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SIMULATION OF THE OLIGOMERIZATION PROCESS

The regulations of emissions make the usage of an exhaust gas aftertreatment system essential. In diesel engines especially, a diesel particulate filter (DPF) is necessary. Additionally, politics has great interest on biogenic components in fuel. Currently in Germany, the biodiesel content in diesel fuel is limited up to 7 % [1]. Climate change effects and saving fossil resources are the main drivers.

During DPF regeneration, unburned fuel from the piston wall leaks into the engine oil. Due to the high boiling point of biodiesel (circa 360 °C), this fuel does not evaporate from the engine oil. In consequence, autoxidation reactions

leads to a faster degradation of the engine oil resulting in oligomerization.

The aim of this work was the simulation and the chemical understanding of the oligomerization process in the laboratory. Therefore, base oil without additives and squalane as well as their defined mixtures with different fuels were examined. To simulate the chemical stress during the aging in a real engine, an oil stability index apparatus (OSI) was used.

Besides the aging studies, measurements of the acid value of total acid number (TAN) and viscosity as well as investigations with size exclusion chromatography (SEC) and fourier transform infrared spectroscopy (FTIR) were carried out.

MATERIALS AND METHODS

Biodiesel as synonym for fatty acid methyl ester (FAME) is the most commonly used biofuel in Europe. In Germany it is mainly produced from rapeseed oil (rapeseed oil methyl ester, RME). The RME used in the study had a density of 884 kg/m³ and a viscosity of circa 4.5 mm²/s [2]. Furthermore, hydrotreated vegetable oil (HVO) was used in this work. It consists of a multitude of paraffinic hydrocarbons. Primarily, isoparaffins (up to 80 %) are included as well as n-paraffins. HVO as well as FAME is free of sulfur and aromatics [3]. The density of the HVO used was 780 kg/m³ and the viscosity 3 mm²/s [4]. Pure RME as well

Base Oil Aging with Contemporary Biofuels

Because of the regeneration of the diesel particulate filter, unburned fuel from the piston wall leaks into the engine oil and leads to oligomerization. For a better understanding of the autoxidation reaction in the engine oil, simulations of the aging process in the laboratory were carried out at the Technology Transfer Center Automotive of Coburg University. To exclude the influence of additives in engine oil, neat base oil as well as squalane as a model substance were used.

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as pure HVO do not conform to the standard DIN EN 590 (density 820 to 845 kg/m³ and viscosity 2.0 to 4.5 mm²/s). The density of RME was above the permissible limit of the standard while that of HVO was below. Therefore a mixture of HVO and RME was made with a view of creating a new fuel which conforms to the standard.

Kuronen and Mikkonen [5] reported that HVO reduces regulated emissions in heavy duty engines. This aspect is especially important for high emission areas such as inner cities in which environmental zones have been instituted to improve air quality. For these reasons a new fuel called Diesel regenerativ was created consisting of HVO and

RME without any fossil diesel fuel. In order to obey DIN EN 590, a blend of 93 % HVO and 7 % RME was composed. The aim of the project was to create a city fuel. RME assured the fuel lubricity.

In all tested passenger cars, Diesel regenerativ showed with the exception of nitrogen oxides (NO_x) lower emissions; NO_x increased. However, because of its density of 786 kg/m³, this fuel didn't fulfill DIN EN 590 [2, 6]. The viscosity was 3 mm²/s.

Based on Diesel regenerativ, a new fuel was developed which conformed to the standard. The follow-up project, Diesel R33 aimed at market testing and a subsequent possible market introduc-

tion in a controlled manner. Diesel R33 obtains 7 % biodiesel from used cooking oil (UCOME from Tecosol GmbH, Germany), 26 % HVO (from Neste Oil, Finland), a quality high-grade diesel fuel (DF) and a sophisticated additive package (from ERC Emissions-Reduzierungs-Concepte GmbH, Germany). The biogenic content of 33 % led to the label Diesel R33. The density is between 823 kg/m³ and 831 kg/m³ and the viscosity 3 mm²/s. O'Connor calculated approximately 17 % reduction of greenhouse gas potential for Diesel R33 versus fossil diesel fuel. However, Diesel R33 leads to increased NO_x emissions in passenger cars [7]. From the final report of Diesel R33, the fuel used for this stu-

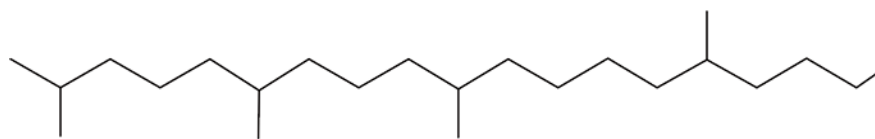


FIGURE 1 Structure of squalane (© Coburg University)

dies consisted of 26 % HVO, 7 % RME and 67 % DF without additives [7].

