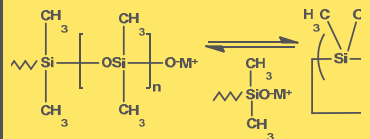
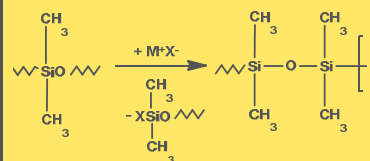
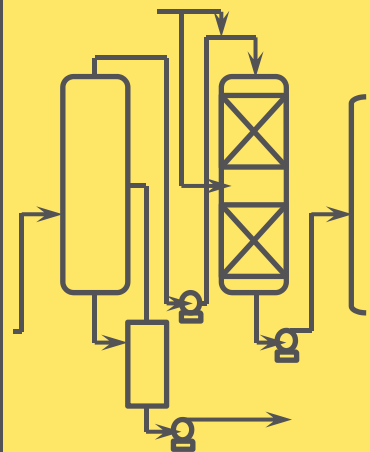


Silicon-containing species in used lube oil re-refining

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Turku/Åbo, 2015

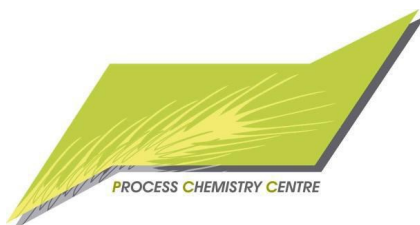


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PREFACE

The work outlined in this dissertation was carried out at Åbo Akademi University. The research was conducted under the supervision of Professor D. Yu. Murzin in the Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, between October 2011 and March 2015. The work is a part of activities at the Åbo Akademi Process Chemistry Centre (PCC), a centre of excellence financed by Åbo Akademi University.

First of all, I would like to express my gratitude to Professor Dmitry Yu. Murzin and Academy Professor Tapio Salmi for giving me the opportunity to do research work that led to this thesis. Professor Dmitry Yu. Murzin is acknowledged for his scientific guidance, valuable input and advices over the years, which helped me to complete this work. Furthermore, I would like to thank Dr. Petri Rautanen for introducing me to a fascinating research area.

I owe appreciation to my colleagues within the research group. Each has contributed to this thesis in some way. I hereby express my thanks to all the co-authors and co-workers I have worked with during my time at Åbo Akademi University. I am grateful to Docent Päivi Mäki-Arvela for her help and support throughout these years, to Dr. Henrik Grénman for his comments and suggestions on my work. I thank Dr. Kari Eränen for his collaboration and assistance. Professor Johan Wärnå is gratefully acknowledged for sharing his knowledge in kinetic modeling.

I am also indebted to my colleague and friend, Anton Tokarev, who was always willing to take time for adding new ideas to my project and teaching me experimental techniques. I especially thank Steliana Aldea, for showing me the importance of using curiosity as the driving force behind research.

Herein I am happy to acknowledge my friends in Finland and abroad. Many thanks to my fellow researchers, in particular to Alice, Elena, Martina, Andrea and Sabrina. I very much enjoyed our daily exchange of ideas and thoughts, and the fun moments together.

Finally, I take this opportunity to express my gratitude to my family for their love, unfailing encouragement and support.

ABSTRACT

Silicon-containing species in used lube oil re-refining

Keywords: tetramethyldisiloxane, used oil re-refining, alkali treatment, base-catalyzed transformations, sodium silanolates, reaction mechanism.

Nowadays, the re-refining of the used lube oils has gained worldwide a lot of attention due to the necessity for added environmental protection and increasingly stringent environmental legislation. One of the parameters determining the quality of the produced base oils is the composition of feedstock. Estimation of the chemical composition of the used oil collected from several European locations showed that the hydrocarbon structure of the motor oil is changed insignificantly during its operation and the major part of the changes is accounted for with depleted oil additives.

In the lube oil re-refining industry silicon, coming mainly from antifoaming agents, is recognized to be a contaminant generating undesired solid deposits in various locations in the re-refining units.

In this thesis, a particular attention was paid to the mechanism of solid product formation during the alkali treatment process of silicon-containing used lube oils. The transformations of a model siloxane, tetramethyldisiloxane (TMDS), were studied in a batch reactor at industrially relevant alkali treatment conditions (low temperature, short reaction time) using different alkali agents.

The reaction mechanism involving solid alkali metal silanolates was proposed. The experimental data obtained demonstrated that the solids were dominant products at low temperature and short reaction time. The liquid products in the low temperature reactions were represented mainly by linear siloxanes. The prolongation of reaction time resulted in reduction of solids, whereas both temperature and time increase led to dominance of cyclic products in the reaction mixture. Experiments with the varied reaction time demonstrated that the concentration of cyclic trimer being the dominant in the beginning of the reaction diminished with time, whereas the cyclic tetramer tended to increase. Experiments with lower sodium hydroxide concentration showed the same effect. In addition, a decrease of alkali agent concentration in the initial reaction mixture accelerated TMDS transformation reactions resulting in solely liquid cyclic siloxanes yields.

Comparison of sodium and potassium hydroxides applied as an alkali agent demonstrated that potassium hydroxide was more efficient, since the activation energy in KOH presence was almost 2-fold lower than that for sodium hydroxide containing reaction mixture. Application of potassium hydroxide for TMDS transformation at 100° C with 3 hours reaction time resulted in 20 % decrease of solid yields compared to NaOH-containing mixture. Moreover, TMDS transformations in the presence of sodium silanolate applied as an alkali agent led to formation of only liquid products without formation of the undesired solids.

On the basis of experimental data and the proposed reaction mechanism, a kinetic model was developed, which provided a satisfactory description of the experimental results.

Suitability of the selected siloxane as a relevant model of industrial silicon-containing compounds was verified by investigation of the commercially available antifoam agent in base-catalyzed conditions.

REFERAT

Silikoninnehållande föreningar i återaffinering av använd smörjolja

Nyckelord: tetrametyldisiloxan, raffinering av använd olja, alkalibehandling, baskatalyserade omvandlingar, natriumsilanolater, reaktionsmekanism.

Numera har återaffineringen av använda smörjoljor fått mycket uppmärksamhet runt världen på grund av ett ökat behov av miljöskydd och allt strängare miljölagstiftning. En av de parametrarna som avgör kvaliteten på de producerade basoljorna är sammansättningen av råmaterialet. En uppskattning av den kemiska sammansättningen av den använda oljan som samlas in från flera europeiska orter har visat att kolvätestrukturen av motorolja förändras betydligt under dess användning och att de största förändringarna beror på förlorade tillsatser.

I återaffineringsindustrin för smörjoljor kommer kisel främst från skumdämpare och det erkänns vara en förorening som förorsakar oönskade fasta avlagringar på olika ställen av återaffineringsanläggningar.

I denna avhandling ägnades särskild uppmärksamhet åt mekanismen för fasta produkters bildning under alkalisk behandling av kiselinnehållande smörjoljor. Omvandling av en modellmolekyl, siloxan, tetrametyldisiloxan (TMDS), studerades i en satsreaktor vid industriellt relevanta alkaliska behandlingsförhållanden (låg temperatur, kort reaktionstid) med hjälp av olika alkaliska ämnen.

En reaktionsmekanism som involverar fasta alkalimetall - silanolater föreslogs. De experimentella data visade att de fasta produkterna var de dominerande vid låga temperaturer och korta reaktionstider. De flytande produkterna vid låga temperaturer var främst linjära siloxaner. Förlängning av reaktionstiden resulterade i minskning av fasta produkter, medan en ökning av temperaturen och förlängning av reaktionstiden ledde till en dominans av cykliska produkter i reaktionsblandningen. Experiment med varierade reaktionstider visade att koncentrationen av cykliska trimerer, som är dominerande i början av reaktionen, minskade med tiden, medan koncentrationen av cykliska tetramerer tenderade att öka. Experiment med lägre natriumhydroxidkoncentrationer visade samma effekt. Dessutom, en minskning av alkalikoncentrationen i reaktionsblandningen accelererade TMDS:s omvandlingsreaktioner, vilket resulterade i enbart flytande cykliska siloxaner.

Jämförelse av natrium- och kaliumhydroxider som alkali visade att kaliumhydroxid var mer effektiv, eftersom aktiveringsenergin med KOH var nästan dubbelt lägre än med natriumhydroxid. Användning av kaliumhydroxid för TMDS:s omvandling vid 100°C med tre timmars reaktionstid gav en 20 % minskning av fasta produkter jämfört med NaOH. Dessutom ledde TMDS:s transformationer i närvaro av natriumsilanolat som alkali till bildning av endast flytande produkter, utan några oönskade fasta material.

På basis av experimentella data och en föreslagen reaktionsmekanism utvecklades en kinetisk modell, som gav en tillfredsställande beskrivning av de experimentella resultaten.

Användbarheten av den valda siloxanen som en relevant modell för industriella kiselinnehållande föreningar verifierades genom undersökning av kommersiellt tillgängliga antiskummedel under baskatalyserade betingelser.

РЕФЕРАТ

Кремнийорганические соединения в процессе переработки отработанных смазочных масел

Ключевые слова: тетраметилдисилоксан, переработка отработанных масел, щелочная очистка, катализируемые основанием реакции, силаноляты натрия, механизм реакции.

В настоящее время переработка отработанных масел приобретает все большую популярность в мире в связи с ужесточением требований природоохранных мер и экологического законодательства. Одним из показателей, определяющих качество переработанных базовых масел, является состав используемого сырья. Оценка химического состава отработанного масла, поступившего с нескольких различных пунктов сбора в Европе, показала, что углеводородный состав моторного масла претерпевает незначительные изменения в процессе его эксплуатации, основные же перемены приходится на разложившиеся присадки масел.

В процессе переработки отработанного масла, кремнийорганические соединения, которые чаще всего добавляются в индустриальные масла в виде противоположных присадок, рассматриваются как загрязнители, так как способствуют образованию нежелательных твердых отложений в различных узлах перерабатывающих заводов.

В данной работе основное внимание было уделено механизму образования твердых продуктов в процессе щелочной очистки отработанных масел, содержащих кремнийорганические соединения. Реакции преобразования модельного вещества, тетраметилдисилоксана (ТМДС) были изучены в реакторе периодического действия при условиях, аналогичных условиям щелочной очистки, применяемых в перерабатывающей промышленности (низкая температура, короткое время реакции) с использованием различных щелочных агентов.

Был предложен механизм реакции, включающий образование твердых силанолятов щелочных металлов. Согласно полученным экспериментальным данным твердые вещества были основными продуктами реакции в условиях низких температур и короткого времени реакции. Жидкие продукты были представлены главным образом линейными силоксанами при проведении реакции при низких температурах. Увеличение времени реакции способствовало снижению выхода твердых продуктов, более того, при одновременном увеличении температуры и времени реакции циклические силоксаны становились основными продуктами в жидкой фазе. Концентрация циклического тримера, образующегося в значительных количествах в начале реакции, снижалась с течением реакции, в то время как концентрация циклического тетрамера возрастала. Аналогичная тенденция наблюдалась при снижении концентрации гидроксида натрия в реакционной смеси. Более того, снижение концентрации щелочи способствовало увеличению скорости реакций преобразования ТМДС и выходу только жидких продуктов.

Сравнение гидроксидов натрия и калия, используемых в качестве щелочных агентов, показало более высокую эффективность гидроксида калия, так как энергия активации в смеси с КОН была практически в два раза ниже. В присутствии КОН выход твердых продуктов в 3-х часовой реакции преобразования ТМДС при 100° С был на 20 % ниже, чем в реакционной смеси с NaOH. Более того, удалось полностью избежать образования твердых продуктов при использовании силанолятов натрия в качестве щелочного агента.

На основе предложенного механизма реакции была разработана кинетическая модель, которая была успешно применена для описания экспериментальных данных.

Пригодность выбранного модельного силоксана для описания поведения кремнийорганических соединений в условиях щелочной очистки отработанных масел была подтверждена экспериментами с коммерчески доступной противопенной присадкой.

Таким образом, данная работа вносит существенный вклад в понимание и развитие процессов переработки отработанных смазочных масел. В частности, на основании предложенного механизма реакции станет возможным избежать образования нежелательных твердых веществ в процессе щелочной очистки отработанных масел, содержащих кремнийорганические соединения.

LIST OF PUBLICATIONS

- I. **Kupareva A.**, Mäki-Arvela P., Murzin D.Yu.: *Technology for rerefining used lube oils applied in Europe: a review*. J. Chem. Technol. Biotechnol. 88, 1780 – 1793 (2013).
- II. **Kupareva A.**, Mäki-Arvela P., Grénman H., Eränen K., Sjöholm R., Reunanen M., Murzin D.Yu.: *Chemical characterization of lube oils*. Energy Fuels. 27, 27 – 34 (2013).
- III. **Kupareva A.**, Mäki-Arvela P., Grénman H., Eränen K., Murzin D.Yu.: *Base-catalyzed transformation of tetramethyldisiloxane*. Ind. Eng. Chem. Res. 55, 10080 – 10088 (2013).
- IV. **Kupareva A.**, Mäki-Arvela P., Grénman H., Eränen K., Murzin D.Yu.: *The base-catalyzed transformation of tetramethyldisiloxane: influence of reaction media*. J. Chem. Technol. Biotechnol. 90, 34 – 43 (2015).
- V. **Kupareva A.**, Wärnä J., Grénman H., Murzin D.Yu.: *Transformation of tetramethyldisiloxane in used oil alkali treatment conditions: Mechanism and kinetic modeling*. J. Chem. Technol. Biotechnol. DOI: 10.1002/jctb.4673 (2015).
- VI. **Kupareva A.**, Mäki-Arvela P., Grénman H., Eränen K., Hemming J., Murzin D.Yu.: *The transformation of silicon species contained in the used oils under industrially relevant alkali treatment conditions*. J. Chem. Technol. Biotechnol. DOI: 10.1002/jctb.4582 (2014).

