. The heating curve and pressure increase during the experiment was monitored and can be seen in Figure 7. The first sample was taken at 10 minutes during the initial heating phase at 225 °C as a reference. Another sample was taken at 20 minutes when the temperature in the reactor had reached the desired 280 °C. The next 4 samples were then taken every 30 minutes after the 20-minute mark and the final sample was taken after the reactor had cooled down.

The sample sizes were between 600 mg and 1.4 g; therefore, the fractionation was done in larger scale separatory funnels with 15 (+15) ml hexane, 15 ml methanol and 300 µl 25%-ammonia solution. The hexane phases from the samples were collected, transferred to smaller test tubes, and evaporated. The samples were then placed in a 40 °C vacuum oven overnight to ensure complete evaporation of the solvent.

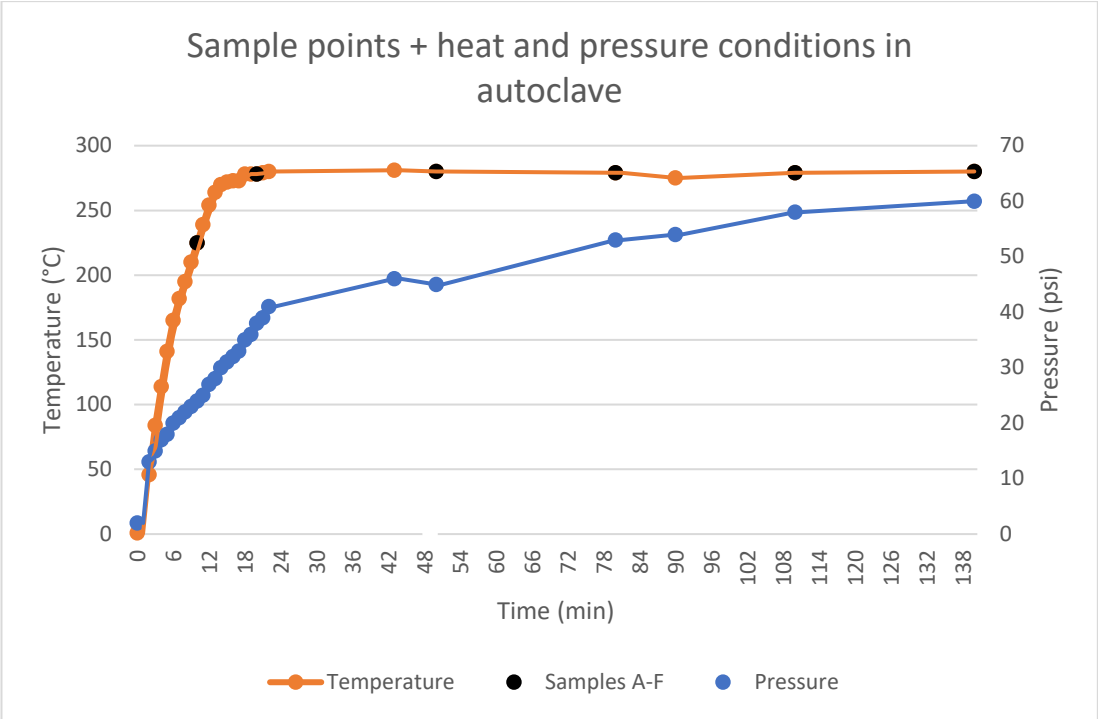


Figure 7. Heating of PDMS + bio-oil 1 (20:80) autoclave experiment conditions.

3.4 Adsorbent effect on degradation

3.4.1 Thermal degradation of PDMS in bio-oil 3 with adsorbent

A silicon-based adsorbent is often introduced before hydrotreatment in industrial processes, and its effect on PDMS degradation was therefore tested. In the first experiment, 250 mg samples of PDMS mixed in a bio-oil 3 matrix with a ratio of 20:80 were prepared in Ace pressure tubes. One weight-% of adsorbent was then added to the samples. The tubes were flushed with argon, sealed, and subsequently heated to 250 °C under constant stirring in a sand bath. The first sample was removed after 30 minutes and the second after 60 minutes. An untreated reference sample was also prepared.

After the reaction, the samples were extracted using the methanol and hexane extraction method. After collecting the hexane phase and evaporating the solvent, the samples were placed in a 40 °C vacuum oven overnight. The samples were then diluted to 3 mg/ml in THF for HP-SEC analysis.

3.4.2 Thermal degradation of PDMS in bio-oil 1 with an adsorbent

The same experimental method and setup as 3.4.1 was deployed in this experiment, only this time bio-oil 1 was used as matrix instead of bio-oil 3. The samples were diluted to 3 mg/ml in THF for HP-SEC analysis.

3.5 PDMS degradation products in bio-oil 3 and bio-oil 4 and the effect of Calcium ions

3.5.1 PDMS degradation products in bio-oil 3 and bio-oil 4

A simple heating experiment of two 250 mg samples, one containing 20% PDMS and 80% bio-oil 3 and the other 20% PDMS and 80% bio-oil 4 was conducted in order to detect PDMS degradation products in these matrixes using GC-MS and GC-FID. The samples were filled with argon, sealed, and then placed in a sand bath at 250 °C under constant stirring for 90 minutes.

3.5.2 Calcium ion effect on PDMS degradation in bio-oil 2

As the matrixes containing the most cations such as calcium and sodium showed the fastest degradation, and as the catalytic effect of calcium ions has been described in literature, the effect of calcium ions on PDMS degradation was tested. Bio-oil 2 was chosen as a matrix as it did not show any significant degradation in the earlier experiments. Two samples containing 250 mg of 20% PDMS and 80% bio-oil 2 were prepared, and 5 µl distilled water was added to the first sample while 5 µl of 5 mg/ml $CaCl_2$ (0,025 mg) was added to the other. The two samples were filled with argon, sealed, and heated in a sand bath at 250 °C under constant stirring for 90 minutes. The samples were then diluted to 3 mg/ml in THF and prepared for HP-SEC analysis.

4 RESULTS AND DISCUSSION

4.1 Preliminary experiments

4.1.1 Heating of PDMS in bio-oil 1 matrix

The initial experiment (3.2.1) where pure PDMS was heated to 240 °C showed no degradation as expected, as the onset degradation temperature in inert atmospheres is somewhere around 400 °C. In this experiment, where PDMS was heated in a bio-oil 1 matrix, at least some degradation was expected to occur in accordance with the studies conducted by Anton Örn.[52] Therefore, an initial residence time of 3 hours in the reactor was chosen to ensure that the HP-SEC results would indicate some degradation.

High MW PDMS elutes at around 14 minutes, while the bio-oil 1 components will show up between 19 and 23 minutes. In the resulting HP-SEC chromatogram (Figure 8), practically all of the initial high MW PDMS was degraded into presumably smaller components after 3 hours of residence time. In this chromatogram, only the steryl esters at around 20 minutes were seen from the bio-oil 1 components, as the other components were transferred to the methanol phase during the extraction.

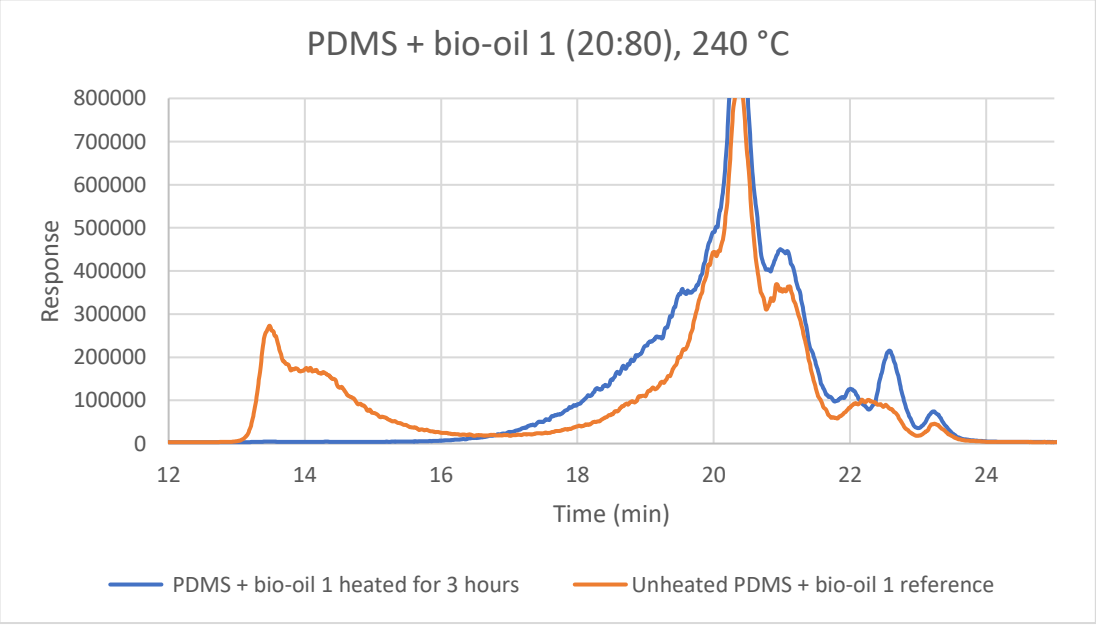


Figure 8. HP-SEC chromatogram of 20% PDMS in bio-oil 1 heated to 240 °C for 3 hours and an unheated reference sample.

4.1.2 Catalytic efficiency of bio-oil 1 on PDMS degradation

As a catalytic effect of bio-oil 1 on PDMS degradation could be demonstrated in the previous experiment, this experiment was conducted to obtain a picture of to what extent bio-oil 1 catalyses the degradation.

With 80% PDMS and 20% bio-oil 1, the resulting HP-SEC chromatogram (Figure 9) showed a clear degradation of the high MW PDMS, with the elution peak at 14 minutes decreasing and shifting to the right with increased time. The large spike visible at the beginning of the high MW PDMS peak is caused by the initial analyte not interacting with the column as it should, giving a sharp elution peak of molecules that have no retention in the columns. This phenomenon can be seen in all of the chromatograms. The shift towards the right indicated a shortening of the polymer chain, however, large amounts of high MW PDMS were still detectable, even after 3 hours of residence time at 260 °C, suggesting that larger amounts of bio-oil 1 are required for the high MW PDMS to fully degrade, even with long residence times.

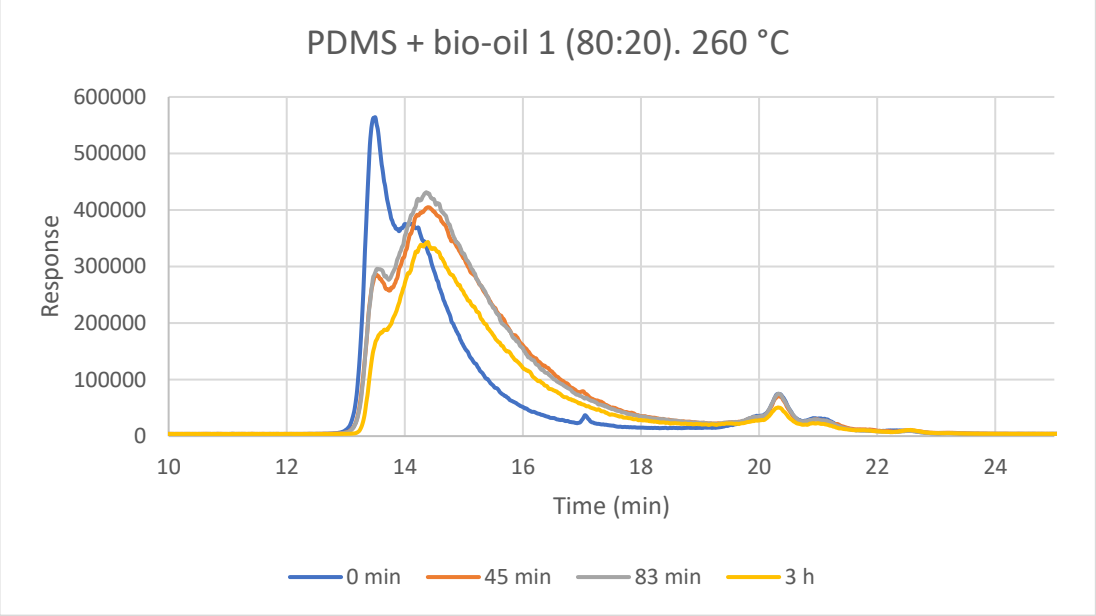


Figure 9. HP-SEC chromatogram of PDMS + bio-oil 1 (80:20), 260 °C.

4.2 Thermal degradation of PDMS

4.2.1 Thermal degradation of PDMS in bio-oil 1 matrix with long residence time

Similarly to the preliminary heating experiment 3.2.2, this experiment involved heating PDMS in bio-oil 1 in a 20:80 ratio to 250 °C for 3 hours. This was done in order to try and replicate the results from the previous experiment, introduce stirring of the mixture for more representative results, compare fractionated and extracted samples from unfractionated ones, and to try and identify the degradation products.

The HP-SEC chromatogram of the unfractionated samples (Figure 10) shows both PDMS and all the bio-oil components. The steryl esters eluted at 20 minutes and the fatty- and resin acids eluted at around 22 and 23 minutes. Here, the high MW PDMS at 14 minutes again seems to have fully degraded into smaller components. In contrast, the HP-SEC results of the more concentrated and fractionated samples (Figure 11) showed that there was still about 20% of the original amount of high MW PDMS left after 3 hours, calculated from the peak areas. This might be due to unreacted PDMS that has not been in contact with the bio-oil or simply due to differences in concentration. Both samples show that degradation is clearly occurring, but in order to gain a more complete understanding of the fate of PDMS, the use of the hexane-methanol fractionation method is preferable.