CONTRIBUTION OF THE AUTHOR

Antonina Kupareva made the experiments and wrote the article manuscripts I-VI.

OTHER PUBLICATIONS RELATED TO THE TOPIC

1. Kupareva A., Mäki-Arvela P., Grénman H., Eränen K., Murzin D.Yu.: *The transformation reaction of silicon-containing compounds at industrially relevant alkali treatment conditions.* // 4th International Congress on Green Process Engineering, April 2014, Sevilla, Spain, oral presentation.
2. Kupareva A., Mäki-Arvela P., Grénman H., Eränen K., Murzin D.Yu.: *Novel approach to identify polydimethylsiloxanes base-catalyzed transformations* // The 17th International Symposium on Silicon Chemistry, August 2014, Berlin, Germany, poster presentation.

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1. INTRODUCTION

Nowadays, the re-refining of the used lube oils has gained worldwide a lot of attention due to the necessity for additional environmental protection and increasingly stringent environmental legislation. Moreover, an economically attractive waste oil re-refining process allows production of valuable base oils with quality comparable with virgin base oils. According to the European Re-refining Industry section of the Independent Union of the European Lubricants Industry (GEIR) [1] the regenerated base oils represent one-third of the European market for lubricant volume. The re-refining process could be divided in the following four steps: dewatering and defueling, de-asphalting, fractionation and finishing process, as illustrated in Figure 1 [2]. Nowadays the acid-clay treatment technology, which was the first regeneration process used, has been banned in most countries due to generation of hazardous waste by-products.

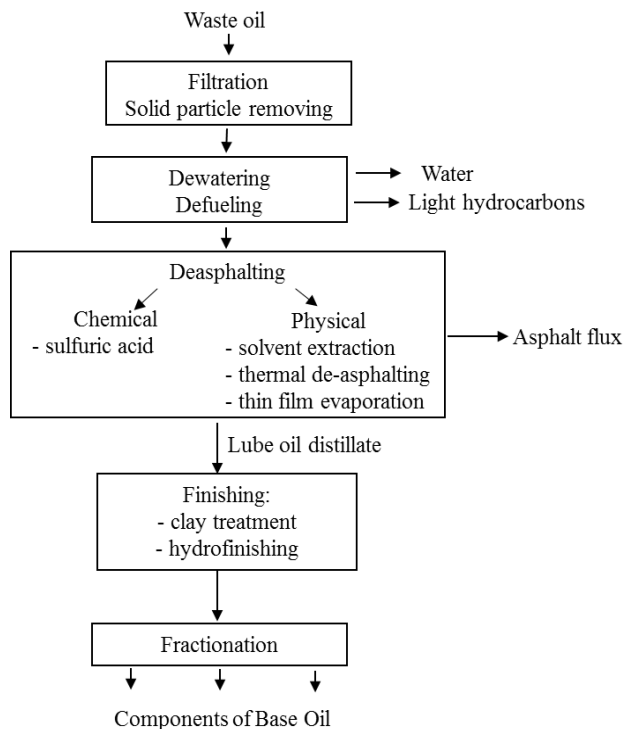


Figure 1. Flow diagram of a typical re-refining process.

An overview of re-refining methods [I] demonstrated that in the majority of European countries currently applied technologies are based on solvent extraction and hydroprocessing. Leading industrial processes combine these technologies in different ways, trying to optimize investment and operational costs, while producing a competitive quality product without creating environmental problems. Currently in Europe the following re-refining methods are widely used: combined thermal de-asphalting and hydrofinishing (Revivoil), solvent extraction (MRD process, Interline), solvent extraction and hydrofinishing (Cyclon, Snamprogetti), thin film evaporation and different finishing processes (Ecohuile, Vaxon, CEP) and hydroprocessing (Hylube) [I].

Composition of the waste oil, feedstock determines the quality of the product base oils depending on the type of applied technology. As exemplified in [I], the quality of base oils produced with recycling technologies based on solvent extraction is directly related to the quality of feedstock, while hydrofinishing technology guarantees high-quality products independently of raw material. The major drawback of hydroprocessing is the catalyst sensitivity and poisoning; in this regard feedstock pretreatment is necessary to prevent catalyst deactivation. Furthermore, since synthetic and semi-synthetic lubricating oils tend to replace the conventional mineral oils due to their enhanced performance characteristics, for the re-refining technologies applying alkaline treatment (CEP, Vaxon, Interline) and hydrofinishing steps (Cyclon, Snamprogetti, Revivoil) the fraction of lube oils based on esters in the feedstock should be eliminated due to their instability under alkali and hydrofinishing conditions. Thus, the yield and selection of the operation conditions are strongly dependent on the composition and properties of the feedstock. The data for the used lube oil composition is limited although it is known that automotive oils represent 65 % of the collectable waste oil and industrial oils comprise the balance of 35 % [3]. Therefore, the chemical composition of the waste oil, collected from several European locations, was estimated on the basis of comparative analysis of the used and commercially available fresh motor oils compositions [III].

1.1. Composition of the used lube oil [III]

Composition of new motor oils and new oil additives is changing because of continuous engine modification. Mineral oil components continue to form the quantitatively most important foundation of lubricants and represent mixtures of different types of hydrocarbons mainly with aliphatic ones and chemical additives. Significant growth in synthetic and semi-synthetic oils markets has been observed. In contrast to mineral oils, synthetic base oils usually are prepared from a few well-defined chemical compounds such as alkylated aromatic compounds, polybutenes, dibasic acid esters, polyalphaolefins, poly(alkylene glycol)s, neopentyl polyol esters, silicones, perfluoralkyl polyethers and several others. In many cases synthetic oils can be also based on petroleum. Similar to mineral base oil synthetic base oils generally cannot satisfy the requirements of high performance lubricants without modern additives. Novel oil compositions are certainly known to oil manufacturers, while this information is unavailable to re-refineries processing used oil. Therefore for optimal re-refining, data on the used oil chemical structure is needed.

Thus, in order to get an overview of the chemical composition of the used lube oil, which is a current feedstock for re-refineries, comparative analysis of commercially available fresh synthetic motor oil, the same type of synthetic motor oil after use, and the used oil from a re-refinery was performed via gas chromatography–mass spectrometry (GC–MS), nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and elemental analysis (CHNS/O analysis) techniques [III].

According to NMR results, the hydrocarbon composition of the motor oil does not change significantly during its use. The modern fresh oil had the following chemical composition: 99.7 % aliphatic hydrocarbons, 0.27 % aromatic hydrocarbons, and 0.03 % olefins. During application, oxidation processes occurred, resulting in a slight increase of aromatic hydrocarbons and sulfur contents in the used oil, although these changes could be probably related to the presence of used industrial oil (5- 15 %) with a higher amount of the latter compounds in the analyzed samples. Determination of the hydrocarbon structure of the used oil showed a presence of aliphatics (98.9

%), 0.94 % aromatics, and 0.08 % of olefins. Differences in the concentration of aliphatic hydrocarbons and their structures in the modern fresh and used motor oils were elucidated. The used oil showed a higher content of methyl protons than the fresh oil; thus, the used oil is more branched.

FTIR spectroscopy results demonstrated the decrease of carbonyl groups with lube oil use, which leads to a decrease of the viscosity index of the oil. GC–MS and NMR results showed the depletion of phenol-containing antioxidants. Hence, combined analysis of the obtained results demonstrated that the hydrocarbon structure of the motor oil is changed insignificantly during its operation and the major part of the changes is accounted for with depleted oil additives.

1.2. Base-catalyzed transformations of the silicon-containing used lube oils

Most often, industrial companies own only the license for re-refining processing without knowing chemistry and mechanisms of reactions occurring in the re-refinery units. However, understanding of reaction mechanism in the used oil recycling could contribute to most efficient re-refining technology, improving the quality of the final products, base oils. Therefore, this work focused on the unit of used lube oil alkali treatment, the entrance point of some modern re-refining processes such as Vaxon [4], Sotulub [5] and Chemical Engineering Partners (CEP) [6]. The latter is depicted in Figure 2.

Addition of caustic into the used oil aims in removal of the undesirable impurities of the oil, that resulting in lubricating oil having a low total acid number, no objectionable odor, and improved oxidation stability. Usually the process is conducted at temperatures of about 100 °C and with short reaction times. The caustic treatment is usually accompanying with the subsequent water separation unit. CEP process employs the dewatering process based on evaporation, where water and light hydrocarbons are flashed off from the oil phase (Fig.2).

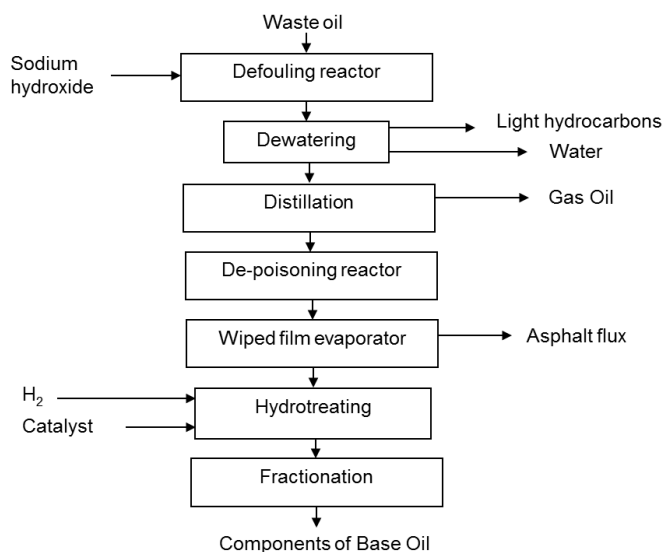


Figure 2. Block flow diagram of the CEP process adapted from Refs 4, 6.

Owing to the complex structure of the used oil, represented by hydrocarbons supplemented with various chemical additives, the present research focused only on base-catalyzed transformations of the silicon species contained in the used oil. Moreover, silicon speciation is of great interest in the oil re-refining industry because of the negative effect of silicon compounds on the performance of hydrotreating catalysts [7], and the formation of undesired solid deposits in various locations in the re-refining units. In the used oil re-refining industry, silicon mainly originates from the use of polydimethylsiloxane-based antifoam agents in industrial oils and species of silicon-based brake fluids in motor oils. Different transformation reactions of polysiloxanes, being currently widely used industrially as lubricants, coatings, and adhesives because of their high chemo- and thermstability have been reported in the literature.

A considerable amount of data [8–12] has been accumulated on the thermal degradation of polysiloxanes and especially of polydimethylsiloxane. Since the reactions of ring-opening polymerization of cyclic siloxanes and silanols polycondensation allow synthesizing high molecular weight polysiloxanes, there are a lot of studies on kinetics of these reactions [13–18]. According to Grzelka et al. [13, 14] base- and acid-catalyzed polycondensation of polysiloxanol is accompanied

with disproportionation reactions. In the presence of a superacid [13] condensation was the dominant reaction, whereas the disproportionation rate was found to be higher in the presence of a superbase [14]. Carmichael and Heffel [17] reported that for high molecular weight polymers the equilibrium constant for the formation of each cyclic compound is approximately equal to its equilibrium concentration. Since the polymerization involves a thermodynamic equilibrium between the cyclic oligomers and linear polymers, polymethyldisiloxane can be depolymerized to cyclosiloxane oligomers by removing the oligomers continuously from the equilibrium [19].

The process of anionic polymerization of cyclic siloxanes has been broadly explored since Grubb and Osthoff [20] performed their pioneering work related to cyclic dimethylsiloxanes polymerization catalyzed by a strong base, where it was assumed that free silanolate ions are the reactive species. The anionic polymerization reaction proceeds accordingly to the mechanism advanced in the study of Hurd et al. [21] and illustrated in Figure 3. The initiation leads to formation of an active propagation centre, a silanolate anion, which is able to extend polysiloxane chain by an addition of cyclosiloxanes. The propagation step is reversible; depropagation produces cyclic compounds of various sizes. In accordance to Oku et al. [22] the cyclic siloxane formation can proceed through the end- and back-biting mechanism, depicted in Figure 4.

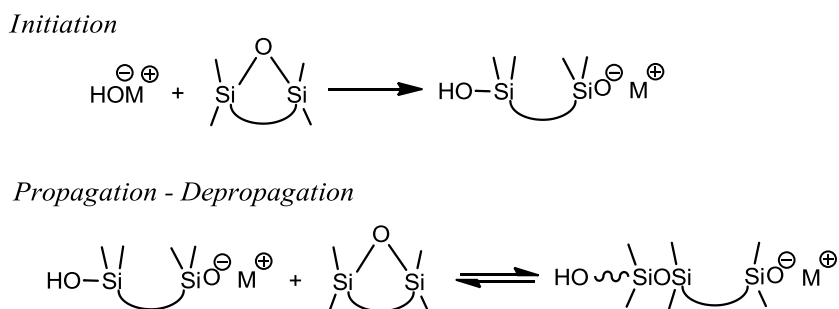


Figure 3. Mechanism of anionic ring-opening polymerization adapted from Refs 15, 23 (M – alkali metal ion).

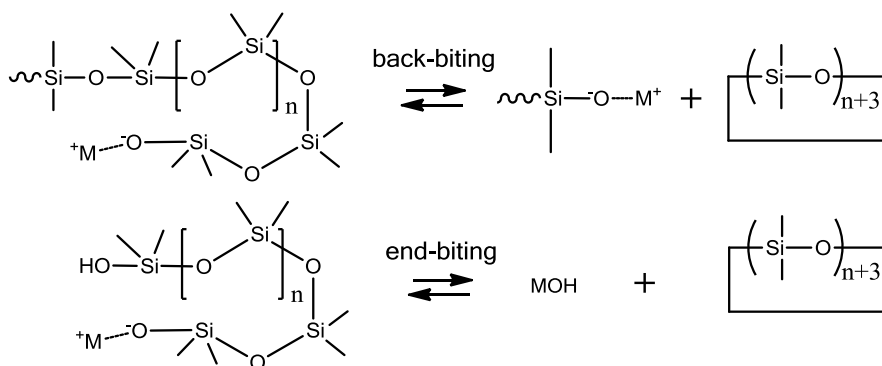


Figure 4. Depolymerization mechanism of polydimethylsiloxanes adapted from Ref 22 ($n \geq 0$, M – alkali metal ion).

A detailed kinetic investigation [23] discovered that the formation of the silanolate ion aggregates determines the kinetic pattern of the anionic polymerization. According to the studies done so far free silanolate groups are active while silanolate in the aggregate constitutes a dormant center [23, 24]. Moreover the silanolate pair association phenomena affected the thermodynamics of anionic polymerization systems [25].

Despite a plenty of studies reported in the literature on different polydimethylsiloxanes reactions, almost no studies exist reporting siloxane behavior at low temperatures, for short reaction times and especially in the presence of hydrocarbons. Therefore, the overall objective of this research was to improve understanding of silicon speciation in the oil re-refining industry, namely in the process of alkali treatment of silicon-containing used lube oils. Tetramethyldisiloxane (TMDS), as a readily available model compound of a simple structure, was investigated for the reason that it is a monomer of the industrially used silicon-containing compounds. Furthermore, this short chain siloxane was selected as a model compound to check an assumption that the polymerization reactions take place under industrially relevant base-catalyzed conditions and result in the formation of long chain solid polymers. Moreover, in order to gain a deeper understanding of the mechanism of silicon species transformation during the process of alkali treatment of the used oil, the selected model siloxane was a hydrogen-terminated one considered to be more reactive compared to dimethylsiloxanes.

An influence of the temperature, time and TMDS concentration in the reaction mixture on the base-catalyzed transformation reactions of TMDS in a hydrocarbon solvent (dodecane) was studied in the batch reactor [III]. The influence of the alkali type on the reaction performance was elucidated via comparison of the reaction rates and product distributions in the mixtures with sodium and potassium hydroxides [IV]. Since several studies have reported that the addition of alcoholic solvents affects the reaction rates of siloxane depolymerization [26], polymerization [21] and condensation [27], the sodium hydroxide catalyzed transformation of TMDS was studied in the presence of methanol [IV]. The studied reaction kinetics and mechanism were addressed in publication [V]. The model siloxane compound transformations were conducted using sodium silanolates with different molecular weights as an alkali agent, instead of alkali metal hydroxides [IV] in order to increase selectivity to the desired reaction products, liquid siloxanes.

It is well-known that polysiloxanes added as an antifoam additive in the lube oils usually do not have any hydrogen-silicon bonds and certain differences exist in properties of Si-H and Si-CH₃ bonds. Therefore, suitability of the selected hydrogen-terminated two-membered model siloxane for the study of the transformations of industrially relevant silicon-containing compounds represented by long chain polydimethylsiloxanes was verified [VI]. That was done by studying the transformation reaction of a commercially available antifoam concentrate at industrially relevant alkali treatment conditions using sodium hydroxide and silanolate as alkali agents.

2. EXPERIMENTAL

2.1. Materials

The model siloxane compound, 1,1,3,3-tetramethyldisiloxane (97 %) was supplied by Sigma-Aldrich. Dodecane (Aldrich, ≥ 99 %) was applied as a solvent and 33 wt % sodium (Merck, > 99.98 %) [III, IV, V, VI] and potassium hydroxides (Merck, > 85 %) [IV] solutions in water were used as alkali agents. The reaction kinetics and product distribution was studied at different reaction times [III, IV], temperature [III, IV] and sodium hydroxide [V] concentrations.

A series of experiments was performed with alkali agents represented by sodium trimethylsilanolate (Aldrich, 95 %) and high molecular weight sodium silanolate collected after 3 hours of reaction of TMDS in a 33 wt % aqueous solution of sodium hydroxide at 100° C [VI]. The formed sodium silanolate was dried in an oven at 60 °C for 2 days before being used as an alkali agent.

Dodecane (Aldrich, ≥ 99 %) was used as a solvent. Since some of the reaction products (5-membered linear and cyclic siloxanes) were not visible in GC-MS spectra due to overlapping with dodecane, the base-catalyzed transformation reactions of TMDS with an aqueous solution of sodium hydroxide [IV] and high molecular weight sodium silanolate [VI] were carried out in the presence of decane (Sigma-Aldrich, ≥ 99 %) as a solvent. Siloxane transformations are not influenced by the type of hydrocarbon solvent therefore the amounts of pentasiloxanes were calculated for all experiments with dodecane, based on the liquid product distribution of the decane-contained reaction mixtures. Moreover, influence of methanol (Fluka Analytical, > 99.99 %) on the TMDS transformation reaction in the presence of sodium hydroxide [IV] and different sodium silanolates [VI] was investigated. The transformations of antifoam concentrate A (Sigma, active silicone polymer 100 %) was studied in an aqueous solution of sodium hydroxide and in a methanol solution of sodium silanolate [VI].

2.2. Experimental procedure

The experiments were performed in a 300 mL stainless steel batch reactor, in which 150 mL was used for the liquid volume. The alkali agent (sodium and potassium hydroxides, sodium silanolates) and the non-polar solvent were mixed outside the reactor. In some experiments methanol was added at this stage. Thereafter the reaction mixture was charged into the reactor and heated up to the reaction temperature. Siloxane was then injected into the reactor, the stirring (1000 rpm) was started and a zero sample was taken. The temperature was kept constant during the experiments.

2.3. Analytical techniques

Gas chromatography – mass spectrometry (GC-MS) was used to determine the conversion of the initial siloxane and the concentrations of the liquid products in TMDS transformation reactions [III, IV, V, VI]. The final product compositions in the reactions of the antifoam agent and different alkali agents were also identified by GC-MS [VI]. The data were obtained using Agilent 6890N Network Gas Chromatograph equipped with an Agilent 5973 Network mass selective spectrometer detector coupled to an Agilent DB-PETRO 128-1056 capillary column with a length of 50 m, internal diameter of 200 μm , and 0.50 μm film thickness. The injector was operated in splitless mode and the injection volume was 1.0 μL . Helium was used as the carrier gas with flow rate 0.8 mL/min. The oven temperature profile was 45 °C (5 min) to 300 °C (5 min) with a ramp of 5 °C/min. The concentrations of the siloxane compounds were measured by assuming a response factor of unity.

The composition of the fresh antifoam agent [VI] was studied via high-pressure size exclusion chromatography (HPSEC), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy techniques. Moreover the antifoam agent was loaded in the oven and heated in air to 1073 K at the rate of 5.4 K min^{-1} ; thereafter the formed ash was analyzed by FTIR and energy-dispersive X-ray analysis (EDXA).

High-pressure size exclusion chromatography was used to detect the high molecular weight antifoam agent conversion. The zero and 3h – samples were dissolved in tetrahydrofuran (Sigma-Aldrich, $\geq 99.9\%$) in the concentration about 1 mg/ mL. A HPSEC system using polystyrene standards for calibration after recording retention volumes with an ELS-detector (Evaporative Light-Scattering Detector) was applied. The following PDMSs were analyzed by HPSEC to confirm the applicability of polystyrene as a calibration standard: dodecamethylpentasiloxane (Aldrich, 97 %) of molecular weight 384.84 Da, dimethylpolysiloxane (Sigma) of average molecular weight 2000 Da, and dimethylpolysiloxane (Sigma) of average molecular weight 17250 Da. The three-column system, 2 x JordiGel DVB 500 Å 300 mm x 7.8 mm and Guard column JordiGel DVB 500 Å 50 mm x 7.8 mm was used in analysis. Tetrahydrofuran containing 1 % (v/v) acetic acid was applied as the elution solvent, with the flow rate being 0.8 mL/min.

The composition of the solid products obtained in the reactions between TMDS and different alkali agents (NaOH [III] and KOH [IV]) was investigated by FTIR, TGA and temperature-programmed oxidation–mass spectrometry (TPO–MS). The solids were pre-dried at 60° C for 2 days. Analogously, the composition of the solid products resulting from the reaction between the antifoam agent and sodium hydroxide [VI] was analyzed by FTIR and TPO-MS techniques.

Infra-red spectra of the solid product were recorded on a Bruker IFS 66v/S spectrometer equipped with a DTGS detector and a MIR source. Scans were carried out in the 4000 – 500 cm^{-1} range. Solid sample pellets were prepared by mixing 2 mg of the samples and 200 mg of a potassium bromide (KBr). Background spectra were obtained by scanning a neat KBr pellet.

Thermogravimetric analysis was performed on a CAHN D200 instrument to determine the water and organics contents in the solids. All experiments were conducted in a nitrogen atmosphere, and for all measurements, the baseline was subtracted. The samples were heated from 293 to 728 K at a heating rate of 5.4 K min^{-1} . Isothermal conditions were maintained at the maximum temperature for 5 min.

Temperature-programmed oxidation (TPO) of the solid products was carried out by heating the solids in the following atmosphere: 2.5 wt % oxygen in helium carrier gas with the flow rate 50 cm³/min and temperature programmed to 5.4 K/min up to 1073 K by using Micromeritics (Autochem 2910) apparatus and analyzing the desorbing gases with a quadrupole mass spectrometer (Balzers Instrument, Omnistar). Mass spectrometry was set up to analyze the presence of water, carbon monoxide and dioxide in the oxidation products coming after TPO.

The morphology and elemental composition of the thermally decomposed antifoam agent [VI] were analyzed by scanning electron microscopy and energy dispersive X-ray technique using a Leo Gemini 1530 with a ThermoNORAN Vantage X-ray detector.

The specific surface area of the solid products formed during the reaction between TMDS and 33 wt % aqueous sodium hydroxide was determined by nitrogen adsorption using Sorptometer 1900 (Carlo Erba instruments). The sample was outgassed at 120 °C for 3 h before the measurement. For the determination of the specific surface area BET equation was applied.

3. RESULTS AND DISCUSSION

3.1. Effect of alkali agent type on TMDS transformations [III, IV]

At industrially relevant alkali treatment conditions, the transformation of silicon containing used lube oil is carried out in alkali metal hydroxide aqueous solutions. The process is usually carried out at temperatures below 110 °C with short reaction time (~ 3 hours). Hydrogen-substituted tetramethyldisiloxane (3.72 mmol) was used to examine the siloxane transformation under industrially relevant alkali treatment conditions. The TMDS transformations were investigated in the temperature range of 60-110 °C with widely used in industry 33 wt % aqueous sodium and potassium hydroxides applied as alkali agents. Dodecane (145 ml) was chosen as the solvent imitating a hydrocarbon solution. The influence of an alkali agent type on the reaction performance was elucidated via comparison of the reaction rates and product composition in the mixtures with NaOH and KOH with 3 hours and longer reaction durations.

3.1.1. Effect of temperature on TMDS transformations

Experiments conducted in the temperature range of 60- 110° C demonstrated that the rates of TMDS transformation reactions were found to increase with increasing reaction temperature for both NaOH- and KOH-contained reaction mixtures [III, IV]. In fact, in NaOH- mixture at the highest temperatures (100 and 110 °C), the siloxane conversion after 3 h was about 100 %, whereas at 80 and 60 °C, the conversions were less than 40 % and 10 %, respectively. However, KOH was found to be more efficient than NaOH since in the potassium hydroxide presence the TMDS conversion after 3 h was about 100 % already at 80 °C. Moreover, while no conversion was observed in the reaction between TMDS and NaOH at a temperature of 40 °C, 20 % of TMDS was converted in the presence of KOH.

Comparison of the reaction rates with alkali agents evaluated in the time interval 60– 120 min is depicted in Figure 5. From Fig. 5 it can be seen that at the highest temperatures 100– 110 °C the reaction rates are the same independently on the alkali agent type. However, in the presence of

KOH the dependence of the reaction rate on temperature is not as strong as for the NaOH-containing mixture. The temperature dependence of the rate constant was used to evaluate the

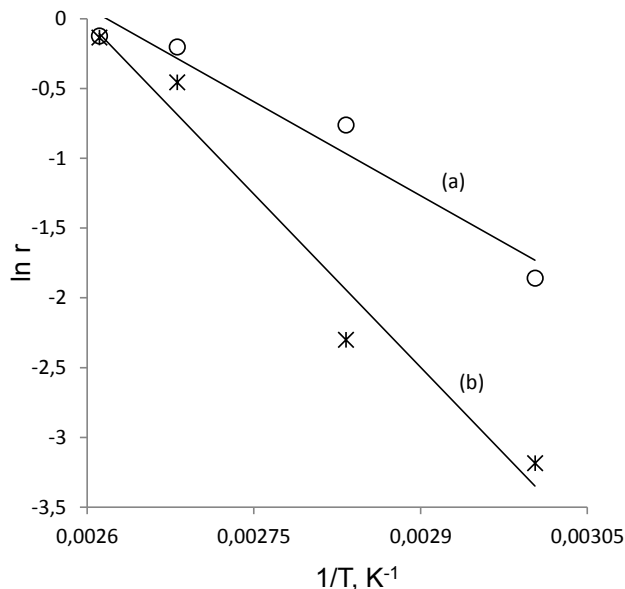


Figure 5. Effect of temperature on the reaction rate of TMDS transformation of the reaction mixture containing: (a) – KOH; (b) – NaOH.

overall activation energy for the investigated reaction mixtures, giving a value for the activation energy of 68 and 37 kJ mol⁻¹, for NaOH- and KOH-containing mixtures, respectively.