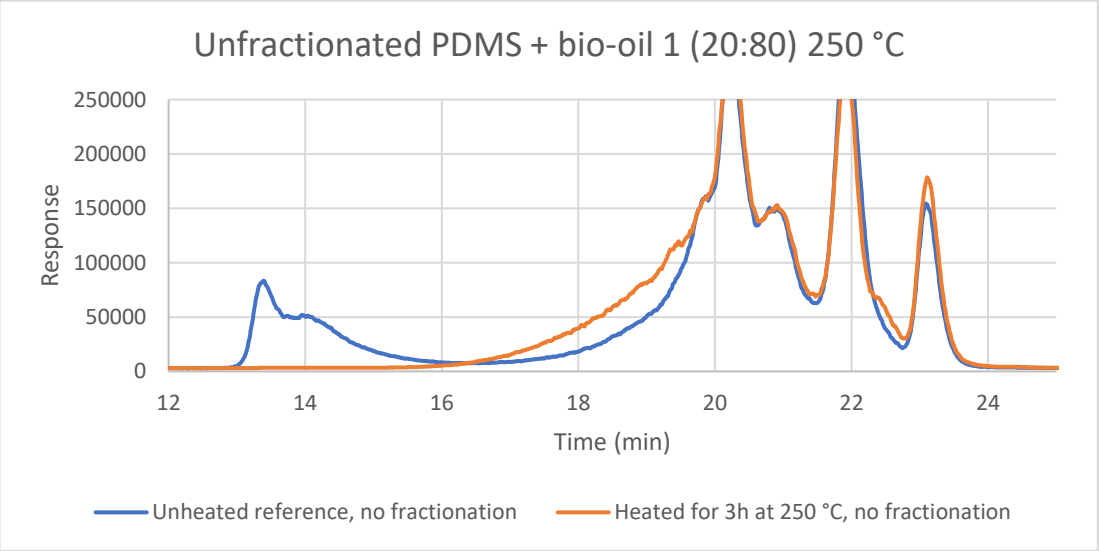


Figure 10. HP-SEC chromatogram of unfractionated PDMS + bio-oil 1 samples (20:80), 250 °C.

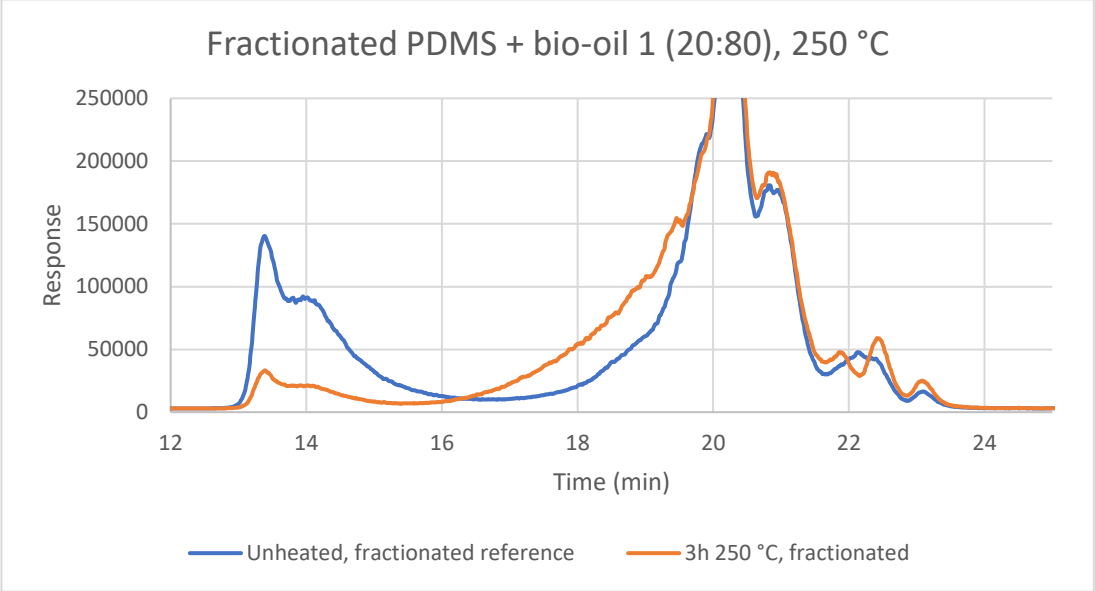


Figure 11. HP-SEC chromatogram of fractionated PDMS + bio-oil 1 samples (20:80), 260 °C.

A short column GC analysis was also conducted on an unfractionated sample and on the hexane phase of a fractionated sample. Both samples were silylated using the method described in 3.1.3. In the resulting chromatograms (Figure 12), the unfractionated sample is depicted in black and the fractionated sample in blue. The peaks at 18–21 min are steryl esters, the peaks at 5.2–6.6 minutes are fatty acids and the peaks at 6.6–8 minutes are resin acids. Both the fatty acids and resin acids have mostly disappeared in the fractionated sample. This is because they form salts with the ammonia solution and end up in the methanol phase. What is interesting is the peak at around 3 minutes. This is an unknown peak which is not present in pure bio-oil 1 chromatograms and could therefore be of interest.

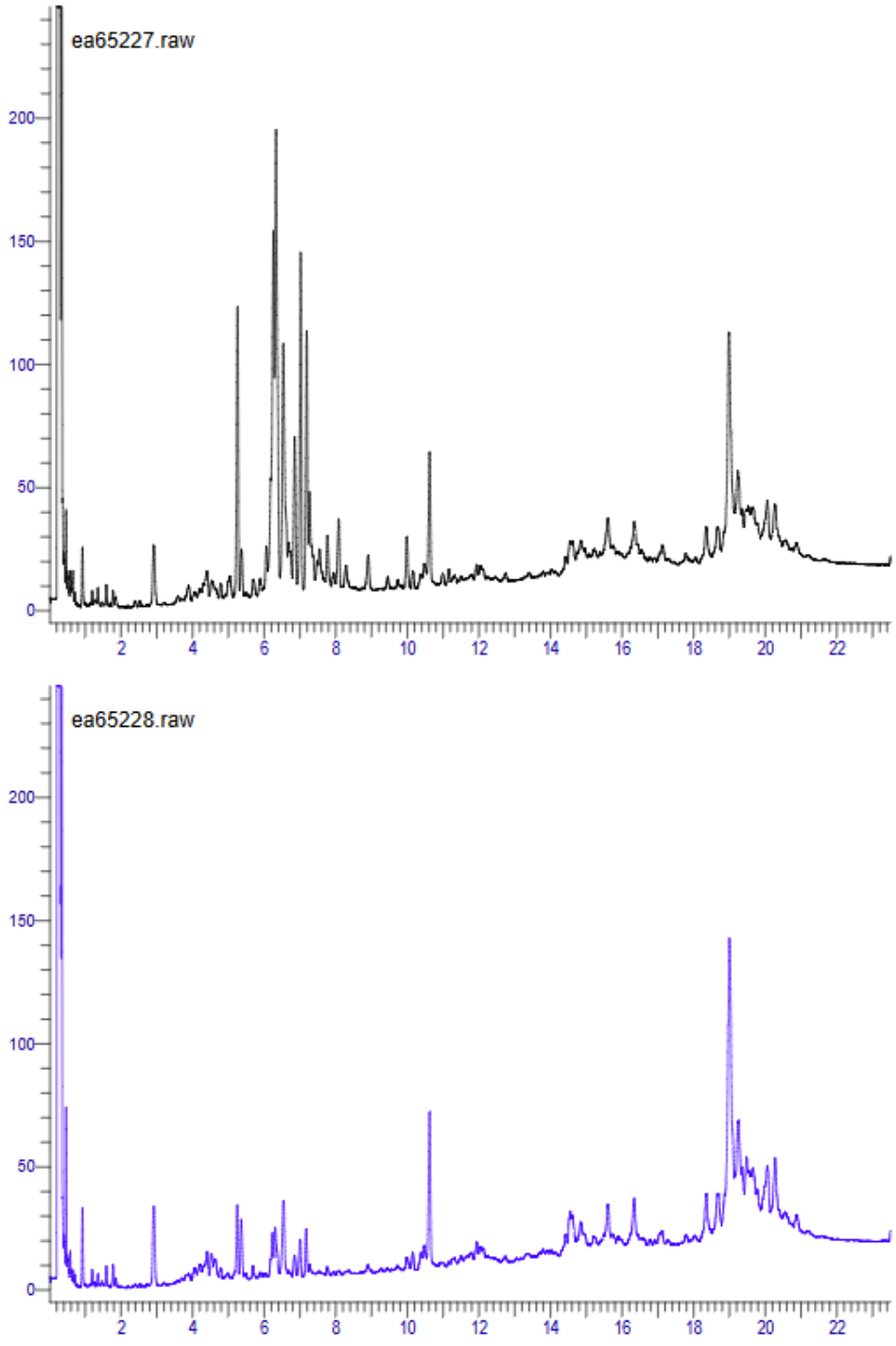


Figure 12. Short column GC of an unextracted PDMS + bio-oil 1 sample (black) and the hexane phase of a fractionated PDMS + bio-oil 1 sample (blue).

An NMR analysis on the heated PDMS + bio-oil 1 sample (green) was conducted and compared to a sample of PDMS + bio-oil 1 spiked with D3 and D4 cyclosiloxanes (red). The results from the ^{1}H-NMR (Figure 13) show that D3 and D4 have formed as degradation products from high MW PDMS. The NMR results are also consistent with literature

discussed in 2.2.4, where the chemical shift of D3 and D4 is said to be at around 0.17 and 0.9 ppm, respectively. The coupling from the siloxane chain is expected to be at around 0.075 ppm.[29] In this spectra, a peak can be seen at 0.07–0.08 ppm which potentially could be from the siloxane chain or some other degradation products. By running a sample of pure high MW PDMS (blue), the siloxane chain could be observed at around 0.07–0.08 ppm, although the concentration of the sample was somewhat high for a more exact chemical shift.

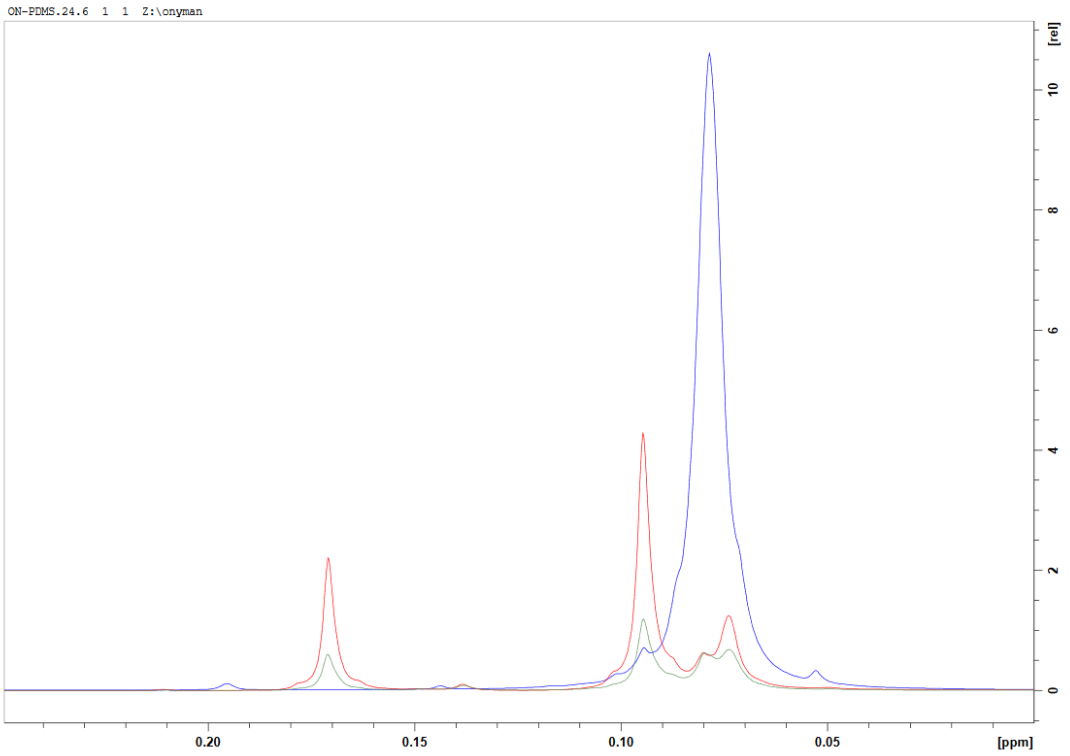


Figure 13. 1H-NMR of PDMS + bio-oil 1 (green), PDMS + bio-oil 1 spiked with D3 and D4 (red) and pure untreated high MW PDMS (blue).

4.2.2 Thermal degradation of PDMS in bio-oil 1 matrix with shorter residence time

In industrial processes, the residence times in the reactors are typically shorter than three hours. The thermal degradation of PDMS in a bio-oil 1 matrix with shorter residence times was therefore investigated. Residence times of 30, 60 and 90 minutes where chosen and samples with 20% PDMS and 80% bio-oil 1 were heated to 250 °C. The samples where fractionated using the hexane-methanol dissolution method.

The HP-SEC results can be seen in Figure 14. After only 30 minutes, the high MW PDMS peak at around 14 minutes has flattened and shifted to the right, meaning it has started to

degrade. After 90 minutes, practically all of the high MW PDMS was degraded (Figure 15) and signals from smaller components seen between 15 and 18 minutes in the HP-SEC chromatogram were increased. There is, however, an overlap between the bio-oil 1 components that start to elute at around 18 minutes and the formed degradation products, making it difficult to distinguish the elution time of the final degradation products.

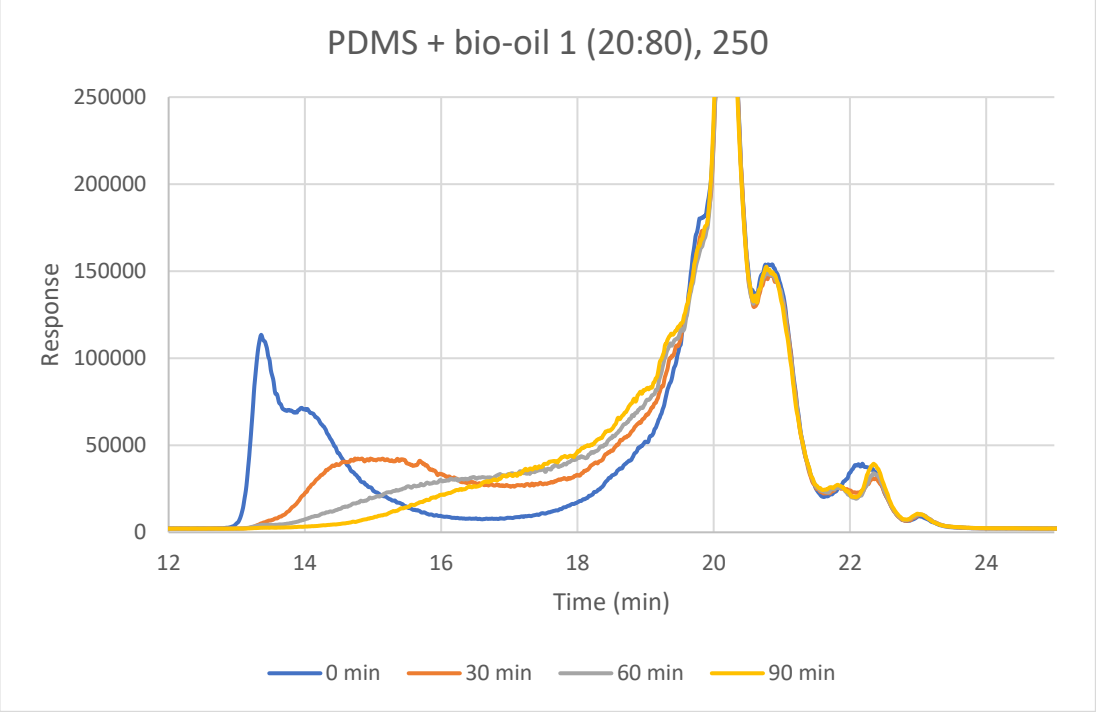


Figure 14. HP-SEC chromatogram of PDMS + bio-oil 1 (20:80), 250 °C.