Higher reactivity of KOH compared with NaOH is in agreement with a hypothesis made by Hurd et al. [21], suggesting that the first step in the base-catalyzed reaction is coordination of the oxygen atom in the alkali metal hydroxide to a silicon

atom in a siloxane chain, and subsequent rearrangement of the activated complex with the chain cleavage. Thus, increasing the efficiency of oxygen as an electron donor should decrease the temperature at which the base is soluble in the siloxane and accelerate the reaction, or in other words the reactivity is related directly to the size of the cation.

The TMDS base-catalyzed reactions resulted in formation of different liquid and solid products, which are given in Figure 6. Solid products were found to be the dominant ones for all performed reactions. In sodium hydroxide containing reaction mixtures the solid content increased with increasing reaction temperature and reached 77 % at the highest reaction temperature. However, in the case of KOH-mixtures the pattern of the solids formation dependence on the reaction temperature was different. At the lowest reaction temperature of 60 °C, when the reaction rate was relatively slow, the solid products were dominant. As reaction temperature was increased

to 80 °C the yield of the solids reached 72 % of the maximum value experimentally observed. Further temperature increase resulted in the reduction of solid products formation, since at 100° and 110 °C the solid yields were about 49 and 41 %. Thus, under the conditions studied the TMDS transformation proceeded through generation of the solid products, assumed to be alkali metal silanolates, which depending on the conditions could be a final product or could be consumed for cyclic liquid siloxanes formation, in accordance with Fig. 4. The difference in the solid products yield dependence on the reaction temperature for NaOH- and KOH-containing mixtures can be explained by a higher overall rate of the TMDS transformation reactions in the presence of KOH, compared to NaOH. Additionally, the activation energy for the latter one was almost 2 fold higher.

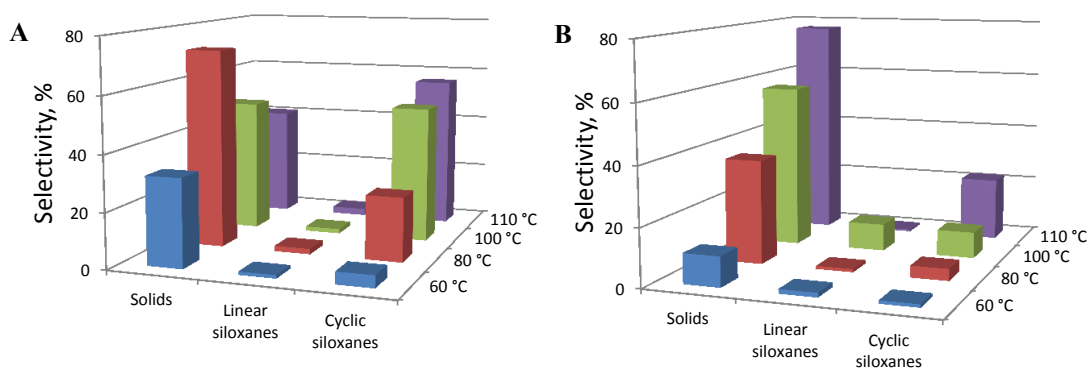


Figure 6. Effect of temperature on the product composition of the reaction mixture containing: (A) – KOH; (B) – NaOH (3 h reaction).

Liquid products were found to consist of linear and cyclic siloxane oligomers (Fig. 6) containing 3- 10 silicon atoms, with cyclic trimer and tetramer being the most abundant products with decreasing fractions of higher oligomers. All formed linear products were hydrogen-terminated according to GC-MS. The studied H-terminated model siloxane (TMDS) comprised of two – silicon atoms, which implies that siloxane hydrolysis and subsequent silanols condensation with generation of high-membered linear siloxanes took place (Fig. 7). Thereafter, based on the reaction product compositions for both alkali agents, metal ions and alkoxy groups attached to the silicon atom form linear silanolates, which depending on the reaction conditions could be a final solid product or

could be consumed in cyclization reactions through back- or end-biting depolymerization mechanisms.

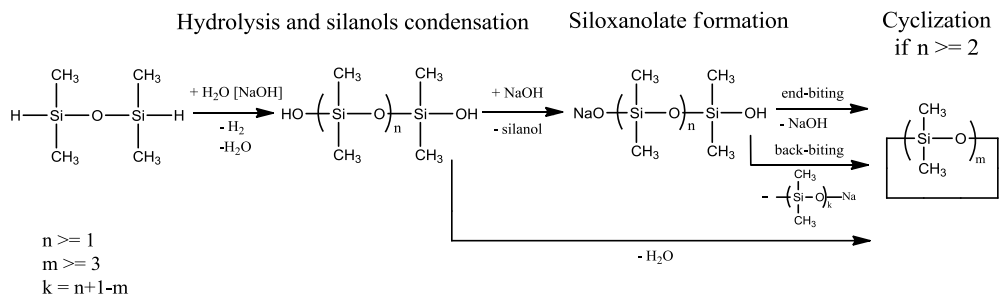


Figure 7. Pathways of TMDS transformation under base-catalyzed conditions.

The liquid products distribution was also found to be dependent on the reaction temperature (Fig. 6). Relative concentrations of cyclic oligomers in the final reaction mixtures increased with elevation of reaction temperature, while amounts of the linear products decreased independently on the type of the alkali agent. The obtained data are in agreement with the proposal from the literature [28] that, as more linear components accumulate, cyclization reactions become dominant, because ring production consumes linear components. Since the overall reaction rates were higher in KOH-containing mixture compared with NaOH, the fast growth of cyclic siloxanes concentration with reaction temperature elevation was observed in mixtures with potassium hydroxide (Fig. 6).

3.1.2. Effect of reaction duration on TMDS transformation

To confirm the proposed reaction pathway (Fig. 7) the transformation reaction of TMDS (3.72 mmol) and 33 wt % aqueous sodium hydroxide (12.5 mmol) was investigated with prolonged reaction time [III]. Experiments were conducted at 100 °C with 3, 6 and 12 hours reaction duration. In addition, a reaction for 70 h was performed at 110 °C. The product compositions for different reaction times were determined (Figs. 8, 9). The yields of the liquid products tended to increase with time, whereas cyclic oligomers became almost the only products in the final reaction mixture at 110 °C after 70 h of the reaction. At 3 and 6 h, cyclic trisiloxane was the dominant among the cyclic siloxanes, whereas at 70 h the concentration of cyclic tetrasiloxane was 4.5 times higher than

cyclic trisiloxane. These results are in agreement with the reaction mechanism proposed in ref [22],

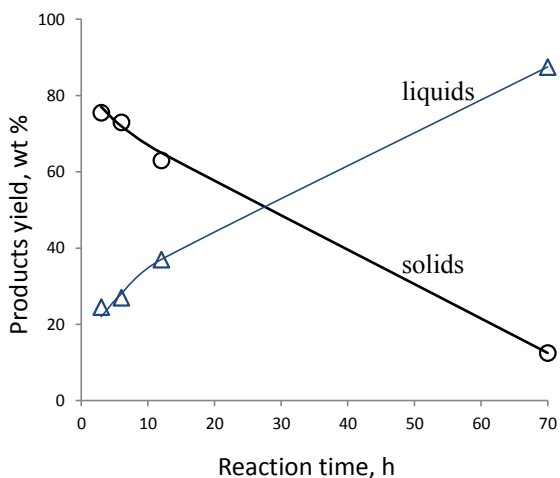


Figure 8. Product compositions as a function of time.

where solid sodium silanates are intermediate products, being transformed into short-chain cyclic oligomers.

To gain additional data regarding the influence of the alkali agent on the reaction scheme, the transformation of TMDS was investigated in the presence of different alkali agents KOH and NaOH with prolonged reaction time. The conditions of

experiments were the following: 110 °C, 7 h [IV].

The composition of the reaction mixture was analyzed for each periodically taken sample by GC-

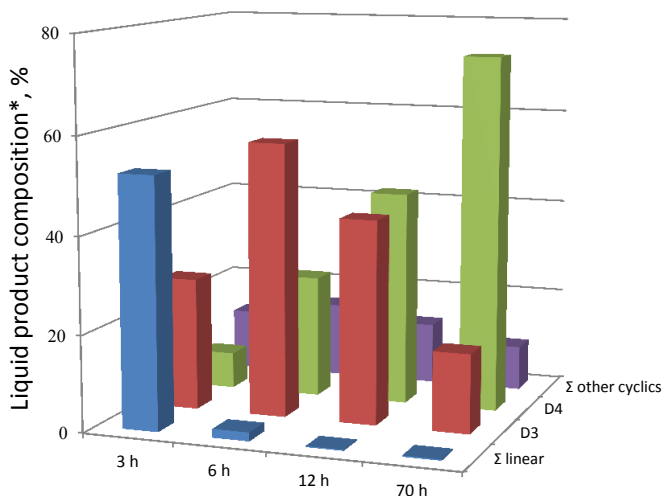


Figure 9. Effect of reaction time on the liquid products composition.

*Here and below L and D denote linear and cyclic siloxanes, respectively; the number following is the number of Si-atoms in the siloxane molecule.

MS. Among the peaks of linear and cyclic siloxanes in GC-MS spectra 6- 8 membered silanols were observed in the time interval 0 – 120 min and 0 – 180 min for KOH- and NaOH-containing reaction mixtures, respectively. The silanols formation is explained by the fact that the

reaction was carried out under the hydroxyl group excess,

leading to siloxane hydrolysis. This finding is in agreement with the reaction mechanism proposed in the literature [29], where siloxane should dissolve under the attack by hydroxyl ion and pentavalent silicon intermediate would be formed (Fig. 10). Thereafter the reaction might proceed

by cleavage of either the silicon–carbon or the silicon–oxygen bond. Since the initial siloxane and

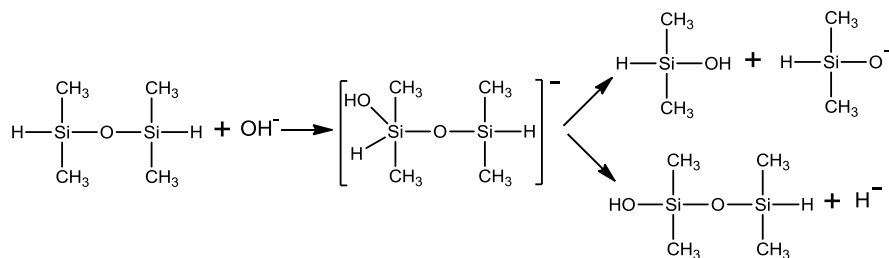


Figure 10. The proposed mechanism of siloxane transformation reaction under alkali treatment [29].

all observed in GC-MS spectra linear siloxanes coming from the reaction mixture are hydrogen-terminated siloxanes, thus the studied reaction might proceed by cleavage either of the silicon–oxygen or silicon–hydrogen bond. Both scenarios lead to formation of silanols. According to Sprung [30], the rupture of the Si–H bond results in release of a hydride ion, which is then immediately attacked by a proton from the water molecule. The alkaline cleavage of the silicon–hydrogen bond in hydrogen-terminated siloxanes resulting in silanol formation and hydrogen release was reported in the literature [31, 32]. Since the initial reaction mixture contained only TMDS, the low-membered silanols also should be present in the reaction mixture. The absence of the silanol peaks in the GC-MS spectra could be explained by high reaction rates of their consumption reactions. Since the reaction mixture composition, independently of the type of alkali agent, comprised linear and cyclic siloxanes it can be assumed that the formed silanols are consumed by condensation reactions with formation of linear siloxanes. The latter ones are then attacked by the hydroxyl group again to form longer-chain silanols. Thereafter the reaction proceeds in accordance with scheme proposed in Figure 7.

The TMDS conversion for reactions with both NaOH and KOH was about 100 % already after 3 h at 110° C (Figure 11 a). Figures 11 b and 11 c illustrate how the concentration of the major compounds in the reaction mixture (3 and 4 linear and cyclic siloxanes) changed as a function of time. From Figure 11 b it can be seen that linear siloxanes were dominant at the beginning of the reactions. Moreover the NaOH-contained mixture showed higher linear siloxanes concentrations

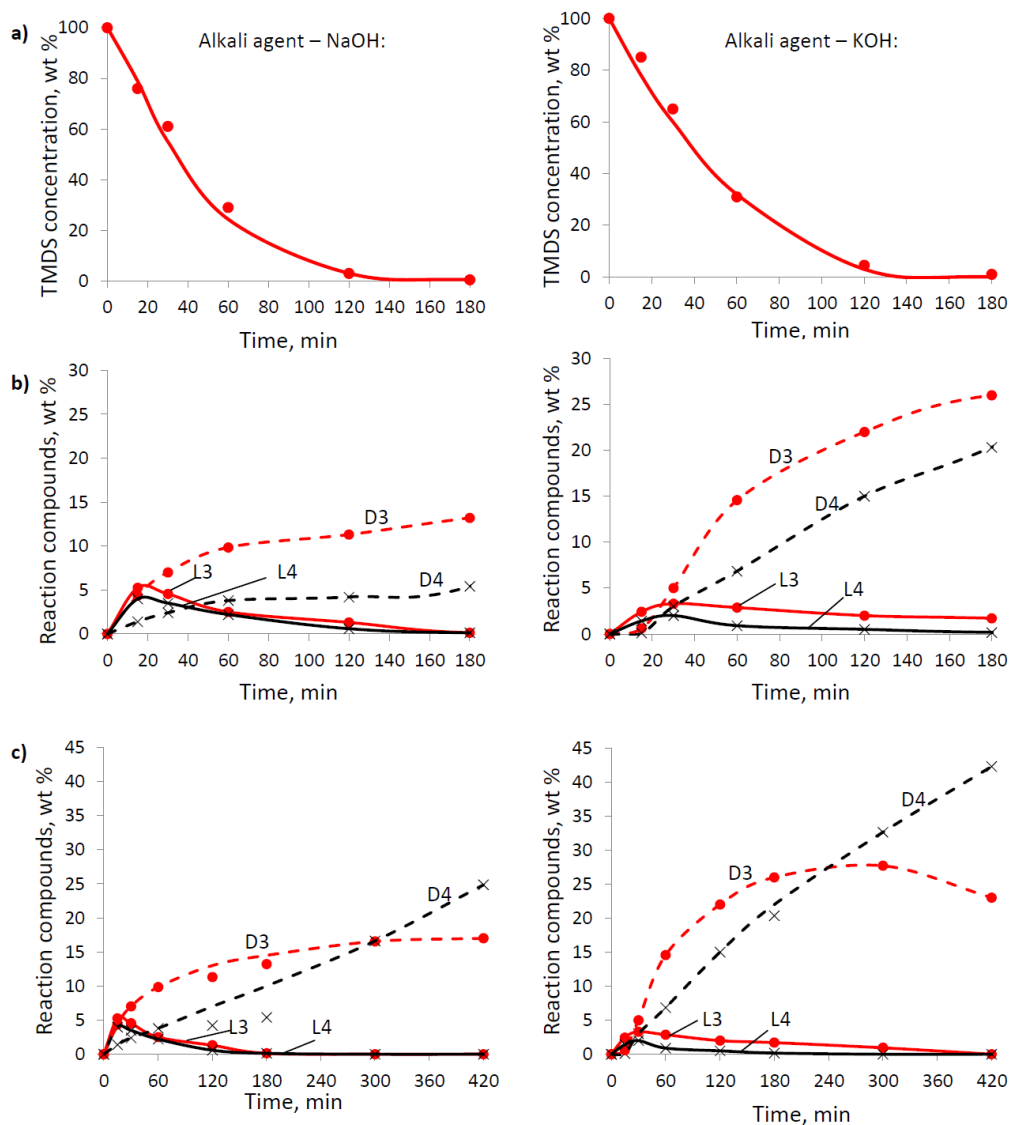


Figure 11. Concentration changes for components in NaOH- and KOH- contained reaction mixture as function of time: (a) TMDS concentration wt % in reaction time 0-180 min; (b) – concentration of linear and cyclic trimer and tetramer siloxanes at 0 - 180 min; (c) - concentration of linear and cyclic trimer and tetramer siloxanes at 0 - 420 min.

compared to KOH. The explanation can be found in the low rate of the subsequent cyclization reactions of linear siloxanes for NaOH-contained mixture. As more linear components accumulate, the cyclization reactions became dominant, because ring production consumed linear components, which were represented by alkali metal silanolates. Both reaction mixtures confirmed that the concentrations of the cyclic siloxanes increased with reaction time. In the NaOH-reaction mixture the cyclic compound D3 dominated over L3 after 20 min of reaction, whereas the concentration of

D4 exceeded the L4 concentration in about 40 min of reaction. The amount of cyclic D3 and D4 products in KOH-mixture increased more rapidly than in the NaOH-mixture and both cyclic compounds became dominant at the same reaction time of about 25 min (Figure 11 b). Since the cyclization reaction proceeds through the stage of the formation of linear alkali metal silanolates it could be assumed that the rate of sodium silanolates cyclization reaction is significantly lower than that for potassium silanolates. As a confirmation of this in the NaOH-contained reaction mixture the yields of solid products, which are silanolate salts, were more than 3 fold higher than the total yield of liquid products at different temperatures for 3 h- reaction time [III], whereas the KOH-mixture demonstrated domination of the liquid products for 3 h-reaction at temperature above 100° C [IV]. Figure 11b shows that after 3 h of reaction the amount of linear compounds in both reaction mixtures was almost zero, whereas the concentrations of cyclic D3 and D4 products were significant. Moreover, for both mixtures cyclic trisiloxane was the dominant liquid product, which can be an evidence that it is kinetically favoured. Comparison of the compositions of the 3 h- reaction mixtures for NaOH and KOH demonstrated that D3 and D4 content in KOH-reaction was two and four fold higher, respectively, than for NaOH-mixture. Moreover, further reaction continuation showed that D4 became a dominant product after 4 and 5 hours for KOH and NaOH-contained mixtures, respectively (Figure 11 c). The concentration of D3 reached about 15 % in NaOH- mixture and 25 % in KOH mixture, whereas the formation of D4 continued due to silanolate salts cyclization. This finding is an agreement with the study of Zhang et al. [28], where dominance of D4 with reaction time was also observed.

3.1.3. Solid products composition

The composition of solids resulting in the base-catalyzed reactions of TMDS in the presence of potassium [IV] and sodium hydroxides [III] was analyzed via FTIR, TGA and TPO-MS techniques. The results and comparative analysis of solid products formed in NaOH – and KOH-contained mixtures are summarized in Table 1.

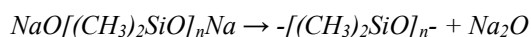
Table 1. Results of analysis of solid products formed in the TMDS base-catalyzed transformation in the NaOH [III] and KOH [IV].

NaOH + TMDS	KOH + TMDS	Comments
Thermogravimetric Analysis (TGA)		
<ul style="list-style-type: none"> Total water content: 5 wt % 175 – 277 °C weight loss: 35 wt % 	<ul style="list-style-type: none"> 12 wt % 19 wt % 	<p>The process of water crystallization with silanolate salts occurs more in the case of KOH than with NaOH.</p> <p>The solids are mixtures of 4–7 membered linear dimethylsilanolates of sodium and potassium. Sodium silanolates have shorter siloxane chains than those in potassium silanolates.</p>
Temperature-programmed oxidation combined with mass spectrometry (TPO-MS)		
<ul style="list-style-type: none"> Free and ionically bonded water, TCD signals at temperature, °C [33]: 61 and 93 Cyclic siloxanes release, TCD signals at temperature, °C: 230 and 320 	<ul style="list-style-type: none"> 77 and 126 145, 195 and 255 	<p>The mass spectra of both samples are correlated with TPO spectra and confirmed that at decomposition temperatures below 130 °C, only water release occurred. This data is an agreement with the TGA results.</p> <p>In the MS spectra of both samples a release of carbon monoxide and dioxide was registered. Thus, the mechanism of thermal degradation of the solids implies the hemolytic Si–CH₃ bond scission with formation of methane, which thereafter is oxidized to carbon dioxide and water [34].</p> <p>TPO results are not in line with TGA, demonstrating lower molecular weight of potassium silanolates compared to that in sodium silanolates.</p>
Fourier transform infrared (FTIR) spectroscopy of the solids before the TGA		
<ul style="list-style-type: none"> Water presence (~ 3200 cm⁻¹) [35] Alkali metal hydroxides presence (abundant bands in the range of 1450–1370 cm⁻¹, 880 cm⁻¹ and 700 cm⁻¹) [IV, VI] Si–O–Si stretching vibrations (1110–1000 cm⁻¹) [33, 36] Si–CH₃ (1255 cm⁻¹); Si(CH₃)₂ (798 cm⁻¹) [36, 37] 		<p>Potassium silanolate spectra demonstrated higher intensity of water related band than that in sodium silanolate, confirming higher water content in KOH-sample recorded by TGA and TPO analysis.</p> <p>Both samples demonstrated abundant bands in the range attributed to remaining in the solid product NaOH and KOH, which were taken in excess, for sodium and potassium silanolates, respectively.</p> <p>The band of Si–O–Si in the potassium silanolate is broader and more complex, showing several overlapping bands, contrary to the results for the solid products formed in the reaction between NaOH and TMDS. Thus, according to Launer [36] the siloxane chains in the KOH-solids are longer than those in the NaOH-solid products. The data are in agreement with TGA results.</p> <p>Both samples exhibited polydimethylsiloxanes characteristic bands for the silicon–dimethyl absorption and a band for Si–CH₃ bonds, confirming the presence of siloxane chains in studied silanolates.</p>
Fourier transform infrared (FTIR) spectroscopy of the solids after the TGA		
<ul style="list-style-type: none"> Alkali metal hydroxides bands in the range of 1450–1370 cm⁻¹, 880 cm⁻¹ and 700 cm⁻¹) [IV, VI] 		<p>The ash resulting after TGA analysis of both samples did not show any presence of Si–O–Si structures, Si–CH₃, Si–(CH₃)₂ and water, while exhibited only the bands attributed to the alkali metal hydroxides. These results indicate that during TGA silanolates decomposed through a condensation reaction with the release of volatile cyclic dimethylsiloxane oligomers and alkali metal oxide.</p>

Based on TGA results, weight losses in low temperatures were observed in both NaOH- and KOH- contained solids. These weight losses correspond to evaporation of free and ionically bonded

water [33]. In potassium silanolate sample water evaporation was continuing at relatively high temperature about 150 °C. According to Hyde [38], this could be caused by water contained in the reaction mixture crystallized with a portion of potassium silanolate salts as the hydrate.

At high TGA temperatures the samples were thermally decomposed. As was shown by Clarke et al. [37] thermal degradation of the alkali metal silanolate salts results in release of a number of liquid cyclic siloxane polymers which evaporate when temperature during TGA analysis reaches their boiling points and the alkali metal stays in the ash in the form of oxide:



Such evaporation is seen as a weight loss in the TGA curve. The composition of the potassium and sodium silanolates was estimated (Table 1) based on the same study [37], which proposed that the number of silicon atoms in linear silanolate salts can be evaluated based on TGA results and the boiling points of cyclic siloxane oligomers reported in the literature [19, 39].

The TPO results (Table 1) were analyzed based on thermal conductivity detector (TCD) signals exhibited at decomposition temperatures of the samples. The TGA and TPO results are in line regarding water content in the samples. However, TGA results contrary to TPO demonstrated longer siloxane chains in potassium silanolate than in sodium silanolates. This disagreement could be due to different conditions applied in TGA and TPO analysis.

FTIR was used to investigate the chemical composition of the solid products obtained in the 3 h reaction between potassium/ sodium hydroxide and TMDS at 100 °C and the ash resulting from the TGA analysis of these samples (Table 1). The results confirmed that the formed solids were represented by sodium and potassium dimethylsilanolates. Moreover, the FTIR spectra of the ash resulting in TGA analysis of the samples, demonstrated that during TGA silanolates decomposed through a condensation reaction with the release of volatile cyclic dimethylsiloxane oligomers and alkali metal oxide. The FTIR results were in agreement with TGA, indicating longer siloxane chains in potassium silanolates than in sodium silanolates.

3.1.4. Sodium silanolate as an alkali agent [VI]

As can be seen from data described in previous sections, the transformation of TMDS in the presence of any type of alkali metal hydroxide at temperatures about 100 °C with short reaction time (3 h) resulted in formation of the solid product as a dominant one. From an industrial point of view the formation of solids should be diminished during the alkali treatment as they can be deposited in various locations in the re-refining units, causing significant problems. In order to verify the proposed reaction scheme (Fig. 7), which implies the formation of the solids (silanolate salts) and their further consumption by cyclization reactions, the commercially available sodium trimethylsilanolate was added into the reaction mixture as an alkali agent instead of sodium hydroxide with the same weight concentration (0.5 wt %). Experimental results confirmed an increase of the overall reaction rate in the presence of sodium trimethylsilanolate ($(CH_3)_3SiONa$), since TMDS was completely converted after 30 min. It is apparent that when starting with the silanolate salts almost no solid products were formed (Fig. 12). Moreover, comparative FTIR

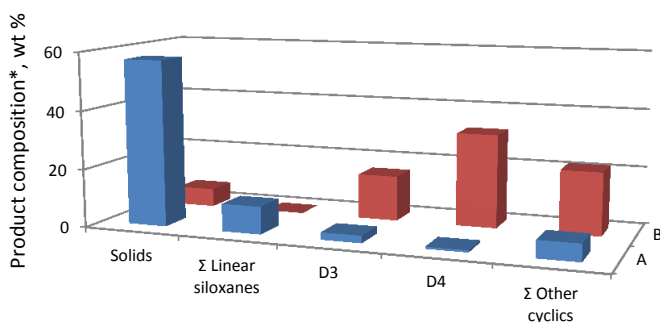


Figure 12. Product composition in the reaction mixtures of TMDS and (A) - NaOH; (B) - $(CH_3)_3SiONa$.

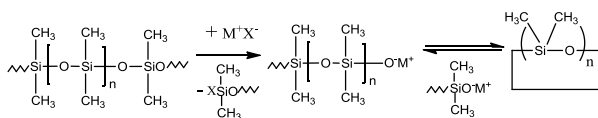
analysis of the initial sodium silanolates and the solid compounds collected after the reactions demonstrated that these solids were unreacted sodium silanolates which were applied as a reagent, since no difference was

observed in the FTIR spectra. The liquid products were found to contain only cyclic siloxane oligomers according to GC analysis, whereas linear oligomers were dominant products in the presence of NaOH [III] (Fig. 12). This fact confirms higher reaction rate of TMDS transformations in sodium silanolate- mixture, than that in NaOH - mixture.

3.1.5. Combined influence of the solvent and alkali agent type [IV, VI]

Commonly in industry, alkali agent compounds act in aqueous solutions. In order to check the role of water in the model siloxane base-catalyzed transformation, the reaction of 3.72 mmol TMDS was carried out in a water-free sodium hydroxide (12.5 mmol) [III]. The conversion of TMDS was about 20 %, and the major reaction products were solids. Hence, water-free sodium hydroxide under the studied reaction conditions was found to act as a reagent and to lead to the formation of solid products.