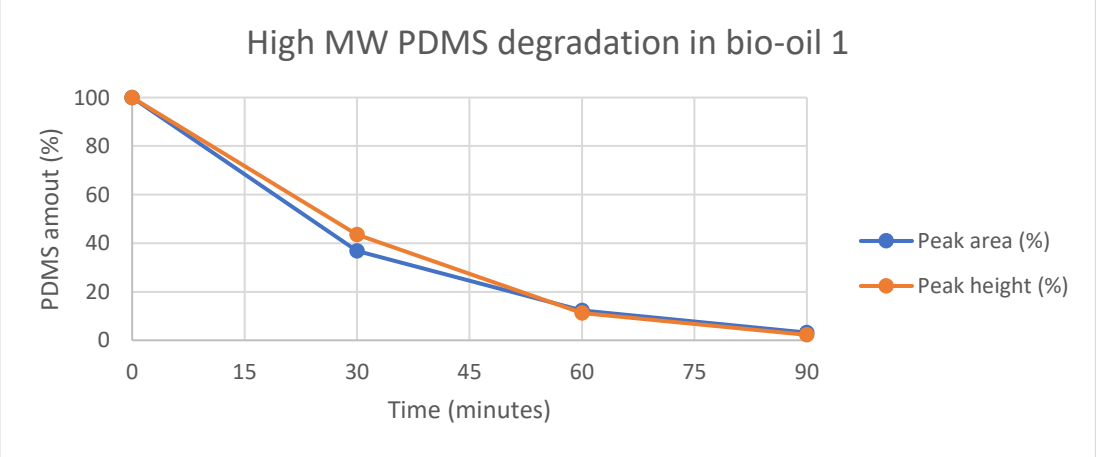


Figure 15. Degradation rate of PDMS in bio-oil 1, calculated from peak area and height in the HP-SEC chromatogram.

4.2.3 Thermal degradation of PDMS in bio-oil 2 matrix

At this point, some of the possible degradation products of PDMS in bio-oil 1 have been observed, namely D3 and D4. However, the cause and the mechanism of this catalytic behaviour was still unknown. Therefore, the thermal degradation of PDMS in 3 other selected bio-oils, bio-oil 1, bio-oil 2 and bio-oil 3, was investigated as a comparison. If the effect is the same, the catalytic effect must be due to some components that are present in all of these matrices.

The resulting HP-SEC chromatogram from the heating of PDMS in bio-oil 2 (Figure 16) indicated that some degradation of high MW PDMS is taking place, as the elution peak at around 14 minutes was gradually becoming smaller. However, the degradation was not very significant, with a decrease of only 10 weight-% high MW PDMS after 90 minutes (Figure 17). The high MW PDMS peak did not seem to shift to the right as much as in the experiments with bio-oil 1 either. This suggested that a component not present in bio-oil 2 was causing the catalytic effect of bio-oil 1.

Something else that could be observed was the elution peak at 18 minutes which was increased with time. This was probably due to triglycerides from bio-oil 2 that were polymerizing. This would also explain the formation of larger particles, which were seen in the THF solution when preparing the samples for HP-SEC.

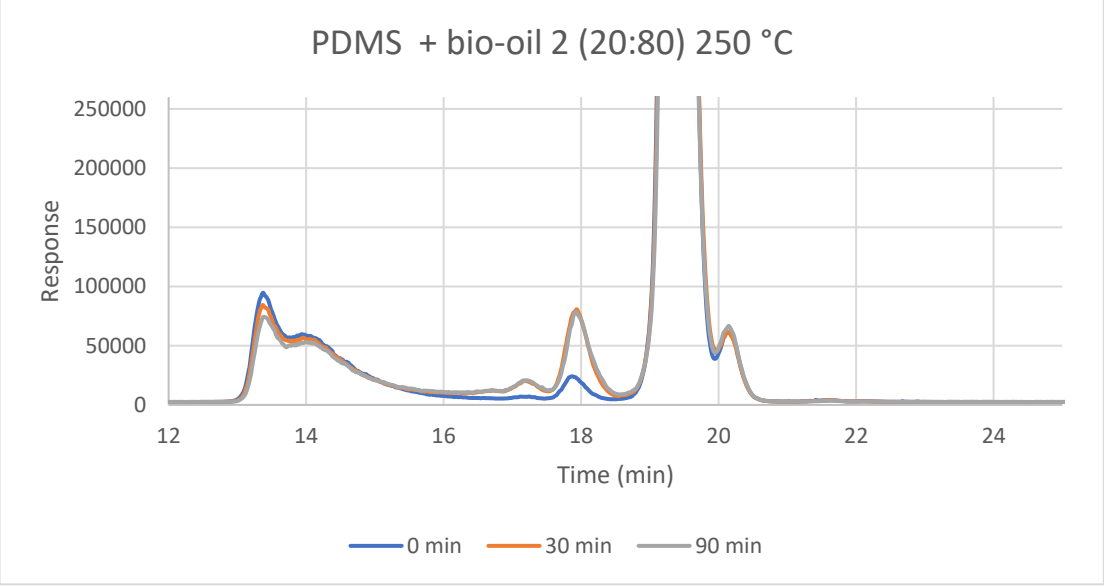


Figure 16. HP-SEC chromatogram of PDMS+ bio-oil 2 (20:80), 250 °C.

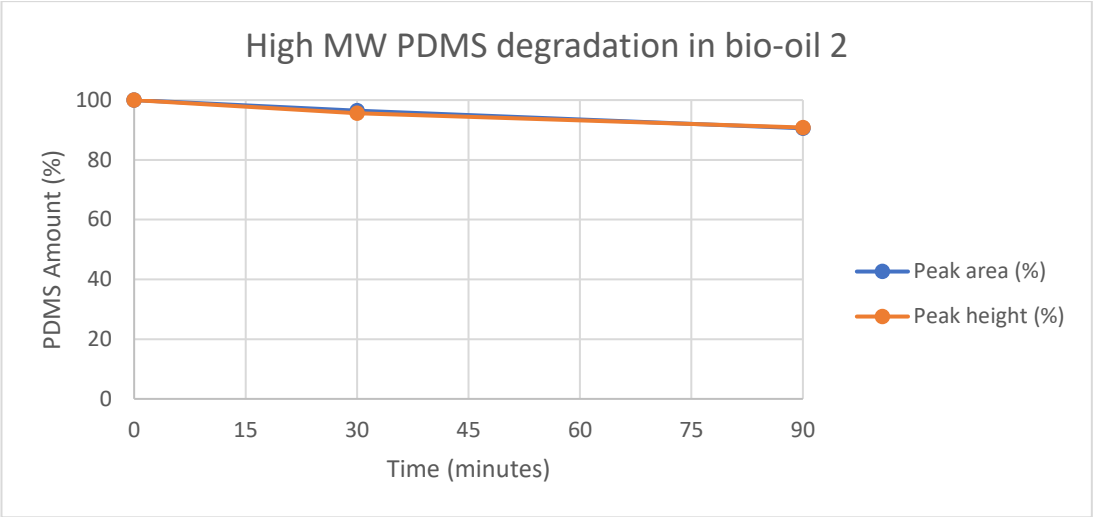


Figure 17. Degradation rate of PDMS in bio-oil 2, calculated from peak area and height in HP-SEC chromatogram.

4.2.4 Thermal degradation of PDMS in bio-oil 3 matrix

The thermal degradation of PDMS in bio-oil 3 (Figure 18) yielded different results compared to those of PDMS in bio-oil 2, even though their compositions are similar. In the HP-SEC results, degradation of PDMS was again observed from the elution peak at 14 minutes which was both decreasing and shifting to the right with increased residence time. The degradation was significant, albeit slightly slower than in the bio-oil 1 matrix, with a peak area decrease of ~35% and height decrease of 70% after 90 minutes (Figure 19). There was still a large number of products high MW compounds that eluted at 14–15 minutes even after 90 min of residence time, whereas in bio-oil 1 there were practically none. These findings suggest that either the catalytic component is limited in this matrix, or that another, slower degradation mechanism is taking place in the bio-oil 3 matrix compared to the other matrices.

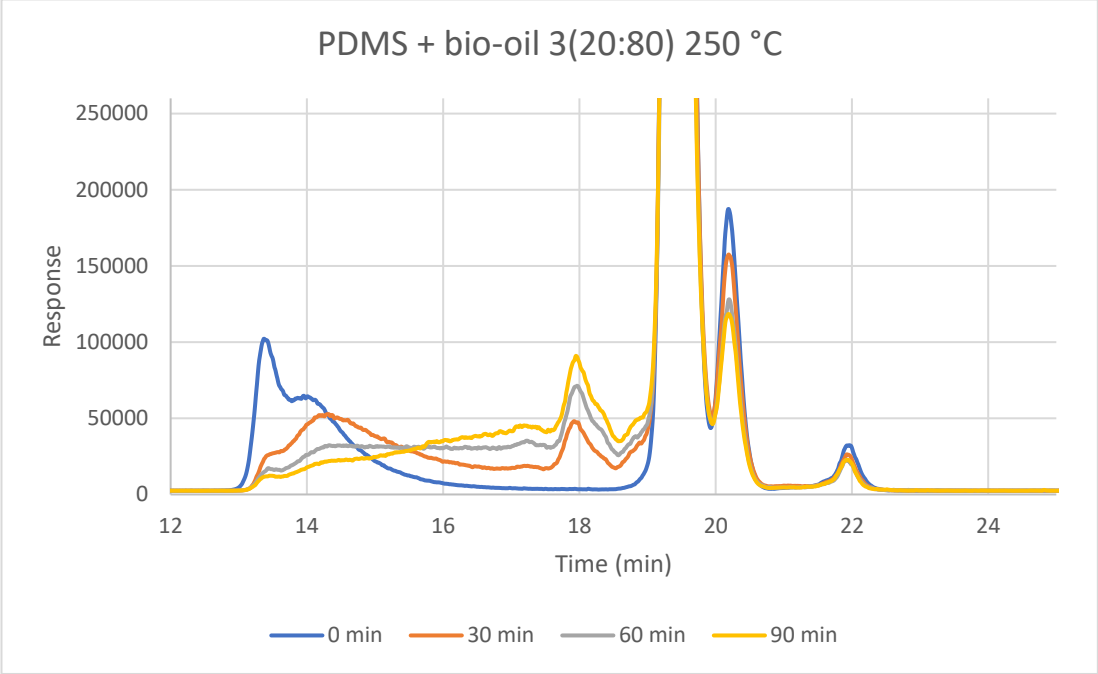


Figure 18. HP-SEC chromatogram of PDMS + bio-oil 3 (20:80), 250 °C.

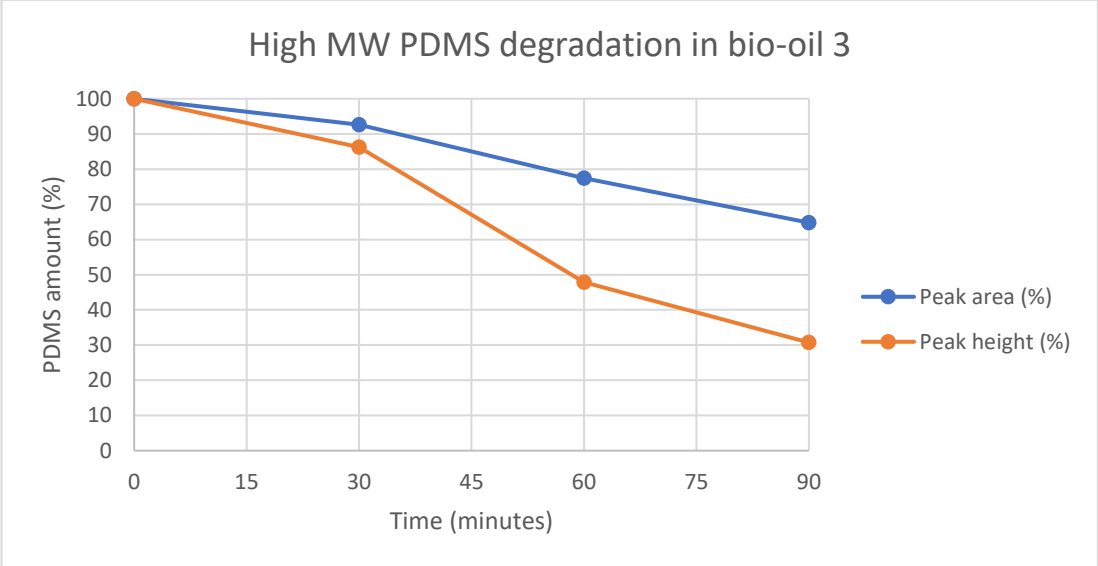


Figure 19. Degradation rate of PDMS in bio-oil 3, calculated from PDMS peak area and height in HP-SEC chromatogram.

Another HP-SEC was run on pure bio-oil 3 to verify that the intermediate products between 15 and 17 minutes did not stem from the bio-oil 3 components (Figure 20). From the resulting chromatogram, an increase of the elution peak at 18 minutes was observed. This

was probably the same phenomenon of polymerizing triglycerides, which was also seen in the previous experiment. This chromatogram also showed no elution products between 15 and 17 minutes, reinforcing the suspicion that the products of intermediate size in Figure 18 are in fact PDMS breakdown products.