According to the section 3.1.3, the TMDS transformation reactions in the presence of alkali metal hydroxides result in the formation of 4 -7 membered linear alkali metal silanolates, which represent the undesired solids in used oil recycling industry. Since the proposed reaction scheme (Fig. 7) implies the consumption of formed silanolates by cyclization reactions with generation of liquid cyclic siloxanes, it can be assumed that the treatment of the used oils with long-chain silanolates could yield only liquid products, in accordance with the mechanism of polysiloxane



M⁺ - alkali metal ion
X⁻ - OH⁻ or another basic anion

Figure 13. Mechanism of anionic depolymerization of polysiloxane.

anionic depolymerization, illustrated in

Figure 13. Therefore, sodium silanolates

collected as the final products in the

reaction between TMDS and sodium

hydroxide, were added into water-free

reaction mixture as an alkali agent [VI]. Their relative concentration in the mixture was diminished

(0.1 wt %), since an excess of the alkali agent remains in the final reaction mixture (see Section

3.1.4). Despite a low surface area of the chosen silanolate (13 m²/g), the initial rate of TMDS

transformation was significantly higher compared to water-free sodium hydroxide [III]. The

siloxane conversion after 3 h was about 73 % for sodium silanolates, whereas for the NaOH-

contained mixture the conversion was less than 20 % and the solids were the major reaction

products. Analogously, as for the water-containing reaction mixture (Section 3.1.4), the reactions

between the TMDS and dry sodium silanolates yielded mainly liquid products with the linear

oligomers being the dominant ones (Table 2, A). Thus, water presence is essential in the sodium hydroxide-contained reaction mixture, where TMDS transformations start with hydrolysis.

Table 2. Influence of methanol addition on product distribution.

Reaction mixture	Yield of solids, wt %	Yield of liquids, wt %	Liquid product composition at 73 % conversion, wt %			
			Σ linear siloxanes	D3	D4	Σ other cyclic siloxanes
A	5.9	67.1	70.3	6.7	4.9	18.1
B	< 1	73	-	8.5	53.9	37.6
C	52.9	20.1	7.1	55.5	11.5	25.9
D	54.8	18.2	1	50.9	35.6	12.5

Reaction mixture: (A) – 145 ml Dodecane + 0.5 g/3.72 mmol TMDS + 0.06 g sodium silanolate; (B) – 145 ml Dodecane + 0.5 g/3.72 mmol TMDS + 0.06 g sodium silanolate + 0.35 g/ 11 mmol CH₃OH; (C) – 145 ml Dodecane + 3.72 mmol TMDS + 12.5 mmol NaOH + 55.5 mmol H₂O + 3.72 mmol CH₃OH; (D) – 145 ml Dodecane + 3.72 mmol TMDS + 12.5 mmol NaOH + 55.5 mmol H₂O + 11 mmol CH₃OH.

Since several studies have reported that the addition of an alcoholic solvent affects the reaction rates of various siloxane transformations [21, 26-27], the reaction between TMDS and different alkali agents (sodium hydroxide **[IV]**, sodium silanolates **[VI]**) was studied in the presence of methanol. Hurd et al. [21] have proposed that the base-catalyzed siloxane polymerization reaction proceeds through the coordination of the oxygen atom in the alkali metal hydroxide to a silicon atom in a siloxane chain and a subsequent rearrangement of the activated complex with the chain cleavage. Thus, high degree of the alkali metal hydroxide ionization will cause its high reactivity. Moreover, addition of a polar solvent increases the degree of ionization and results in a more rapid polymerization.

The effect of methanol addition was investigated for 3.72 mmol TMDS transformation reaction with 33 wt % NaOH aqueous solutions at several methanol concentrations: 3.72 and 11 mmol **[IV]**. Additionally transformation of 3.72 mmol TMDS was studied in the presence of a high-membered sodium silanolate (0.1 wt %) dissolved in 11 mmol methanol **[VI]**. Since these silanolates are solids, addition of methanol created a homogeneous initial reaction mixture. In all methanol-contained reaction mixtures the addition of methanol substantially accelerated the reaction rates. Thus, in NaOH-mixture TMDS was completely converted after 1 hour of reaction for the reaction mixture with the highest methanol concentration, and in sodium silanolate salts mixture

TMDS was converted within 15 min. A possible explanation of the methanol effect on the rate of TMDS transformation reactions is that the siloxane undergoes the nucleophilic attack by hydroxyl coming from methanol and all the bonds between silicon and its neighbors are weakened. The activation energy required for the siloxane hydrolysis reactions is decreases, thus, the overall rate of TMDS transformation reaction increases.

The evaluation of product composition in methanol-contained reaction mixtures with sodium hydroxide demonstrated that the addition of methanol to the reaction mixture did not affect the yield of solid products, however led to predominance of cyclic products in the final products (Table 2, C, and D). Moreover, high methanol concentration (D) resulted in low yields of high molecular weight products compared to lower methanol concentration (C). A possible explanation is [21] that, under excess of the hydroxyl groups, which are attached to one end of a siloxane chain, they act as a chain-terminating unit and result in lower molecular weight products.

The product distribution obtained in the TMDS transformation reaction catalyzed by high molecular weight sodium silanolate salts in the methanol solution showed that the methanol addition led solely to the formation of liquid products, since the yield of solids was less than 1 wt %, whereas in methanol-free reaction mixture it reached 8 wt %. The liquid product composition (B) comprised of only cyclic siloxanes, with cyclic tetrasiloxane being the dominant product, as opposed to the methanol-free reaction mixture contained mainly linear siloxanes (A). The amount of high-membered siloxanes was insignificant, analogously to NaOH-contained mixture described above.

Hence, independently on the type of an alkali agent the addition of methanol into the reaction mixture substantially increased the overall reaction rate of TMDS transformations. Moreover, methanol was found to affect the liquid product distribution, resulting in dominance of cyclic siloxanes with low molecular weights in the final reaction mixtures.

3.2. Influence of the alkali agent concentration on the TMDS transformation [V]

As it was mentioned in the Introduction, the transformation of organosilicones during the used oil re-refining process is of great interest because of the negative effect of silicon compounds on the performance of hydrotreating catalysts and formation of undesired solids in various locations in the re-refining units. Various alkali agents can be used for the alkali treatment process of the used oils. Sodium hydroxide applied as an alkali agent has the most attractive price. Therefore, influence of NaOH relative concentration in the reaction mixture on TMDS conversion and product distribution was studied in detail [V]. A series of experiments was performed with varied relative concentration of the alkali agent and TMDS. In the first experiment a mixture of TMDS (3.72 mmol) and sodium hydroxide (6.25 mmol) in water solution (55.6 mmol) was intensively stirred at 100° C for 3 hours in dodecane (150 ml). The concentrations of all reaction compounds were the same in the second run except a decreased amount of NaOH (1.25 mmol). The TMDS transformation reaction order was found to be negative with respect to NaOH [V].

According to the results described in section 3.1, the investigated reaction rate can be characterized based on the solid products content, linear and cyclic product distribution and cyclic trimer – tetramer relative concentration in the reaction mixture. The solids were dominant products at low temperature and short reaction times. The liquid products in the low temperature reactions were represented mainly by linear siloxanes. The prolongation of reaction time resulted in a decrease of solids, whereas both temperature and time increase led to dominance of cyclic products in the reaction mixture. Experiments with the varied reaction time demonstrated that the concentration of cyclic trimer being the dominant in the beginning of the reaction diminished with time, whereas the cyclic tetramer tended to increase. Experiments with a lower sodium hydroxide concentration showed the same effect. Table 3 displays an influence of NaOH content on the main reaction rate characteristics: solid amounts, total linear siloxanes concentration in the final reaction mixture, yields of cyclic trimer (D3) and tetramer (D4).

Table 3. Effect of NaOH concentration on product composition.

NaOH (mmol) in the reaction mixture	Selectivity, wt %				
	Solids	Σ linear siloxanes	D3	D4	Σ other cyclic siloxanes
12.5 [III]	75.5	12.7	6.8	1.9	3.1
6.25	34.5	-	16.8	32.5	16.2
1.25	4.0	-	15.0	37.1	43.9

The reaction with a low NaOH content (1.25 mmol) resulted in the formation of solely liquid products, with the yield of 96 %, represented by only cyclic siloxanes, cyclic tetramer being the dominant one. D3 concentration started to decrease with increasing of D4 after 1 h of reaction. Analogously, a D3-D4 concentration switch was observed in the reaction mixture with 6.25 mmol NaOH, however, only after 2 h of reaction. Moreover, an increase of NaOH content also led to 34.5 % yield of the solid products. Further increase of NaOH concentration up to 12.5 mmol [III] resulted in mainly formation of solids. The yield of the liquid products was less than 25 % with linear siloxanes being the main liquid products. Thus, formation of the undesired solid products, silanulates with different molecular weight is determined by the relative concentration of sodium hydroxide in the initial reaction mixture. A decrease of the alkali agent amount leads to elimination of solids and increase of the overall reaction rate and selectivity to the liquid products.

3.3. Mechanism of TMDS base-catalyzed reaction [V]

Based on the experimental results described in sections 3.1 and 3.2 the base-catalyzed TMDS transformation reaction scheme was proposed (Fig. 14). Since the chosen model compound is hydrogen-terminated siloxane ($M^H M^H$) its transformation starts with hydrolysis which proceeds with a nucleophilic attack by hydroxyl on siloxane (Fig. 10). The alkaline cleavage of the silicon-hydrogen bond in TMDS results in silanol formation and hydrogen release, analogously to literature suggestions [31, 32]. According to Tondeur et al. [32] formation of silanediols takes a place only for siloxanes containing more than 3 silicon atoms, since the first silicon atom bonded to hydroxyl group makes the other silicon through the siloxane link less available for the nucleophilic attack. The absence of silanols and silanediols in GC-MS spectra can be explained by a proposal made by

Chojnowski and Cypryk [15], namely that due to high silanol acidity, the whole base is transformed into solid silanolate. According to the experimental data described above, the solids were found to be initial reaction intermediates. Thereafter they were transformed to liquids or remained in the mixture as the final reaction products. Taking into account instantaneous silanols and silanediols transformations into mono- and disodium silanolates, the reaction scheme was simplified by combining hydrolysis and silanolate formation in one step (Fig. 14).

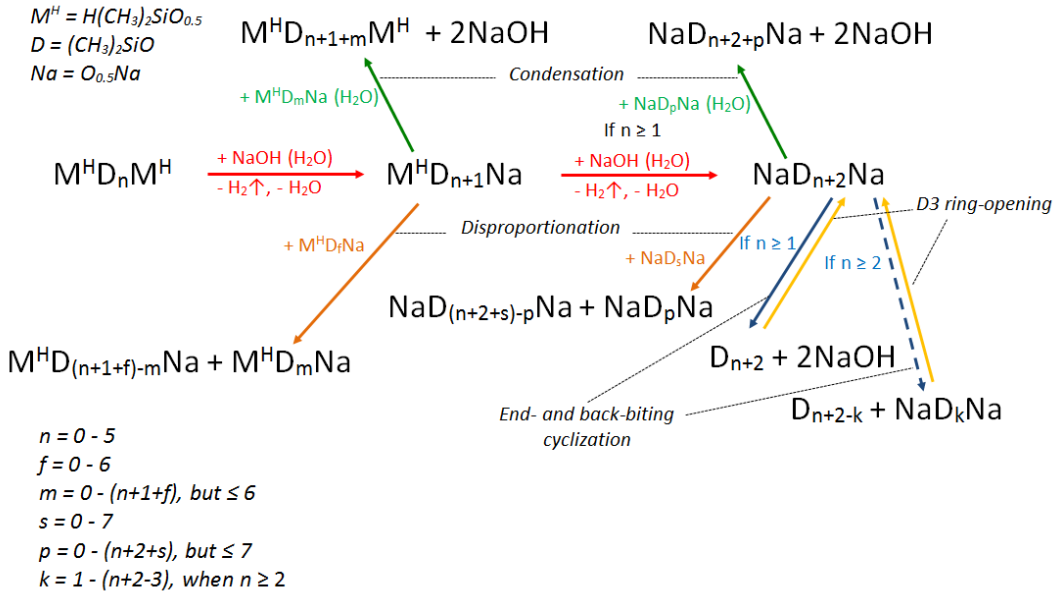
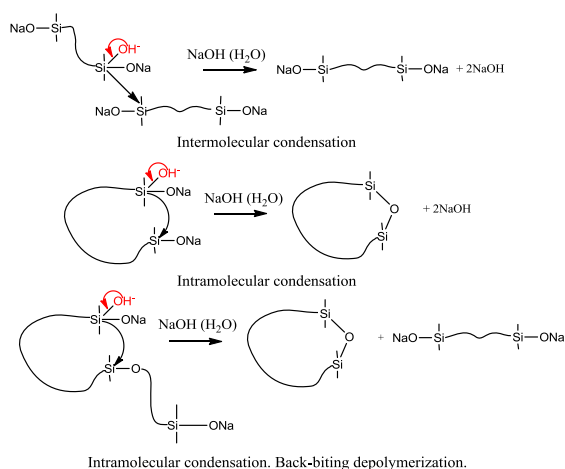


Figure 14. Base-catalyzed TMDS transformation pathways.

The formed single sodium silanolate ($M^H D_{n+1} Na$) containing less than 3 Si-O units can undergo only condensation and disproportionation reactions [13- 15]. The condensation reactions result in hydrogen-terminated linear siloxanes generation ($M^H D_{n+1+m} M^H$) which are usually observed in GC-MS spectra of the reaction samples taken in the beginning. The H-terminated linear siloxanes undergo hydrolysis likewise the initial substrate, TMDS. Sodium oxide released in the condensation and water form sodium hydroxide. In accordance to Fig. 10 hydroxyl ion is essential in the hydrolysis reaction. Therefore it should be noted that OH^- is always regenerated and its concentration remains constant despite the consumption of linear siloxanes.

The disproportionation commonly accompanies condensation and leads to formation of sodium silanolates with different molecular weight (Fig. 14). As it was indicated in [15], disproportionation is particularly important in the presence of strong bases, where it is much faster than condensation. Since in the studied reaction the solid products concentrations were not measured, being calculated from the initial siloxane and liquid product concentration, both disproportionation and condensation reactions were included in the scheme.

Among the mentioned above reactions single sodium silanolates containing more than 3 Si-O units undergo a second hydrolysis reaction, since the silanolates still contain Si-H bonds. Silanediols formed in the hydrolysis are instantaneously transformed into disodium silanolates ($\text{NaD}_{n+2}\text{Na}$). High-membered silanolates can be involved in the same type reactions as condensation and disproportionation and moreover cyclization reactions take place. As exemplified in the study of Chojnowski et al. [40] for the oligosilanols condensation, the base-catalyzed silanolates condensation can proceed through inter- or intramolecular condensation (Fig. 15). The condensation of sodium silanolates shows a competition between intramolecular (unimolecular cyclization) and



intermolecular condensation with linear products generation. Based on [40] dilution of the system retards strongly the intermolecular condensation increasing the yield of the cyclic products. This fact explains the dominance of cyclic products (D_{n+2} , D_{n+2-k}) over linear once in the low NaOH-containing reaction mixtures.

Figure 15. Mechanism of intermolecular and intramolecular condensation.

The mechanism depicted in Figure 15 could explain the behavior of single sodium silanolates. The weight concentrations of linear siloxanes observed in GC-MS spectra of samples collected throughout a typical reaction were used to find a dependence of linear siloxanes

concentrations on their molecular weight or number of silicon atoms in the siloxane chains (Table 4). About 65 % of the total amount of linear siloxanes appeared in molecules having the number of

Table 4. Typical weight distribution of linear siloxanes observed throughout TMDS transformation.

Number of Si-O units in linear siloxane	Concentration, wt %
3	14.6
4	15.4
5	17.0
6	17.5
7	13.2
8	10.4
9	7.8
10	4.1

siloxane units within the range 3- 6. The explanation for such linear siloxane distribution is that short-chain silanolates can undergo only the intermolecular condensation reaction. With an increase of the number of Si-atoms in silanolates, probability of the intramolecular condensation (cyclization) increases. Thus, long enough 3-6-membered silanolates will preferably undergo

intramolecular condensation reactions with formation of cyclic products rather than intermolecular condensation with short-chain silanolates to form 7-and high-membered linear siloxanes.

As depicted in Figures 14 and 15 intramolecular condensation of disodium silanolates can proceed through the end- and back-biting mechanism in accordance with Oku et al. [22]. Cyclization (or depolymerization) theoretically should be accompanied with reversible polymerization resulting in formation of long chain linear siloxanes (Figs. 3 and 13). However, experimental results did not show any polymerization reactions, which leads to a conclusion that under the studied reaction conditions only cyclization or depolymerization reactions take place. Under optimized reaction conditions, such as high temperatures, low sodium hydroxide concentration and prolonged reaction time, initially high concentration of cyclic trimer tends to decrease in the course of the reaction. Thus, in the TMDS transformation scheme (Fig. 14) the anionic ring-opening reactions proceeding according to Figure 13 were taken into account only for the cyclic trimer (D3). As exemplified in the experiment with a low concentration of NaOH the decrease of D3 concentration resulted in D4 increase (Figure 16). Thus, sodium silanolates formed in D3 ring-opening reactions undergo again cyclization reactions with formation of cyclic tetramer.

The formation of nonreactive silanolates complexes was observed in the base-catalyzed

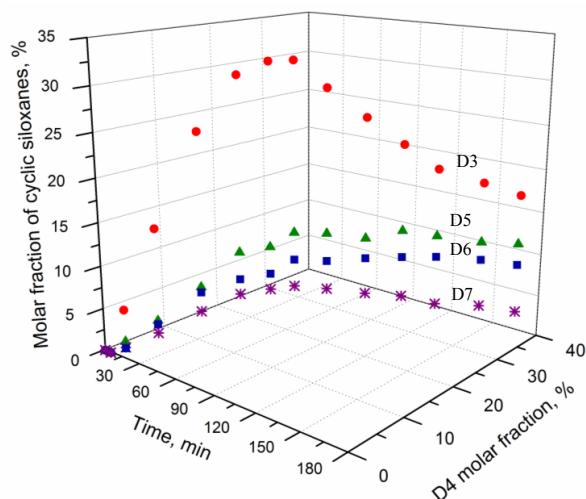


Figure 16. Relative molar concentrations of cyclic siloxanes and D4 in the reaction mixture.

reaction conditions [25]. The aggregated silanolates constitute dormant centers, which are in equilibrium with a small amount of free silanolate groups able to participate in polymerization. The polymerization is negligible since the equilibrium lies well on the side of these aggregates. As it was mentioned above (Fig. 15) in the studied conditions the aggregation results in cyclic products

release. However, an assumption regarding the cyclics formation was done in order to simplify the subsequent kinetic modeling by reducing the number of intermediates with unknown concentrations, such as hydroxyl-terminated sodium single silanolates. The latter ones most probable could be transformed to cyclic siloxanes through end- or back-biting depolymerization with sodium hydroxide and short-membered silanolate releases, respectively [22]. According to Mazurek et al. [25] the intermolecular mechanism for formation of the ring structures containing two or more aggregates is strongly preferred for short chains, since end-groups of these chains always operate at a short mean distance from each other. Hence, if the intermolecular cyclization mechanism prevails, production of cyclic compounds is determined by silanolates concentration. However, in the present study an increase of NaOH content in the initial reaction mixture did not cause high yields of cyclic siloxanes (Section 3.2). Thus intermolecular cyclization was not included in the TMDS transformation scheme (Fig. 14), since the cyclic products formation was dependent only on the length of siloxane chains.

3.4. Kinetic modeling of the TMDS base-catalyzed transformations [V]

The kinetic model was developed in accordance with the reaction network for TMDS base-catalyzed reactions displayed in Figure 14. The experimental data obtained for the low-concentrated sodium hydroxide mixture (1.25 mmol NaOH) [V] was used for modelling of concentration-time dependencies for the studied substrate and various reaction products. The detailed reaction could be illustrated as follows (Scheme 1):

Scheme 1. TMDS base-catalyzed reactions.

No	Reaction step	Constants	Chain length parameter	Number of reactions
1	$M^H D_n M^H + NaOH [H_2O] \rightarrow M^H D_{n+1} Na$	k_1	$n = 0 - 5$	6
2	$M^H D_{n+1} Na + M^H D_m Na \xrightarrow{[H_2O]} M^H D_{n+1+m} M^H + 2NaOH$	k_2	$m = 0 - 4$ only for $n = 0-4$ $0 \leq n+m \leq 4$	11
3	$M^H D_{n+1} Na + M^H D_f Na \rightarrow M^H D_{(n+1+f)-m} Na + M^H D_m Na$	k_3	$f = 0 - 6$ $1 \leq n+f \leq 8$	42
4	$M^H D_{n+1} Na + NaOH [H_2O] \rightarrow NaD_{n+2} Na$	k_1	$n = 1 - 5$	5
5	$NaD_{n+2} Na + NaD_p Na \xrightarrow{[H_2O]} NaD_{n+2+p} Na + 2NaOH$	k_2	$p = 1 - 5$ only for $n = 0-4$ $0 \leq n+p \leq 5$	12
6	$NaD_{n+2} Na + NaD_s Na \rightarrow NaD_{(n+2+s)-p} Na + NaD_p Na$	k_3	$s = 1 - 6$ $2 \leq n+s \leq 9$	42
7	$NaD_{n+2} Na \xrightarrow{[H_2O]} D_{n+2} + 2NaOH$	k_4	$n = 1 - 5$	5
8	$NaD_{n+2} Na \rightarrow D_{n+2} + NaD_k Na$	k_5	$n = 2 - 5$	10
9	$D_3 + 2NaOH \rightarrow NaD_3 Na + H_2O$	k_6	Only for D_3	1
10	$D_3 + NaD_k Na \rightarrow NaD_{3+k} Na$	k_7	$k = 1 - 4$	4

In the development of the model the following assumptions were used. All reactions were assumed to be irreversible. The species reactivity was independent of the chain length. Moreover, the reaction constants of disproportionation (k_3 , Scheme 1) and condensation (k_2 , Scheme 1) were assumed the same for mono- ($M^H D_{n+1} Na$) and disodium ($NaD_{n+2} Na$) silanolates, since formation of the latter one starts only when the siloxane chain is long enough (more than 3 Si-O units) and the second chain end does not affect the reaction rates. Analogously, the constant of combined hydrolysis and silanolate formation reactions for linear siloxanes ($M^H D_n M^H$) and hydrogen-

terminated long-chain silanolates ($M^H D_{n+1} Na$) were considered to be the same (k_1). Formation of sodium silanolate aggregates (see section 3.3) was not taken into account. Due to complexity of the system and lack of experimental data for the solid phase of the reaction mixture, the different solid species were modeled as a lump. In the kinetic model only the main reaction products containing 1-7 Si-O units were described, while the compounds formed in inferior amounts were not taken into account.

In general, in the proposed reaction scheme (Fig. 14 and Scheme 1) the first step is combined linear siloxane hydrolysis resulting in formation of silanol with its further transformation to single sodium silanolate (Scheme 1, entry 1). The formed silanolate then undergoes a series of condensation (Scheme 1, entry 2) and disproportionation reactions (Scheme 1, entry 3). The condensation reaction which can result in TMDS formation was omitted. The disproportionation reactions for $n + f = 1$ were not taken into account since they do not change the concentrations of reactants. When amounts of Si-O units in a single silanolate chain have reached 3, among disproportionation and condensation reactions, hydrolysis accompanying with the subsequent disodium silanolate generation takes place (Scheme 1, entry 4). The formed silanolates could be involved in condensation (Scheme 1, entry 5), disproportionation (Scheme 1, entry 6) and end-biting depolymerization reactions with formation of cyclic products. The silanolate having more than 4 Si-O units can undergo back-biting cyclization (Scheme 1, entry 7). In accordance with the proposed reaction mechanism (Fig. 14) ring-opening reactions with sodium hydroxide (Scheme 1, entry 8) and silanolate (Scheme 1, entry 9) were taken into account only for the cyclic trimer.

For the proposed reaction scheme 138 kinetic equations were derived. The rates of hydrolysis and further transformations of the formed hydroxyl-terminated compound into silanolate for the steps 1 and 4 (Scheme 1) are expressed as follows:

$$r_{hI} = k_1 C_{M^H D_n M^H} C_{OH^-} \quad (1)$$

$$r_{hII} = k_1 C_{M^H D_{n+1} Na} C_{OH^-} \quad (2)$$

According to the equations 1 and 2, the two-step reaction rate is determined by the rate of hydrolysis, since intermediate products - silanols were not detected in GC-MS and their formation and consumption, was considered using the steady-state approximation.

For each elementary condensation reaction of different silanolates (Scheme 1, entry 2, 5), the rate equations are defined in the following way:

$$r_{cI} = k_2 C_{M^H D_{n+1} Na} C_{M^H D_m Na} \quad (3)$$

$$r_{cII} = k_2 C_{Na D_{n+2} Na} C_{Na D_p Na} \quad (4)$$

The rates of disproportionation reactions of different silanolate species formed in steps 3 and 6 (Scheme 1) are obtained from equations:

$$r_{dI} = k_3 C_{M^H D_{n+1} Na} C_{M^H D_f Na} \quad (5)$$

$$r_{dII} = k_3 C_{Na D_{n+2} Na} C_{Na D_s Na} \quad (6)$$

The cyclic products formation or silanolates depolymerization reaction rates are calculated by Equations 7 and 8 for end- and back-biting mechanism, respectively (Scheme, entry 7, 8).

$$r_{dep^E} = k_4 C_{Na D_{n+2} Na} \quad (7)$$

$$r_{dep^B} = k_5 C_{Na D_{n+2} Na} \quad (8)$$

The reaction rates for two types of ring-opening cyclic trisiloxane reactions (Scheme 1, entry 9, 10) are expressed by the following:

$$r_{ROI} = k_6 C_{D_3} C_{OH^-}^2 \quad (9)$$

$$r_{ROII} = k_7 C_{D_3} C_{Na D_k Na} \quad (10)$$

Finally, the generation rates for 25 reaction compounds were derived. Thus, the model consisting of 7 unknown kinetic constants was used to predict concentration dependences of 25 compounds interconnected by 138 reactions. For the parameter estimation concentrations of the substrate and products as a function of time for the experiment with a low NaOH concentration [V] were used. The kinetic modeling was performed using Modest software [41]. The objective function (Q) for the residual sum of squares between the calculated and experimental data was minimized

during the parameter estimation to search for the best-fit values using the Levenberg–Marquardt algorithm implemented in the software. The error function is defined as:

$$Q = \sum (C_{i,t (est)} - C_{i,t (exp)})^2 \quad (11)$$

where i and t denote the components and the corresponding times, respectively.