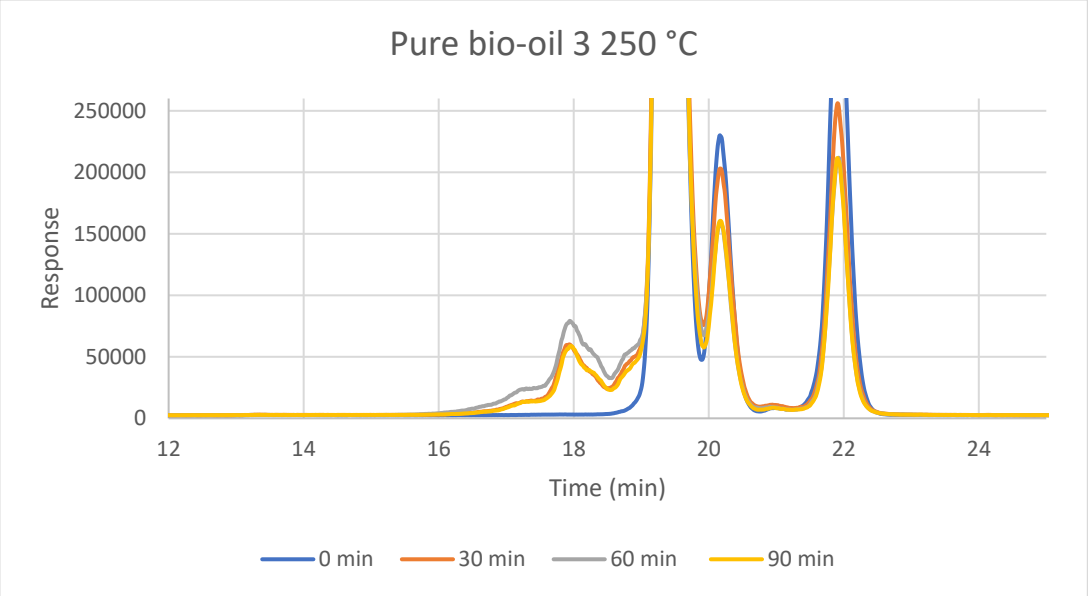


Figure 20. HP-SEC chromatogram for the heating of pure bio-oil 3.

4.2.5 Thermal degradation of PDMS in bio-oil 4 matrix

The thermal degradation of PDMS in bio-oil 4 (Figure 21) was similar to that of PDMS in bio-oil 1, but at an even faster rate. The chromatogram showed clear degradation of PDMS with the elution peak of high MW PDMS at 14 minutes decreasing in size and shifting to the right with time. Already after 60 minutes, all of the high MW PDMS has degraded into smaller components, presumably the same components as in bio-oil 1. The degradation kinetics can be seen in Figure 22.

Note that the scale is not the same as in the other HP-SEC chromatograms. The bio-oil 4 components were easier to separate from PDMS compared to previous experiments and the samples were therefore more concentrated.

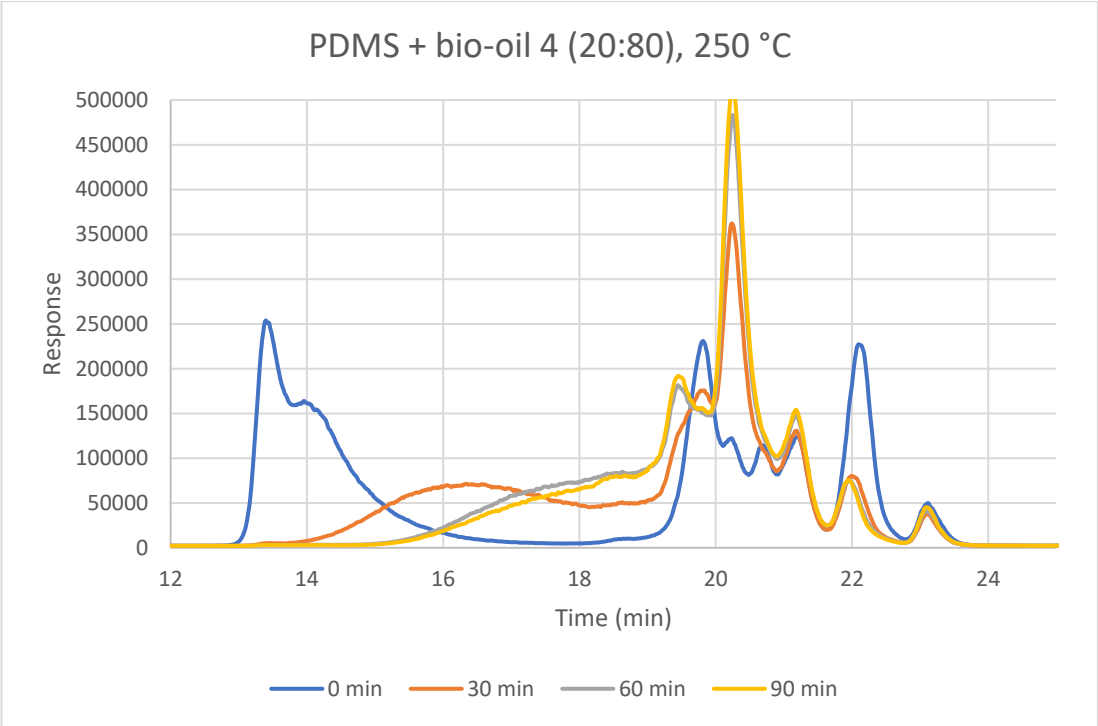


Figure 21. HP-SEC chromatogram of PDMS in bio-oil 4 (20:80), 250 °C.

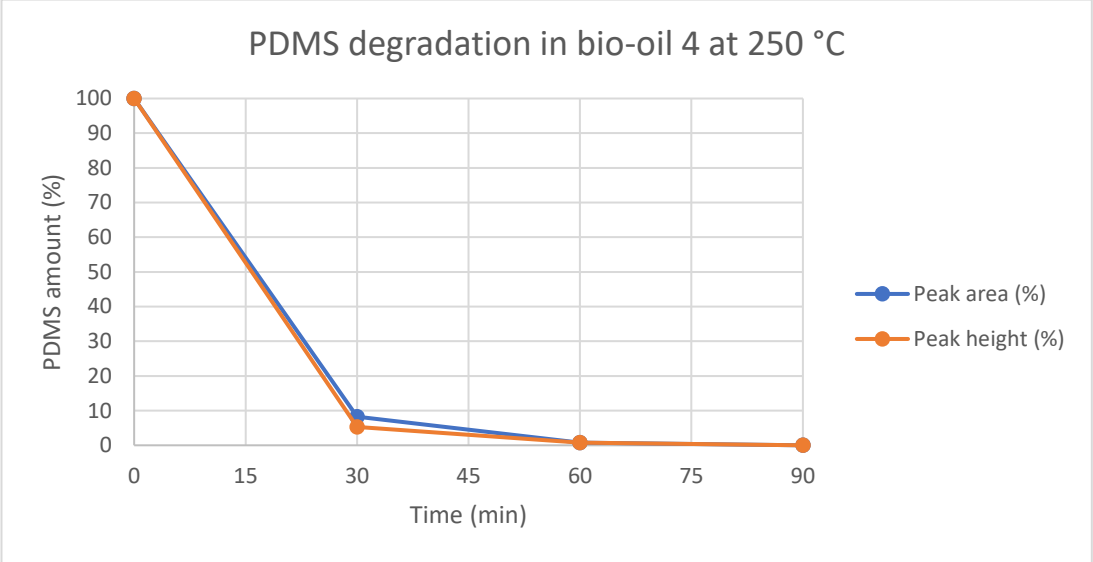


Figure 22. PDMS degradation rate in bio-oil 4 at 250 °C, calculated from peak area and height.

4.2.6 Thermal degradation of PDMS in bio-oil 1 matrix in an autoclave

As the temperatures in the industrial processes often exceed 250 °C, the degradation was investigated in larger scale (50 ml) and at higher temperature.

The HP-SEC analysis for the scaled-up autoclave reactor experiment at 280 °C (Figure 23) resulted in clear signs of degradation with the elution peak at 14 minutes growing gradually smaller and shifting slightly to the right with increased reaction time. The degradation looked very similar to the small-scale reactions at 250 °C, and a complete degradation of the high MW PDMS was observed after 120 minutes (Figure 24).

Sample A was taken at 225 °C before the reactor had reached 280 °C and was larger than the other samples (~1.2 g compared to ~600 mg). Sample B, on the other hand, was taken as soon as the temperature reached 280 °C, followed by a sample every 30 minutes (C, D, E and F) and the last sample (G) after the reaction had cooled down. This sample size difference might have affected the workup, causing peak A to show as slightly smaller than peak B in the chromatogram.

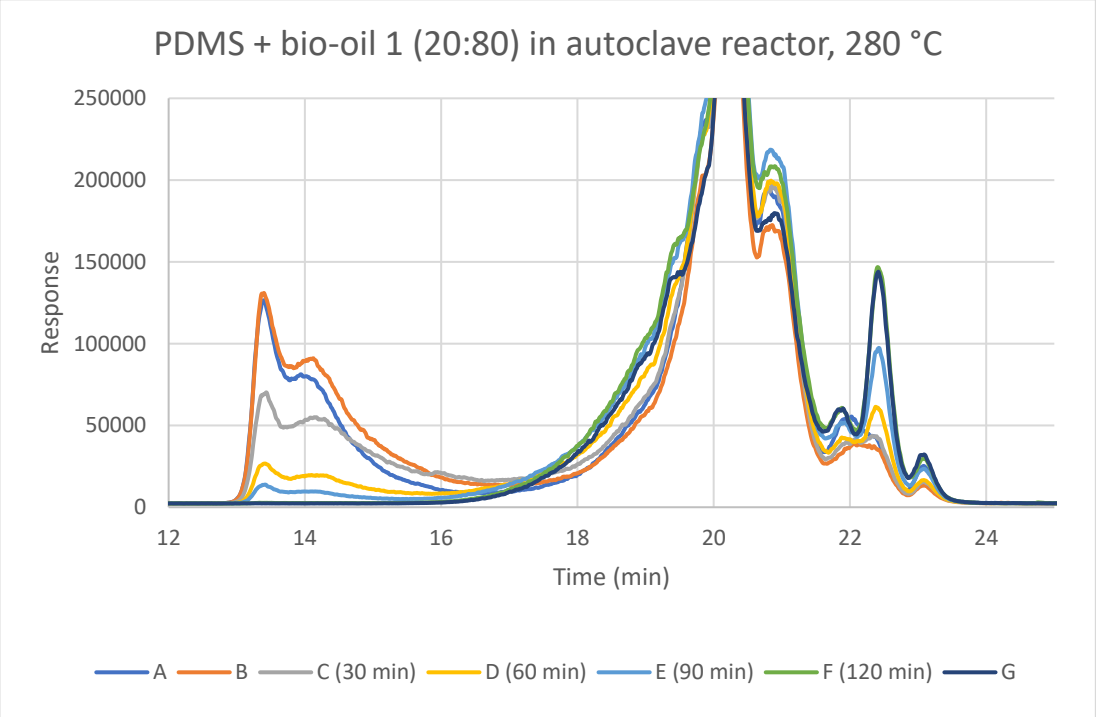


Figure 23. HP-SEC results of the thermal degradation of PDMS in bio-oil 1 at 280 °C in an autoclave.

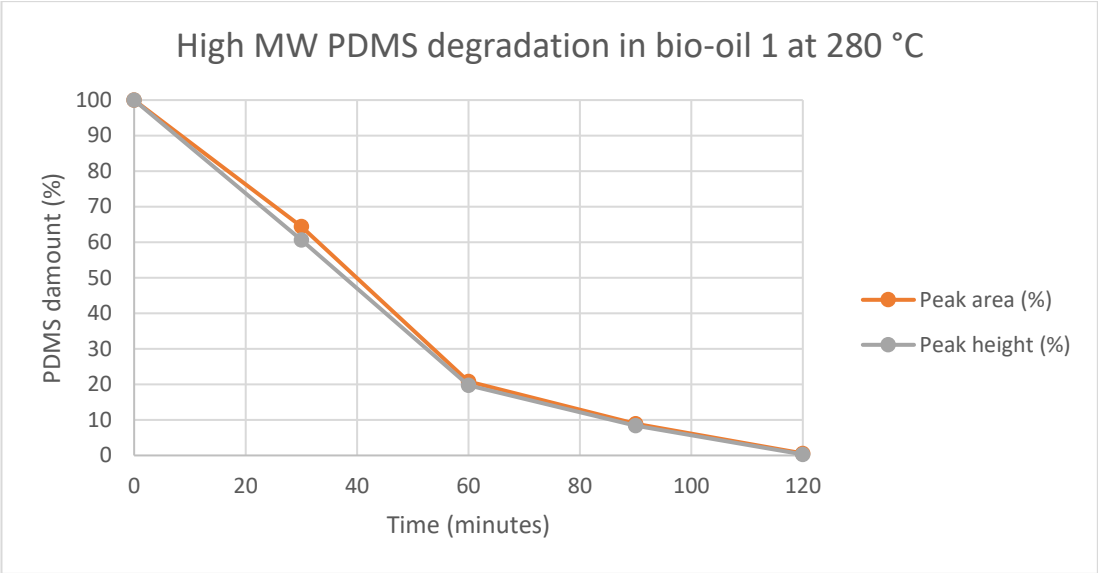


Figure 24. Degradation rate of PDMS in bio-oil 1 at 280 °C calculated from PDMS peak area and height in the HP-SEC chromatogram.

A ^{1}H-NMR analysis of sample G was compared to D3, D4 and PDMS, which can be seen in Figure 25. Due to the very specific chemical shifts of organosilicon compounds with methyl groups, the presence of D3 and D4 can clearly be observed on ^{1}H-NMR. The results were also in accordance with those of literature. The peak at 0.8 ppm does not entirely match with the PDMS peak, suggesting the presence of other silicon compounds.

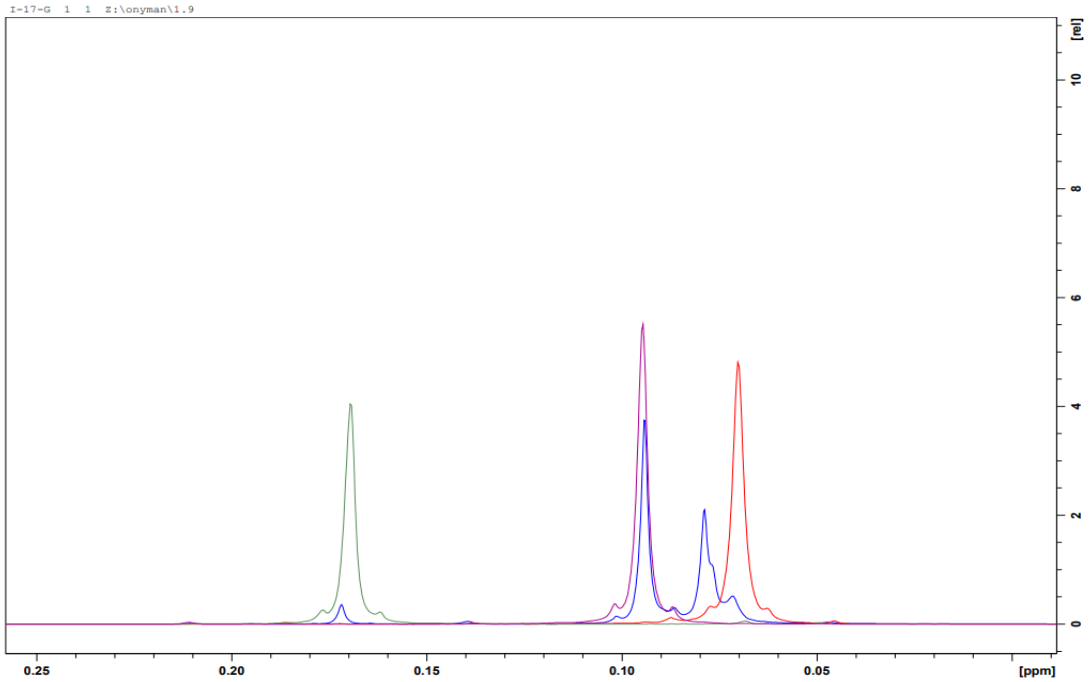


Figure 25. ^{1}H-NMR of Sample G (blue), D3 (green), D4 (purple) and PDMS (red).

Sample G was also analysed using GC-MS, both unsilylated and silylated. The results are shown in Figure 26 and Figure 27. Not only could D3 and D4 be detected, but an entire range of cyclosiloxanes, ranging from D3 to D8. However, D3 was not visible in Figure 26 or Figure 27, because it eluted before 3 minutes.

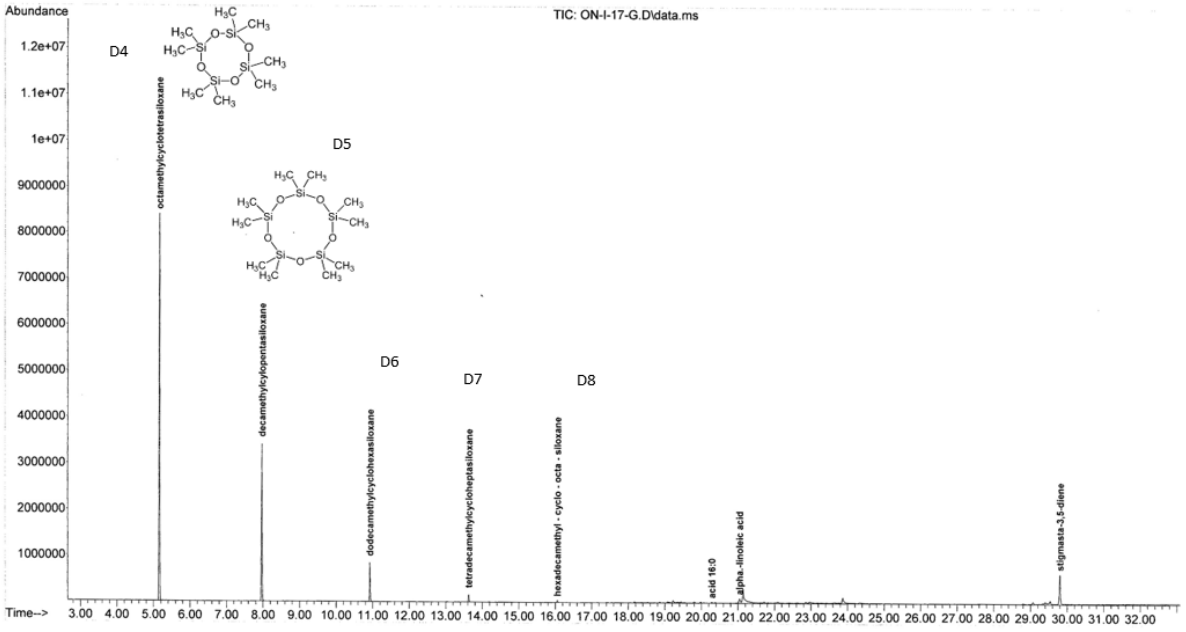


Figure 26. GC-MS on sample G, unsilylated (modified for clarification).

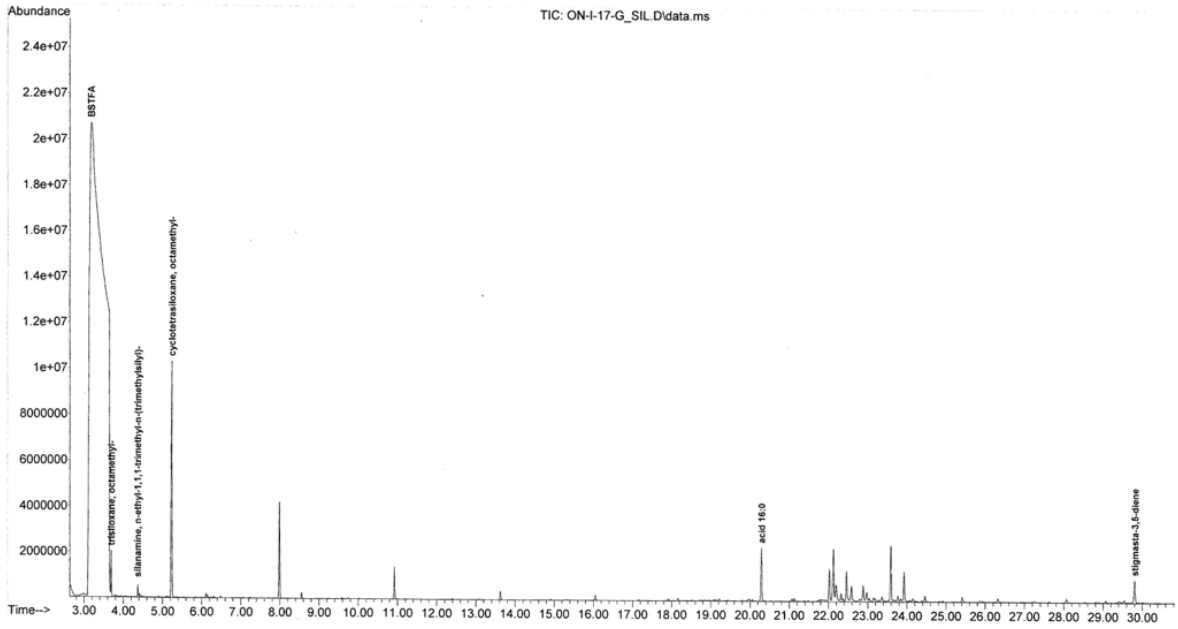


Figure 27. GC-MS on sample G, silylated.

The same thing could be observed from a long-column GC-FID analysis (Figure 28). Here the relative amounts can be seen more clearly, and by comparing the result to a known amount of D4, the following distribution could be calculated:

Compound	Weight-% of total sample
D3	0.93%
D4	8.78%
D5	3.75%
D6	0.89%
D7	0.17%
D8	0.05%
	14.57%

D4 is the most abundant product at 8.78%, followed by D5 at 3.75%, D3 at 0,93 and decreasing amounts of D6–D8. These cyclosiloxanes are probably giving rise to the unknown peak in the NMR spectrum. The presence of these degradation products also indicates the mechanism of degradation, as these products are the same products that form from the back-biting reactions described in 2.2.2. The fact that D4 is the most is the abundant product, and not D3, might be related to the size of the catalytic component. If the reaction is in fact metal catalysed, and thus cation dependent, which was suggested in 2.2.3, then it could be entirely possible that metal residues in bio-oil 1 are driving the reaction by cyclisation of the siloxane chain for these back-biting reactions. D3 cyclosiloxane rings could in that case be too small for a cation to fit inside. Another thing to note is that some of the D3 could potentially be lost from evaporation during the split injection to the GC, however, NMR results confirm that D4 is nonetheless more abundant.

To confirm these results, the same sample was analysed with ICP-MS. The total amount of silicon in the sample was determined to be 5.6%. If we assume that most of the products are in the form of D4, the amount of silicon can be calculated by dividing the total MW of silicon in D4 with the total MW of D4 in the following manner:

$$\frac{\left(28.0855\frac{g}{mol}\right)*4}{\left(15.999\frac{g}{mol}*4\right)+\left(12.011\frac{g}{mol}*8\right)+\left(24*1.00784\frac{g}{mol}\right)+\left(28{,}0855\frac{g}{mol}*4\right)}$$

$$= 0.378748$$

This can then be multiplied to the amount of cyclosiloxanes detected in the GC-FID to yield the total amont of silicon:

$$0.378748 * 14.57\% \approx 5.52\%$$

This is in agreement with the 5.6% detected by the ICP-MS, confirming the accuracy of the results.

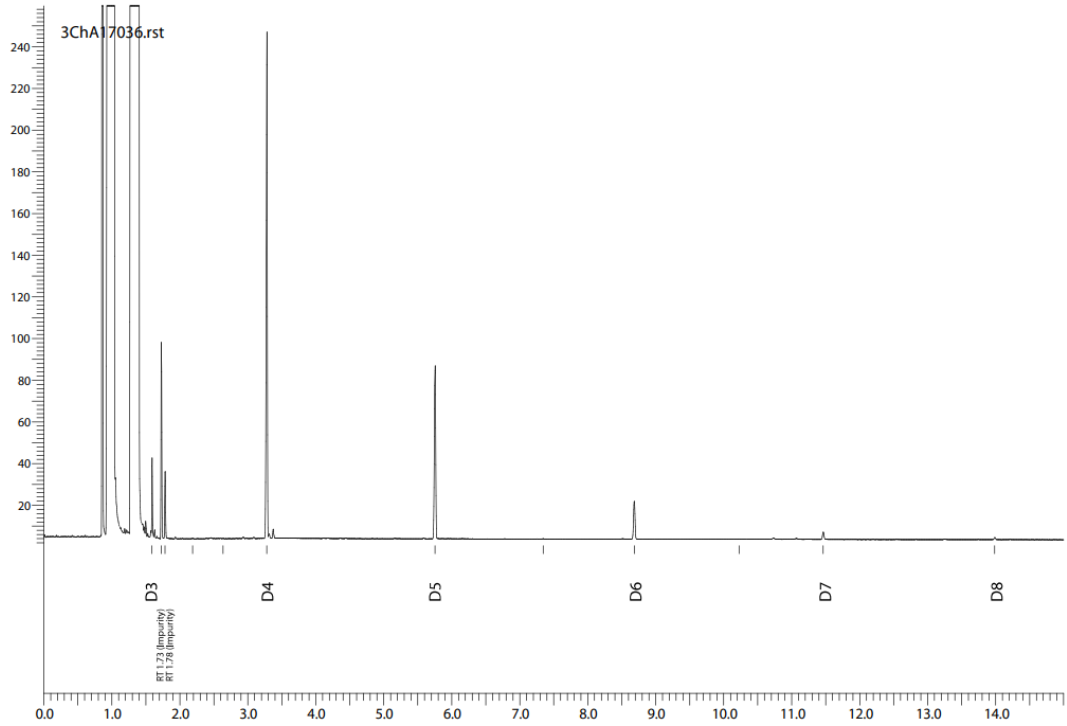


Figure 28. GC-FID result of sample G.

4.2.7 Thermal degradation of PDMS in bio-oil 3 with an adsorbent

Compared to the degradation of PDMS in bio-oil 3 (4.2.4), no significant changes in the degradation behaviour were observed from the HP-SEC chromatogram of PDMS in bio-oil 3 with an adsorbent (Figure 29). The results are presented on top of each other in Figure 30, and no significant difference in kinetics or mechanism could be observed.

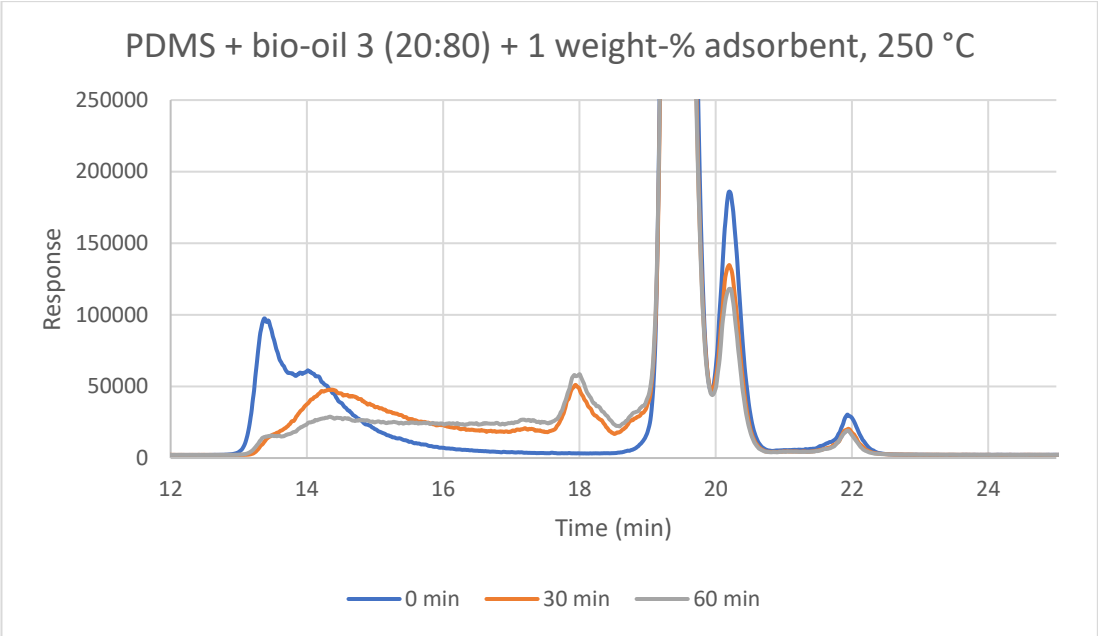


Figure 29. HP-SEC chromatogram of PDMS + bio-oil 3 (20:80) + 1 weight-% adsorbent.