The accuracy of the model description was determined with the R^2 – coefficient or degree of explanation, which reflects comparison between the residuals given by the model with the residuals of the simplest model one may think of, i.e. the average value of all data points. The R^2 value is given by expression:

$$R^2 = 100 \frac{(y_{model} - y_{experiment})^2}{(y_{model} - \bar{y}_{experiment})^2} \quad (12)$$

Values of estimated kinetic parameters for the proposed mechanism of the TMDS base-catalyzed transformation reactions are presented in [V]. Comparison between experimental and calculated data for the all reaction compounds is illustrated in Figure 17. The kinetic model

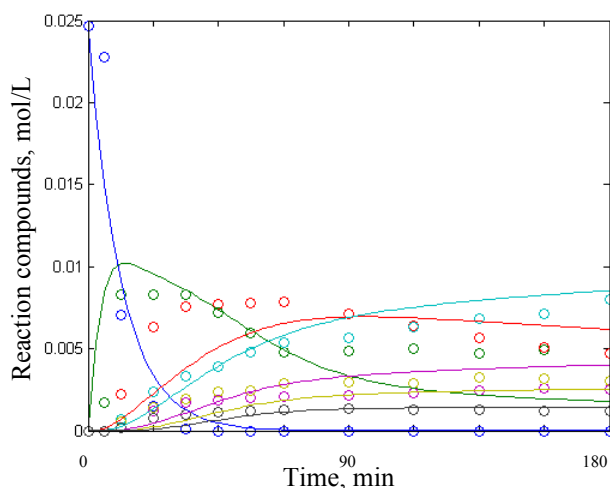


Figure 17. Experimental (symbols) and estimated (lines) concentration profiles for TMDS base-catalyzed reaction.

demonstrates a very good prediction for the compounds present in high concentrations in the reaction mixture. As can be seen from Figure 18a conversion of TMDS is predicted very well. The calculation results for solid compounds (Fig. 18 b) demonstrate an accumulation of the solids in the beginning of the reaction and their further consumption in good

agreement with the experimental data. Moreover, the model indicates a very good prediction for all the cyclic products concentrations, illustrated in Figure 18 c, d for the most abundant cyclic compounds (D3, D4).

The predicted values for the linear siloxanes formed initially in inferior amounts are not in perfect agreement with the experimental data and further model development might be needed to obtain a better description of these compounds. Apart from description of the linear products formation it can be concluded that the proposed kinetic model can satisfactory predict concentration dependences of 25 compounds interconnected by 138 reactions with only 7 fitted kinetic constant.

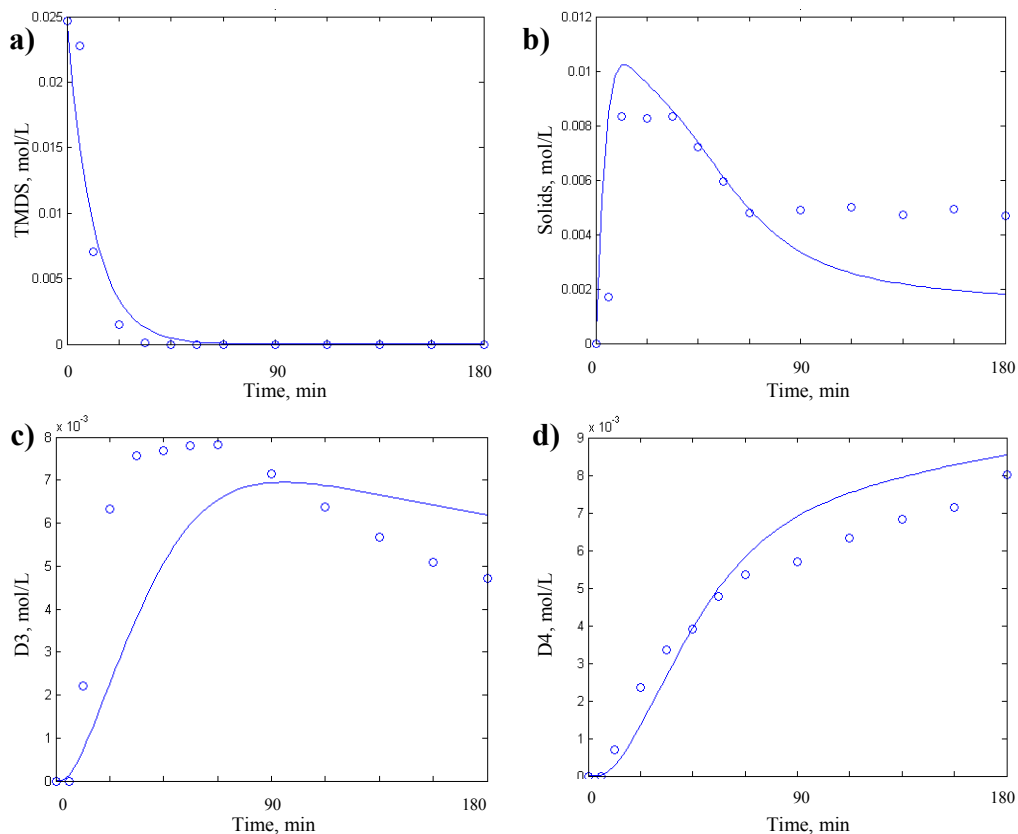


Figure 18. Experimental (symbols) and estimated (lines) concentration profiles for high concentrated reaction compounds.

3.5. Antifoam transformation at alkali treatment conditions [VI]

It is well-known that polysiloxanes added as an antifoam additive in the lube oils usually do not have any hydrogen-silicon bonds and certain differences exist in reactivity of Si-H and Si-CH₃ bonds. Therefore, the suitability of the selected hydrogen-terminated two-membered model siloxane (TMDS) for the study of the transformations of industrially relevant silicon-containing compounds

represented by long chain polydimethylsiloxanes was verified. That was done by studying transformation of a commercially available antifoam concentrate at industrially relevant alkali treatment conditions. The selected antifoam agent was a silicon based polymer [42] with a molecular weight range from 3200 to 16500 Da, whereas HPSEC results calculated based on calibration curves with the use of polystyrene demonstrated somewhat larger average molecular weight of 19000 Da. The TGA, EDXA and FTIR techniques confirmed that the selected antifoam agent was polydimethylsiloxanes-based compound [VI]. In fact, in most cases the silicone based polymer is combined with microscopic hydrophobically treated silica particles, since such mixture shows the best overall performance [43]. According to [44] less than 5 wt % of silica particles is optimally added to an antifoaming agent. Therefore, owing to a low silica concentration its contribution to transformations of various silicon species was neglected.

The transformation of the antifoam (0.5 g) compound was conducted with 33 wt % aqueous solution of sodium hydroxide (0.5 g NaOH, 1 g H₂O) and methanol solution of a high-membered sodium silanolate (0.06 g silanolate, 0.35 g CH₃OH). Analogously to TMDS (Section 3.1) the reaction between the antifoam agent and sodium hydroxide resulted in solid product formation, whereas the use of sodium silanolate as an alkali agent led to a seven fold decrease of the solid

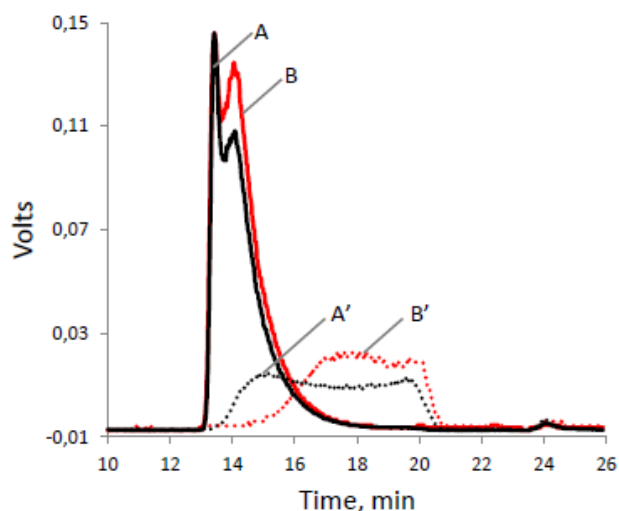


Figure 19. HPSEC chromatograms of the reaction mixtures (A) 0 min and (A') 3 h with NaOH; (B) 0 min and (B') 3h with sodium silanolate.

products yield. Moreover, it was demonstrated by FTIR that the collected solids were unreacted initial sodium silanolate.

According to HPSEC chromatograms shown in Figure 19 the antifoam agent conversion was slightly less than 100 % in the presence of sodium hydroxide. The molecular weight of the reaction products formed

in NaOH mixture was three fold higher than that in the silanolate-contained mixture. The antifoam agent transformation in the presence of sodium silanolate resulted in 70 % yield of the low molecular weight cyclic siloxane oligomers. The degree of polymerization for the studied polydimethylsiloxane decreased eight fold after 3 h of reaction.

The solids, obtained in the reaction between the antifoam agent and sodium hydroxide, were collected and thereafter analyzed by TPO-MS and FTIR. TPO results of the solids generated in the antifoam transformations [VI] were similar to those obtained for the solid products formed in the model TMDS reaction [III]. Thus, TPO results confirmed that the antifoam agent and a model siloxane compound base-catalyzed transformations resulted in the formation of solids with same the structure. Moreover, TMDS-solids contained higher amounts of free and ionically bonded water molecules, compared to the antifoam-solids.

FTIR spectra of the solids formed in the antifoam agent transformation reaction before and after the TPO analysis indicated that these products were sodium silanolate containing NaOH, which was taken in excess in the initial reaction mixture. The obtained results are in agreement with the PDMS depolymerization mechanism proposed in [22] demonstrating that presence of sodium silanolate and hydroxide in the final reaction mixture could mean that the antifoam agent depolymerization proceeded through the back and end-biting mechanisms, respectively. Thus, the final reaction mixture is supposed to contain low molecular weight liquid cyclic siloxanes, solid sodium silanulates and remaining high molecular weight linear siloxanes. According to HPSEC the average molecular weight of linear siloxanes remaining after 3 h reaction time is 7300 Da, representing 38 wt % of the final reaction mixture. Since HPSEC analysis of the sample withdrawn after 3 h reaction of the antifoam agent and NaOH demonstrated relatively low molecular weight of the reaction products, the sample was analyzed by GC-MS [VI]. Based on GC-MS results and the known mass of the collected solid products, the antifoam agent transformation reaction resulted in 80 % yields of the solid products and 20 % yields of short membered cyclic siloxanes in the liquid phase in the presence of sodium hydroxide. Moreover, substitution of sodium hydroxide with

sodium silanolate increased the reaction rate and led to formation of only cyclic products, analogously to the case of the model TMDS transformations.

This leads to the conclusion that selected model siloxane compound (TMDS) was suitable for investigation of the transformations of industrially relevant silicon-containing compounds represented by long chain polydimethylsiloxanes. Hence, all the observations for TMDS transformation reactions could be applied for the antifoam agent.

4. CONCLUSIONS

The most commonly used in Europe technologies of the used lube oil re-refining were summarized and compared. The comparison was based on the product quality and yield, requirements for feedstock and economical attractiveness of the process.

Estimation of the chemical composition of the used oil collected from several European locations was performed on the basis of a comparative analysis of chemical composition of commercially available fresh and used motor oils. The obtained data showed that the hydrocarbon structure of the motor oil is changed insignificantly during its operation and the major part of the changes is accounted for with depleted oil additives. The hydrocarbon structure was represented mainly by aliphatic hydrocarbons with the amounts of aromatic and olefinic hydrocarbons less than 1 and 0.1 %, respectively.

Within the scope of the current work, a particular attention was paid to an alkali treatment process of silicon containing used lube oils. The main motivation was to gain a deeper understanding of the mechanism of the solid product formation during the mentioned process. The transformations of tetramethyldisiloxane under alkali conditions in dodecane were studied in a batch reactor in the temperature range of 60– 110 °C using different alkali agents. It was revealed that at industrially relevant alkali treatment conditions (temperatures below 110 °C, 3 h), the transformation of tetramethyldisiloxane in the presence of aqueous solution of sodium hydroxide led to the formation of solid products with a 60 % yield at 80 % conversion. Potassium hydroxide was found to be more efficient, since the activation energy was almost two-fold lower than that for the sodium hydroxide containing reaction mixture. In addition, using KOH as an alkali agent at temperatures below 110 °C with 3 hours reaction time TMDS transformation yielded only about 50 % of solids at almost 100 % conversion. The liquid products were found to contain linear and cyclic siloxanes, the yields of the latter ones tended to increase with elevation of the reaction temperature in both NaOH and KOH mixtures.

It was determined by means of FTIR, TGA and TPO-MS analysis that the formed solids were silanolates of alkali metals. The revealed reaction mechanism confirmed the linear silanolates formation, which, depending on the reaction conditions, could be the final solid products or could be consumed in cyclic oligomers generation. In addition the revealed reaction mechanism was used for the kinetic modeling, which provided a satisfactory description of the experimental results, thus, confirming plausibility of the proposed mechanism.

The study demonstrated that in the low temperatures and short reaction time the solids were dominant products, whereas minor liquid products were represented mainly by linear siloxanes. The ways to reduce the solid products yield were found. Prolongation of the reaction time resulted in reduction of solids and led to dominance of cyclic products in the reaction mixture. Experiments with the varied reaction time demonstrated that the concentration of cyclic trimer being the dominant in the beginning of the reaction diminished with time, whereas the cyclic tetramer tended to increase. The reduction of alkali agent concentration in the initial reaction mixture accelerated the TMDS transformation reactions resulting in solely liquid cyclic siloxanes yields.

It was found that the addition of methanol into the reaction mixture significantly increased the overall reaction rate and slightly affected the composition of the liquid products, since the increase of methanol concentration in the reaction mixture led to a reduction of the molecular weight of the liquid products.

Sodium silanolate proposed as an alkali agent of TMDS transformations was found to be more efficient than NaOH, because at industrially relevant alkali treatment conditions the transformation of tetramethyldisiloxane in the presence of sodium silanolate led to the formation of the only liquid products without formation of the undesired solids.

The suitability of the selected model siloxane for the study of the transformations of industrially relevant silicon-containing compounds was verified by investigation of the commercially available antifoam agent in the base-catalyzed conditions. Thus, the gained information can be used for optimization of silicon-containing compound treatment in re-refining

units by preventing serious problems, which could be caused by metal silanolates deposition in various locations in the re-refining units.

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