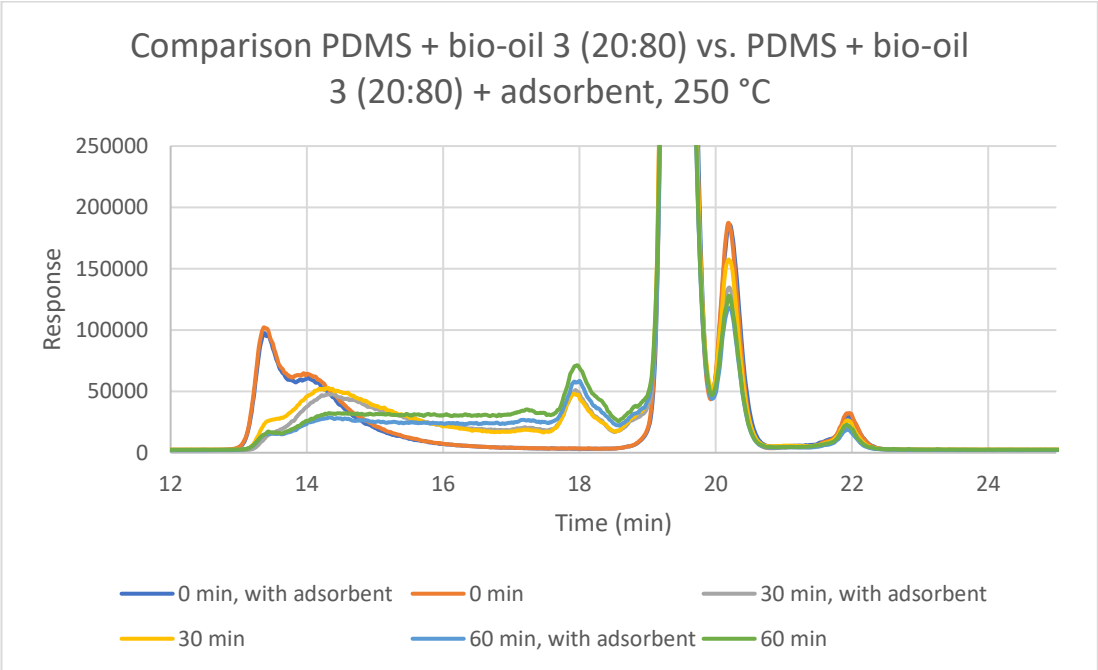


Figure 30. HP-SEC chromatogram comparison of PDMS + bio-oil 3 with and without adsorbent.

4.2.8 Thermal degradation of PDMS in bio-oil 1 with an adsorbent

The thermal degradation of PDMS in bio-oil 1 with an adsorbent can be seen in Figure 31. No significant changes in the degradation behaviour were observed for when the adsorbent

was introduced. In Figure 32, the results are stacked on top of the results from 4.2.2, which is the degradation of PDMS in bio-oil 1 without adsorbent. No significant difference could be observed.

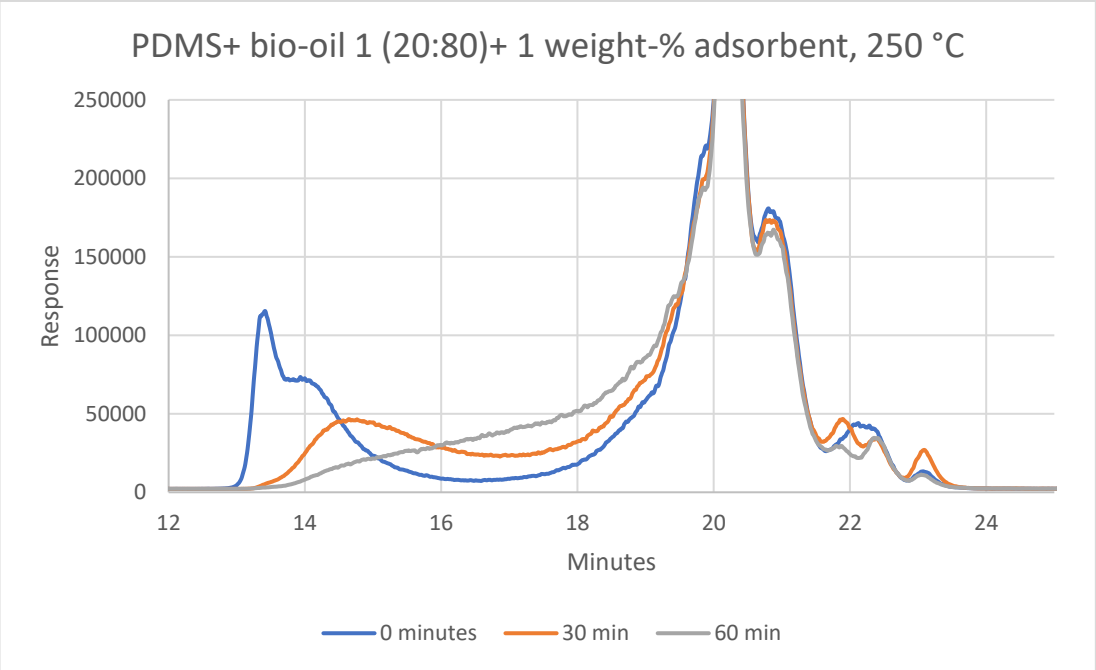


Figure 31. HP-SEC chromatogram of PDMS + bio-oil 1 (20:80) + 1 weight-% adsorbent.

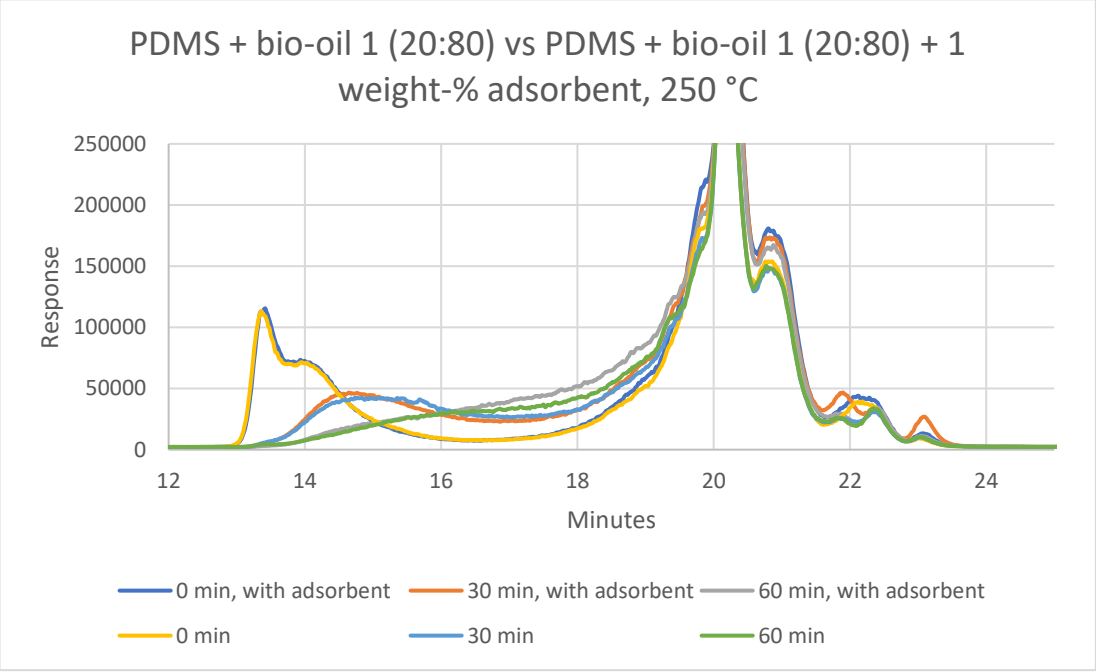
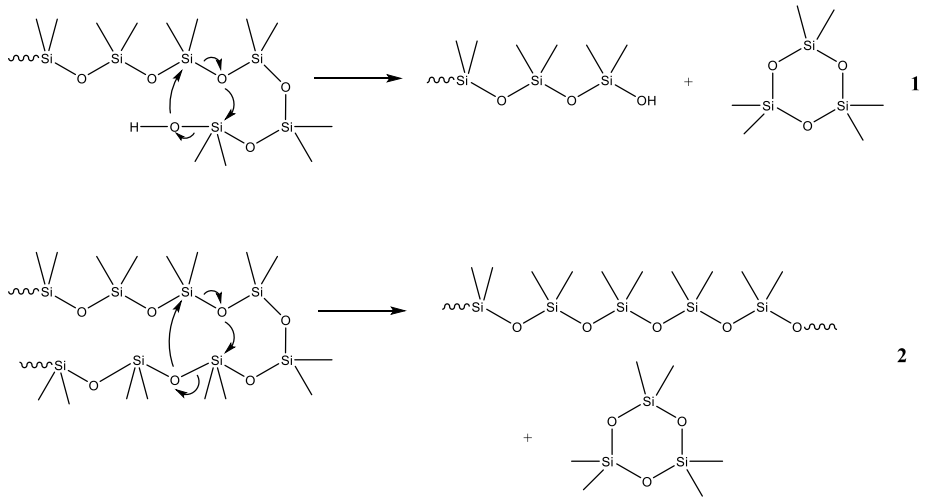


Figure 32. HP-SEC chromatogram comparison of PDMS + bio-oil 1 with and without adsorbent.

4.2.9 PDMS degradation products in bio-oil 3 and bio-oil 4

In the experiments with PDMS in bio-oil 1, cyclic oligomers had been detected, suggesting that the dominating mechanisms of degradation are the back-biting reactions (Scheme 10), either from the chain end (1) or from folding of the polysiloxane chain (2).



Scheme 10. Polysiloxane back-biting reactions.

To find out if this is the dominating mechanism in the other matrixes as well, a heating experiment of PDMS in bio-oil 3 and in bio-oil 4 was conducted. Analysis of the degradation products was done using GC-MS and GC-FID. In the GC-FID results (Figure 33), the two chromatograms are overlaid one another, with the topmost chromatograph representing PDMS in bio-oil 4 and the bottommost graph representing PDMS in bio-oil 3. The results show that also in bio-oil 4, cyclosiloxanes ranging from D3–D8 are formed as degradation products. Trace amounts of these cyclosiloxanes were also detected in bio-oil 3. The percentage of cyclosiloxanes, based on GC-FID peak areas, are the following:

Compound	Bio-oil 3	Bio-oil 4
D3	0.04%	3.23%
D4	0.03%	2.62%
D5	0.02%	0.67%
D6	0.02%	0.22%
D7	0.01%	0.07%
D8	0.01%	0.03%
Sum	0.14%	6.85%

These amounts do not quite add up to the 20% of PDMS the sample was loaded with. The most probable cause for this is due to the relatively short reaction time of 90 minutes, meaning some high to medium-weight PDMS might still be present in sample. However, it could also be due to some other competing mechanism that forms other compounds. If the latter is the case, one reason for why these compounds have not been detected could be due to the preparation of the samples. The samples are dissolved in hexane for GC analysis, meaning possible water-soluble products that might have formed will not show in these chromatograms.

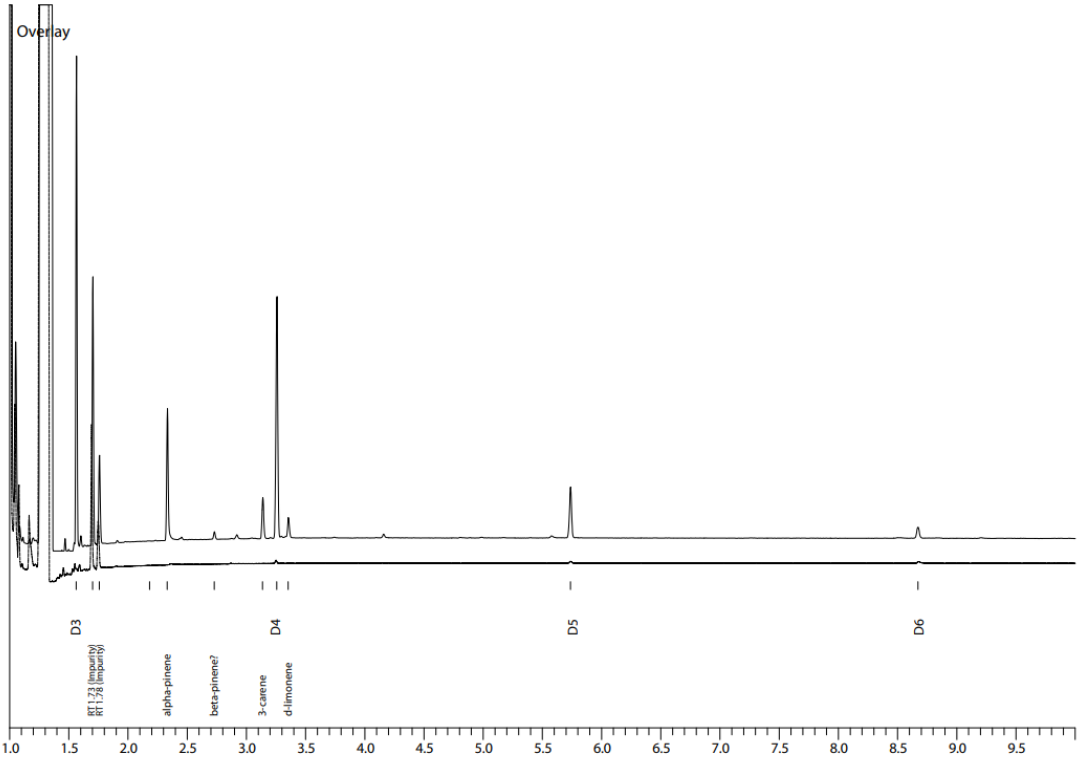


Figure 33 GC-FID results of PDMS + bio-oil 4 (top) and PDMS + bio-oil 3 (bottom) heated for 90 minutes at 250 °C.

The GC-MS analysis (Figure 34) did not yield very reliable results, as several components had more or less identical mass spectra, but some of the cyclosiloxanes were detected.

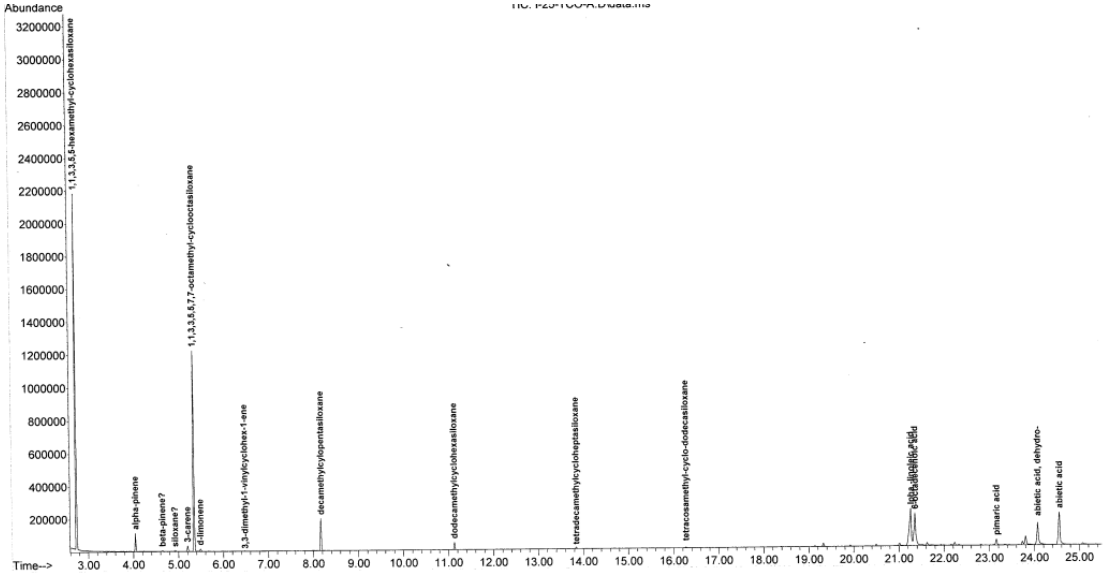


Figure 34 GC-MS chromatogram of PDMS + bio-oil 3 heated for 90 minutes at 250 °C.

Since there is no way of seeing any water-soluble products that may have formed in this experiment, one cannot conclude that the cyclosiloxanes ranging from D3 to D8 are the only degradation products with 100% certainty, however, for PDMS in bio-oil 4, the formation of significant amounts of them have at least been observed, and the degradation mechanism would then be the same as to that of PDMS in bio-oil 1. Only trace amounts of the cyclosiloxanes were detected in the PDMS + bio-oil 3 sample and no conclusion can therefore be drawn based on this experiment alone. One would instead have to repeat the experiment with a longer residence time in the reactor, and potential water-soluble products would also have to be analysed.

4.2.10 Calcium-ion effect on PDMS degradation in bio-oil 2

The driving force for the degradation can be speculated from the composition of the different matrixes, especially the difference between bio-oil 1, bio-oil 3 and bio-oil 4, who all induced degradation, and bio-oil 2, which did not induce any significant degradation.

The most relevant differences in the compositions can be seen from ICP-MS and GPC results presented in Table 4. Firstly, sodium levels for the bio-oil 1 and bio-oil 4 samples

were roughly 56 and 36 times higher (respectively) than in bio-oil 2 and bio-oil 3. Secondly, calcium was found in bio-oil 1, which had the highest amount, and in bio-oil 3 and bio-oil 4, but not in bio-oil 2. Regarding the composition, bio-oil 1, bio-oil 3 and bio-oil 4 had a much higher number of fatty acids than bio-oil 2. Furthermore, bio-oil 1 and bio-oil 4, both of which induced the highest degradation, contained resin acids, which were also not found in bio-oil 2.

Table 4. Most significant matrix composition differences.

	Bio-oil 1	Bio-oil 2	Bio-oil 3	Bio-oil 4
Metals (ICP-MS)				
Sodium	High	Low	Low	High
Calcium	Medium	-	Low	Medium
Composition (GPC)				
Fatty acids	Medium	Very low	Medium	Relatively high
Resin acids	Medium	-	-	Relatively high
Esters	High	-	-	Medium
Di- and triglycerides	-	Very high	Very high	-

The driving force behind these back-biting reactions in the matrixes was therefore hypothesised to be either the cations such as Na^+ and Ca^{2+}, or reactions involving the free fatty and/or resin acids.

The effect of calcium ions was tested by adding 100 ppm of $CaCl_2$ dissolved in distilled water to a sample of PDMS and bio-oil 2 and comparing it to another sample of PDMS and bio-oil 2 with the same amount of distilled water (5 µl) without $CaCl_2$ added. The samples were then heated for 90 minutes and the resulting HP-SEC chromatogram can be seen in

Figure 35. No difference in degradation behaviour could be observed. Any definite conclusions cannot be drawn from this single experiment alone, as factors such as the number of Ca-ions, the addition of water and human errors might have influenced the results, but the findings suggest that it is rather the fatty and/or resin acids components that catalyse the degradation of PDMS, and not the cations.

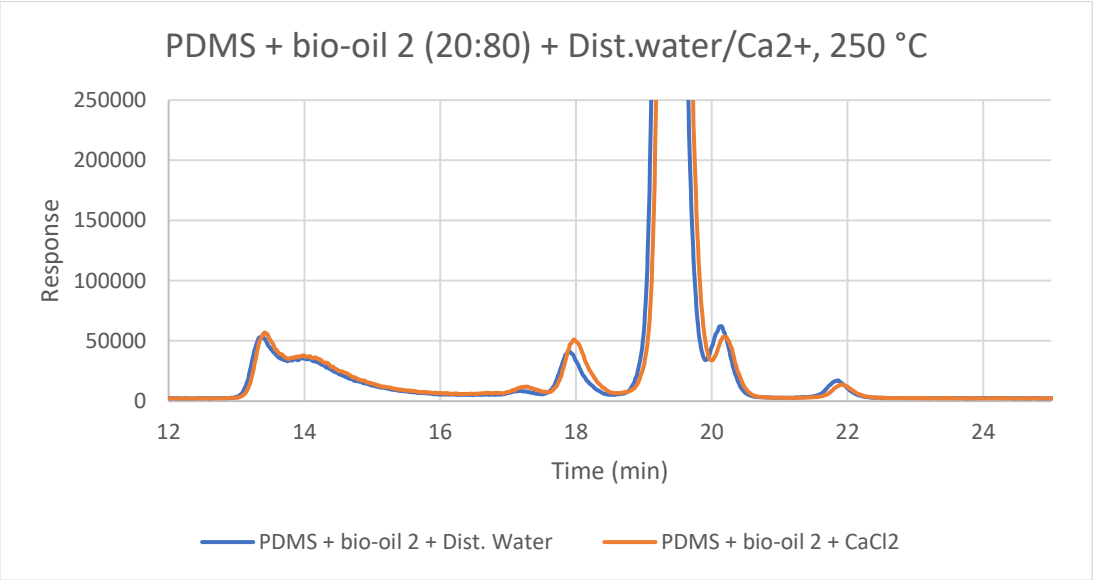


Figure 35. HP-SEC chromatogram of PDMS + bio-oil 2 with and without $CaCl_2$.

5 SUMMARY AND CONCLUSION

The degradation of high MW PDMS at elevated temperatures in renewable oils has been investigated and analysed by HP-SEC, NMR, GC-FID, GC-MS and ICP-MS. A degradation was observed in all matrices using HP-SEC; however, the fastest reaction rates, calculated by peak areas in HP-SEC chromatograms, were observed in bio-oil 4 and bio-oil 1. In the bio-oil 4 matrix, all the high MW PDMS had degraded into smaller products after 60 minutes of residence time in a reactor at 250 °C. For PDMS in bio-oil 1, the same thing could be observed after 90 minutes, whereas in bio-oil 3 only around 35% had degraded after 90 minutes, and in bio-oil 2 merely 10%. No increase in the degradation rate was observed for PDMS in bio-oil 1 after elevating the temperature to 280 °C in an autoclave reactor.

The degradation products of PDMS in bio-oil 1, after over 120 minutes of heating at 280 °C, were analysed by NMR spectroscopy, GC-MS, and GC-FID. The main degradation products of PDMS were found to be cyclosiloxanes ranging from D3-D5, and decreasing numbers of D6-D8, suggesting that the degradation mechanisms are the same back-biting reactions seen in the thermal degradation of PDMS. The accuracy of the experiment was affirmed by comparing the amount of cyclosiloxanes that had formed in the sample, which was about 14.6 weight-%, to the total amount of silicon in the same sample, which in turn had been determined by ICP-MS.

The same cyclosiloxanes were also detected for PDMS in a bio-oil 4 matrix after heating for 90 minutes. The amount of cyclosiloxanes was calculated by peak areas in GC-FID and determined to be about 6.9 weight-%, after initially loading the sample with 20 weight-% high MW PDMS. Due to the relatively short residence time in the reactor, the remaining products were most likely medium weight PDMS polymer and oligomers that had not yet fully degraded. However, the possibility of potential water-soluble degradation products forming cannot be completely ruled out, as the GC samples were dissolved in hexane, meaning water-soluble compounds were not detected.

An adsorbent was also introduced in mixtures of PDMS in bio-oil 1 and PDMS in bio-oil 3. These were heated for 60 minutes at 250 °C and later analysed using HP-SEC. The results showed that the introduction of the adsorbent did not influence the degradation of PDMS.

The driving force for the degradation, or the catalytic component in the matrices, were hypothesised to be either cations or the fatty and/or resin acids. These compounds were hypothesised to be driving the back-biting reactions since the degradation rate of PDMS was increased with increasing amounts of these compounds. Furthermore, the effect of cations and acids on PDMS degradation can also be found in literature. The effect of Ca^{2+}-ions was

tested by dissolving $CaCl_2$ in distilled water (a total of 100 ppm) and adding it to a sample of PDMS in a bio-oil 2 matrix. The same amount of distilled water was added to a reference sample to rule out the influence of water. Both samples were then heated to 250 °C for 90 minutes. No difference in degradation rates was observed, suggesting that the fatty and/or resin acids are catalysing the degradation of PDMS.

For further studies on this subject, I suggest repeating the degradation experiments of PDMS in bio-oil 3 and bio-oil 4, except with longer residence times in the reactor for the PDMS to fully degrade into its final products. Here one could also analyse water-soluble products and rule out other competing degradation mechanisms if none are found. The catalytic effect of acids could also be investigated further by introducing organic acids to PDMS in different matrices. These would preferably then be acids that are similar to the fatty and resin acids, such as butyric acid or larger carboxylic acids, in order for the experiment to be as representative as possible.

6 SAMMANFATTNING PÅ SVENSKA

6.1 Nedbrytning av polydimetylsiloxan i simulerade, industriella processförhållanden

Kisel (Si) är det 14:e grundämnet i det periodiska systemet och det näst vanligaste grundämnet på jorden efter syre. Silikon, eller polysiloxan, är en hydrofobisk polymer som består av alternerande syre- och kiselatomer med organiska föreningar bundna till kiselatomerna, vanligtvis metylgrupper. De långa och flexibla bindningarna i den repeterande Si-O-strukturen ger upphov till unika egenskaper, såsom låg värmekänslighet och låg ytspänning vid gränsytor. Den senare nämnda egenskapen har lett till att den använts som ett skumdämpningsmedel i flera industriella applikationer. I sulfatprocessen, vid framställning av pappersmassa, impregnerar man träet med s.k. vitlut, bestående av natriumsulfid (Na_2S) och natriumhydroxid (NaOH), vid höga temperaturer i en kokare. Vid kokningen frigörs cellulosafibrer från ligninet, och estrar från fettsyror, hartssyror och steroler i träet börjar brytas ner och bilda ytaktiva molekyler. Blandningen av tillsatta kemikalier och upplöst trä kallas svartlut och den separeras från pappersmassan (cellulosafibrerna) genom tvättning. De ytaktiva molekylerna genererar stora mängder skum under tvättningen av pappersmassan och därför tillsätts polydimetylsiloxan (PDMS) som skumdämpare. Efter tvättningen tillåts svartluten sätta sig, och såpa, bestående av fettsyror, lägger sig på ytan av svartluten, varefter den kan skrapas bort. Såpan tas tillvara och neutraliseras med svavelsyra för att bilda tallolja. Talloljan kan sedan vidare destilleras och förädlas till nya produkter. Den har bland annat visat sig vara ett billigt och hållbart alternativ till diverse biooljor för dieseltillverkning i oljeraffineringsindustrin.

Problemet är att man funnit spår av PDMS i talloljan i form av cykliska siloxaner och högmolekylär PDMS, vilket har kommit med vidare i förädlingsprocessen efter att ha tillsatts som skumdämpningsmedel. Denna PDMS har lett till problem i oljeraffinaderier i form av fast avlagring och katalysatorförgiftning under hydrogeneringsprocessen. Målet med denna avhandling var därför att ta reda på hur stabilt PDMS är i industriellt relevanta förhållanden, bland annat vid höjda temperaturer och i blandningar av olika biooljor, samt att ta reda på dess slutliga sönderfallsprodukter. Experimenten utfördes vid Åbo Akademi i autoklav eller i stängda, värme- och trycktåliga glastuber i inert atmosfär som värmdes upp i ett sandbad med värmeplatta och magnetomrörare. Analysmetoderna som användes var HP-SEC, NMR, GC-MS, GC-FID och ICP-MS.

Uträknat från toppareorna i HP-SEC-kromatogrammen konstaterades att PDMS bryts ner snabbast i bioolja 4 och bioolja 1, följt av bioolja 3, och allra minst i bioolja 2. Efter 60

minuter i en 20:80 blandning av PDMS och bioolja 4 vid 250 °C hade all högmolekylär PDMS brutits ner till mellanmolekylära polymerer samt mindre oligomerer och sönderfallsprodukter. Samma kunde konstateras för PDMS i bioolja 1 efter 90 minuter. För PDMS i bioolja 3 hade ca 35 % högmolekylärt PDMS brutits ner efter 90 minuter och i bioolja 2 endast ca 10%, vilket tydde på att en lägre mängd av den katalytiska komponenten i bioolja 3 och bioolja 2.

Sönderfallsprodukterna analyserades med hjälp av NMR, GC-MS och GC-FID. För fallet PDMS i bioolja 1 kunde det konstateras att PDMS bryts ner till cykliska siloxaner i storleksordningen D3–D8 (hexametylcyklotrisiloxan–hexadekametylcyklooctasiloxan), varav den största andelen var D3–D5. Cyklosiloxanernas viktprocent beräknades från GC-FID-resultaten genom att jämföra toppareorna med topparean från en känd mängd D4. Viktprocenten jämfördes sedan med den totala mängden kisel i provet, vilket hade analyserats med ICP-MS. Resultaten stämde överens. D3–D8 bildades även för fallet PDMS i bioolja 4. Här stämde dock mängderna inte överens, vilket kan förklaras med den korta upphettningstiden, vilket troligtvis ledde till att det fortfarande fanns en hel del högmolekylär PDMS och oligomerer kvar i provet. En annan orsak till resultaten kunde vara att GC-proven var upplösta i hexan, vilket gjorde att vattenlösliga produkter inte syntes i kromatogrammet.

Bildningen av cyklosiloxaner tyder på att PDMS:en bryts ner genom så kallade back-biting-reaktioner som också kan observeras vid termisk nedbrytning av ren PDMS. Reaktionen kan ske på två sätt, endera genom att en syreatom i ändan av polymeren reagerar med en kiselatom längre bak i polymeren, vilket frigör cyklisk siloxan. Det andra sättet är att polymeren viker sig dubbelt och en syreatom där reagerar med en kiselatom, vilket i sin tur frigör cyklisk siloxan. Storleken på cyklosiloxanen beror på hur långt bak i polymerkedjan syreatomen attackerar.

De katalyserande komponenterna i oljorna hypotiserades vara antingen katjoner eller fett- och hartssyrorna. Effekten av kalciumjoner testades genom att tillföra 100 ppm kalciumklorid upplöst i 5 µl destillerat vatten till ett prov av PDMS och bioolja 2. Samma mängd rent destillerat vatten tillfördes ett annat prov av PDMS och bioolja 2. Därefter hettades båda proven upp och analyserades med HP-SEC. Ingen skillnad i nedbrytningshastigheten kunde konstateras, vilket tyder på att det är de fria fett- och/eller hartssyrorna som katalyserar nedbrytningen av PDMS och driver back-biting-reaktionerna.

7 REFERENCES

(1) Atul, T.; Soucek, M. D. Preface. In *Concise Encyclopedia of High Performance Silicones*; Atul, T., Soucek, M. D., Eds.; John Wiley & Sons, Incorporated, 2014; pp xvi--xviii.

(2) Noll, W. CHAPTER 1 - General Discussion. In *Chemistry and Technology of Silicones*; Noll, W., Ed.; Academic Press, 1968; pp 1–23. https://doi.org/10.1016/B978-0-12-520750-8.50024-5.

(3) Patterson, R. F. Silicones. In *Handbook of Thermoset Plastics*; William Andrew Publishing, 1998; pp 468–497. https://doi.org/10.1016/B978-081551421-3.50012-6.

(4) O'Lenick, A. J. Silicones—Basic Chemistry and Selected Applications. *Journal of Surfactants and Detergents* **2000**, *3* (2), 229–236. https://doi.org/10.1007/s11743-000-0130-3.

(5) Bergeron, V.; Cooper, P.; Fischer, C.; Giermanska-Kahn, J.; Langevin, D.; Pouchelon, A. Polydimethylsiloxane (PDMS)-Based Antifoams. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1997**, *122* (1–3), 103–120. https://doi.org/10.1016/S0927-7757(96)03774-0.

(6) Aro, T.; Fatehi, P. Tall Oil Production from Black Liquor: Challenges and Opportunities. *Separation and Purification Technology* **2017**, *175*, 469–480. https://doi.org/10.1016/J.SEPPUR.2016.10.027.

(7) Tran, H.; Vakkilainnen, E. K. The Kraft Chemical Recovery Process. *TAPPI Kraft Recovery Course* **2012**, 1–8.

(8) Alén, R. Pulp Mills and Wood-Based Biorefineries. *Industrial Biorefineries & White Biotechnology* **2015**, 91–126. https://doi.org/10.1016/B978-0-444-63453-5.00003-3.

(9) de Buyl, F.; Andriot, M.; DeGroot, J. v; Meeks, R.; Gerlach, E.; Jungk, M.; Wolf, A.; Chao, S. H.; Colas, A.; de Buyl, F.; Dupont, A.; Garaud, J. L.; Gubbels, F.; Lecomte, J. P.; Lenoble, B.; Stassen, S.; Stevens, C.; Thomas, X. Chapter 2 - Silicones in Industrial Applications. In *Inorganic polymers*; de Jaeger, R., Gleria, M., Eds.; Nova Science Pub Inc, 2007; pp 61–161.

(10) Kupareva, A.; Mäki-Arvela, P.; Grénman, H.; Eränen, K.; Hemming, J.; Murzin, D. Y. The Transformation of Silicon Species Contained in Used Oils under Industrially

Relevant Alkali Treatment Conditions. *Journal of Chemical Technology and Biotechnology* **2015**, *90* (11), 1991–1998. https://doi.org/10.1002/jctb.4582.

(11) Chainet, F.; Lienemann, C. P.; Courtiade, M.; Ponthus, J.; Xavier Donard, O. F. Silicon Speciation by Hyphenated Techniques for Environmental, Biological and Industrial Issues: A Review. *Journal of Analytical Atomic Spectrometry* **2011**, *26* (1), 30–51. https://doi.org/10.1039/c0ja00152j.

(12) Griessbach, E. F. C.; Lehmann, R. G. Degradation of Polydimethylsiloxane Fluids in the Environment - a Review. *Chemosphere* **1999**, *38* (6), 1461–1468.

(13) Stevens, C. Environmental Degradation Pathways for the Breakdown of Polydimethylsiloxanes. *Journal of Inorganic Biochemistry* **1998**, *69* (3), 203–207. https://doi.org/10.1016/S0162-0134(97)10019-8.

(14) Lehmann, R. G.; Miller, J. R.; Kozerski, G. E. Degradation of Silicone Polymer in a Field Soil under Natural Conditions. *Chemosphere* **2000**, *41* (5), 743–749. https://doi.org/10.1016/S0045-6535(99)00430-0.

(15) Buch, R. R.; Ingebrigtson, D. N. Rearrangement of Poly(Dimethylsiloxane) Fluids on Soil. *Environmental Science and Technology* **1979**, *13* (6), 676–679. https://doi.org/10.1021/es60154a002.

(16) Lehmann, R. G.; Miller, J. R.; Xu, S.; Singh, U. B.; Reece, C. F. Degradation of Silicone Polymer at Different Soil Moistures. *Environmental Science and Technology* **1998**, *32* (9), 1260–1264. https://doi.org/10.1021/es970918z.

(17) Xu, S.; Lehmann, R. G.; Miller, J. R.; Chandra, G. Degradation of Polydimethylsiloxanes (Silicones) as Influenced by Clay Minerals. *Environmental Science and Technology* **1998**, *32* (9), 1199–1206. https://doi.org/10.1021/es9708676.

(18) Lewis, R. N. Methylphenylpolysiloxanes. *Journal of the American Chemical Society* **1948**, *70*, 1115–1117.

(19) Lewicki, J. P.; Mayer, B. P.; Alviso, C. T.; Maxwell, R. S. Thermal Degradation Behavior and Product Speciation in Model Poly(Dimethylsiloxane) Networks. *Journal of Inorganic and Organometallic Polymers and Materials* **2012**, *22* (3), 636–645. https://doi.org/10.1007/s10904-011-9625-0.

(20) Patnode, W.; Wilcock Vol, D. F.; Si-, C. H. S. Methylpolysiloxanes. *Journal of the American Chemical Society* **1946**, *68*, 358–363.

(21) Jovanovic, J. D.; Govedarica, M. N.; Dvornic, P. R.; Popovic, I. G. The Thermogravimetric Analysis of Some Polysiloxanes. *Polymer Degradation and Stability* **1998**, *61* (1), 87–93. https://doi.org/10.1016/S0141-3910(97)00135-3.

(22) Grassie, N.; Macfarlane, I. G. The Thermal Degradation of Polysiloxanes-I. Poly(Dimethylsiloxane). *European Polymer Journal* **1978**, *14* (11), 875–884. https://doi.org/10.1016/0014-3057(78)90084-8.

(23) Allan, D.; Radzinski, S. C.; Tapsak, M. A.; Liggat, J. J.; Liggat WestChem, J. J. The Thermal Degradation Behaviour of a Series of Siloxane Copolymers - a Study by Thermal Volatilisation Analysis. *Silicon* **2014**, *8*, 553–562. https://doi.org/10.1007/s12633-014-9247-6.

(24) Camino, G.; Lomakin, S. M.; Lageard, M. Thermal Polydimethylsiloxane Degradation. Part 2. The Degradation Mechanisms. *Polymer* **2002**, *43* (7), 2011–2015. https://doi.org/10.1016/S0032-3861(01)00785-6.

(25) Camino, C.; Lomakin, S. M.; Lazzari, M. Polydimethylsiloxane Thermal Degradation Part 1. Kinetic Aspects. *Polymer* **2001**, *42* (6), 2395–2402. https://doi.org/10.1016/S0032-3861(00)00652-2.

(26) Ducom, G.; Laubie, B.; Ohannessian, A.; Chottier, C.; Germain, P.; Chatain, V. Hydrolysis of Polydimethylsiloxane Fluids in Controlled Aqueous Solutions. *Water Science and Technology* **2013**, *68* (4), 813–820. https://doi.org/10.2166/wst.2013.308.

(27) Diehl, B. NMR Applications for Polymer Characterisation. In *NMR Spectroscopy in Pharmaceutical Analysis*; Elsevier, 2008; pp 157–180. https://doi.org/10.1016/B978-0-444-53173-5.00007-X.

(28) Mojsiewicz-Pieńkowska, K.; Jamrógiewicz, Z.; Łukasiak, J. Determination of Polydimethylsiloxanes by 1H-NMR in Wine and Edible Oils. *Food Additives and Contaminants* **2003**, *20* (5), 438–444. https://doi.org/10.1080/0265203031000136288.

(29) Zimmermann, S.; Wischhusen, S.; Müller, J. Micro Flame Ionization Detector and Micro Flame Spectrometer. *Sensors and Actuators, B: Chemical* **2000**, *63* (3), 159–166. https://doi.org/10.1016/S0925-4005(00)00353-1.

(30) Noll, W. Analytical Methods. In *Chemistry and Technology of Silicones*; Elsevier, 1968; pp 663–683. https://doi.org/10.1016/B978-0-12-520750-8.50035-X.

(31) Kaali, P.; Momcilovic, D.; Markström, A.; Aune, R.; Czel, G.; Karlsson, S. Degradation of Biomedical Polydimethylsiloxanes during Exposure to *in Vivo* Biofilm Environment Monitored by FE-SEM, ATR-FTIR, and MALDI-TOF MS. *Journal of Applied Polymer Science* **2010**, *115* (2), 802–810. https://doi.org/10.1002/app.31119.

(32) Alén, R.; Suomen Paperi-Insinöörien Yhdistys. *Biorefining of Forest Resources*, 1st ed.; Alén, R., Ed.; Paperi ja Puu Oy, 2011.

(33) Tikka, P.; Laxén, T. Soap and Tall Oil. In *Chemical Pulping Part 2, Recovery of Chemicals and Energy*; Tikka, P., Ed.; Paperi ja Puu Oy, 2008; pp 359–380.

(34) Demirbas, A. Production of Biodiesel from Tall Oil, Energy Sources, Part A. *Energy Sources, Part A* **2008**, *30* (20), 1896–1902. https://doi.org/10.1080/15567030701468050.

(35) Mikulec, J.; Kleinová, A.; Cvengroš, J.; udmila Joríková; Banič, M. Catalytic Transformation of Tall Oil into Biocomponent of Diesel Fuel. *International Journal of Chemical Engineering* **2012**, *2012*. https://doi.org/10.1155/2012/215258.

(36) White, K.; Lorenz, N.; Potts, T.; Roy Penney, W.; Babcock, R.; Hardison, A.; Canuel, E. A.; Hestekin, J. A. Production of Biodiesel Fuel from Tall Oil Fatty Acids via High Temperature Methanol Reaction. *Fuel* **2011**, *90* (11), 3193–3199. https://doi.org/10.1016/j.fuel.2011.06.017.

(37) Ma, F.; Hanna, M. A. Biodiesel Production: A Review. *Bioresource Technology* **1999**, *70* (1), 1–15. https://doi.org/10.1016/S0960-8524(99)00025-5.

(38) Lestari, S.; Mäki-Arvela, P.; Beltramini, J.; Max Lu, G. Q.; Murzin, D. Yu. Transforming Triglycerides and Fatty Acids into Biofuels. *ChemSusChem* **2009**, *2* (12), 1109–1119. https://doi.org/10.1002/cssc.200900107.

(39) Morales-Delarosa, S.; Campos-Martin, J. M. Catalytic Processes and Catalyst Development in Biorefining. In *Advances in Biorefineries: Biomass and Waste Supply Chain Exploitation*; Elsevier Ltd., 2014; pp 152–198. https://doi.org/10.1533/9780857097385.1.152.

(40) Balat, M.; Balat, H. Progress in Biodiesel Processing. *Applied Energy*. Elsevier Ltd June 2010, pp 1815–1835. https://doi.org/10.1016/j.apenergy.2010.01.012.

(41) Helwani, Z.; Othman, M. R.; Aziz, N.; Fernando, W. J. N.; Kim, J. Technologies for Production of Biodiesel Focusing on Green Catalytic Techniques: A Review. *Fuel Processing Technology* **2009**, *90* (12), 1502–1514. https://doi.org/10.1016/j.fuproc.2009.07.016.

(42) Šimáček, P.; Kubička, D.; Šebor, G.; Pospíšil, M. Hydroprocessed Rapeseed Oil as a Source of Hydrocarbon-Based Biodiesel. *Fuel* **2009**, *88* (3), 456–460. https://doi.org/10.1016/j.fuel.2008.10.022.

(43) Huber, G. W.; O'Connor, P.; Corma, A. Processing Biomass in Conventional Oil Refineries: Production of High Quality Diesel by Hydrotreating Vegetable Oils in Heavy Vacuum Oil Mixtures. *Applied Catalysis A: General* **2007**, *329*, 120–129. https://doi.org/10.1016/j.apcata.2007.07.002.

(44) Murzin, D. Yu. Biomass Processing. In *Chemical Reaction Technology*; DE GRUYTER: Berlin, München, Boston, 2015; pp 127–135. https://doi.org/10.1515/9783110336443.

(45) Tiwari, R.; Rana, B. S.; Kumar, R.; Verma, D.; Kumar, R.; Joshi, R. K.; Garg, M. O.; Sinha, A. K. Hydrotreating and Hydrocracking Catalysts for Processing of Waste Soya-Oil and Refinery-Oil Mixtures. *Catalysis Communications* **2011**, *12* (6), 559–562. https://doi.org/10.1016/j.catcom.2010.12.008.

(46) Afshar Taromi, A.; Kaliaguine, S. Green Diesel Production via Continuous Hydrotreatment of Triglycerides over Mesostructured $Γ$-Alumina Supported NiMo/CoMo Catalysts. *Fuel Processing Technology* **2018**, *171*, 20–30. https://doi.org/10.1016/j.fuproc.2017.10.024.

(47) Arandia, K. Analysis of Silicone Oil in Tall Oil Products, Åbo Akademi, 2018.

(48) Saviainen, J.; Rintola, M.; Saarenko, T. Method of Utilizing Tall Oil Pitch. EP2553052B1, 2011.

(49) Gomes, M. G.; Santos, D. Q.; de Morais, L. C.; Pasquini, D. Purification of Biodiesel by Dry Washing, Employing Starch and Cellulose as Natural Adsorbents. *Fuel* **2015**, *155*, 1–6. https://doi.org/10.1016/j.fuel.2015.04.012.

(50) Atadashi, I. M.; Aroua, M. K.; Aziz, A. A. Biodiesel Separation and Purification: A Review. *Renewable Energy* **2011**, *36* (2), 437–443. https://doi.org/10.1016/j.renene.2010.07.019.

(51) Berrios, M.; Skelton, R. L. Comparison of Purification Methods for Biodiesel. *Chemical Engineering Journal* **2008**, *144* (3), 459–465. https://doi.org/10.1016/j.cej.2008.07.019.

(52) Örn, A. Degradation Studies on Polydimethylsiloxane, Åbo Akademi University 2019.