In this study, pure base oil and pure squalane as well as mixtures with the mentioned fuels with base oil or squalane were used. Neat base oil was used for this investigations to prevent the influence of the additives during the aging. Base oil consists of many hundreds of chemical substances making a detailed analysis impossible. To get a better understanding of the oligomerisation, squalane was used as a model substance for the base oil. In **FIGURE 1** the structure of squalane is shown. The usage of squalane was part of the work of Dugmore [8] and Dugmore and Stark [9]. Furthermore, Knorr [10] showed that base oil and squalane have the same aging behavior at the same conditions.

In a fleet project with different biogenic fuels, Volkswagen AG [11] carried out a worst case scenario with a lot of damages using a mixing ratio of 20 % biodiesel and 5 % diesel fuel in engine oil samples. Another publication of Fang and McCormick [12] examined a biodiesel admixture of 20 up to 30 % in diesel fuel. They have proved that these mixtures have the highest tendency for deposit formation [12]. The sample composition for the used base oil and squalane as well as their mixtures with the mentioned fuels is shown in **TABLE 1**.

For all aging tests Oil Stability Index (OSI) measurements according to the standard DIN EN 15751:2014 [13] for FAME was used. The OSI includes a heated reaction vessel. During the thermal aging process, a stream of air (10 l/h) is passed through the sample. The amount of the sample was 7.5 g. Contrary to the prescribed temperature of 110 °C in the OSI, the used apparatus applied a temperature of 170 °C because in this study. This temperature was applied in previous studies [11, 14] as well as by Dugmore and Starke [9]. The duration of each aging process was 40 h.

The TAN indicates the volume of potassium hydroxide required to neutralize

all acids present in one gram of sample. For the measurements of the TAN an 888 Titrande with 801 Stirrer from the company Metrohm was used.

The kinematic viscosity of the oil/fuel and squalane/fuel mixtures was measured by Stabinger viscometer SVM3000 from Anton Paar. The sample was measured in a small test tube which is located in a temperature controlled chamber. For the analysis of the liquids a temperature of 40 °C was used.

With the SEC, the molecular weight of the built oligomers could be detected. The SEC measurements were done with an Agilent Technologies 1260 Infinity SEC system. 100 mg samples were mixed with 1000 µl THF. Three columns (PSS SDV 50 Å 3 µl, PSS SDV 100 Å 3 µl and PSS SDV 1000 Å 3 µl) were used for the analysis. The heating temperature of the columns was 30 °C and the eluent was tetrahydrofuran. A sample volume of 100 µl was injected and the flow rate was 0.7 ml/min. For the determination of the size of the molecules, the calibration standard Agilent PL2070-100 (highest molecular mass was 21,300 g/mol) was used.

The molecular vibrations of the functional groups of a molecule can be detected by FTIR. For the analysis, a Nicolet

6700 FTIR from Thermo Scientific was used. An ATR-crystal for ATR spectroscopy was equipped in this instrument. The analysis of molecular vibrations were performed by applying a drop of the sample on the crystal. A deuterated tri glycine sulphate detector and an extended range KBr (XT-KBr™) beam splitter were included in the apparatus. For the evaluation of the measurements, the Thermo Scientific Omnic Software was used.

RESULTS

FIGURE 2 shows the FTIR-Spectra of base oil and squalane during the aging process. For both substances, an increase of OH-bonds at 3200 to 3600 cm^{-1} can be observed. These bonds are a result of acid and alcohol generation during the aging process [12]. There were also increasing vibration bonds detected at a wave number of 1650 to 1850 cm^{-1} . The vibrations of squalane are more pronounced than the vibrations of base oil. It can be concluded that more aging products were built with squalane than with base oil.

From Breitmaier and Jung [15] it is known that isoalkanes age faster than n-alkanes because their chemical structure aid a faster autoxidation reaction. The amount of isoalkanes in neat base oil is lower than in squalane which is an isoalkane and this leads to an increased building of radicals with base oil. For the samples in **TABLE 1** the important areas in the spectra were integrated. The results are shown in **FIGURE 3** and **FIGURE 4**.

Base oil	Squalane	RME	HVO	DK	Sample name
100 %					Base oil
80 %		20 %			Base oil + RME
80 %			20 %		Base oil + HVO
80 %		1.4 %	18.6 %		Base oil + Diesel regenerativ
80 %		1.4 %	5.2 %	13.4 %	Base oil + Diesel R33
	100 %				Squalane
	80 %	20 %			Squalane + RME
	80 %		20 %		Squalane + HVO
	80 %	1.4 %	18.6 %		Squalane + Diesel regenerativ
	80 %	1.4 %	5.2 %	13.4 %	Squalane + Diesel R33

TABLE 1 Sample composition (© Coburg University)

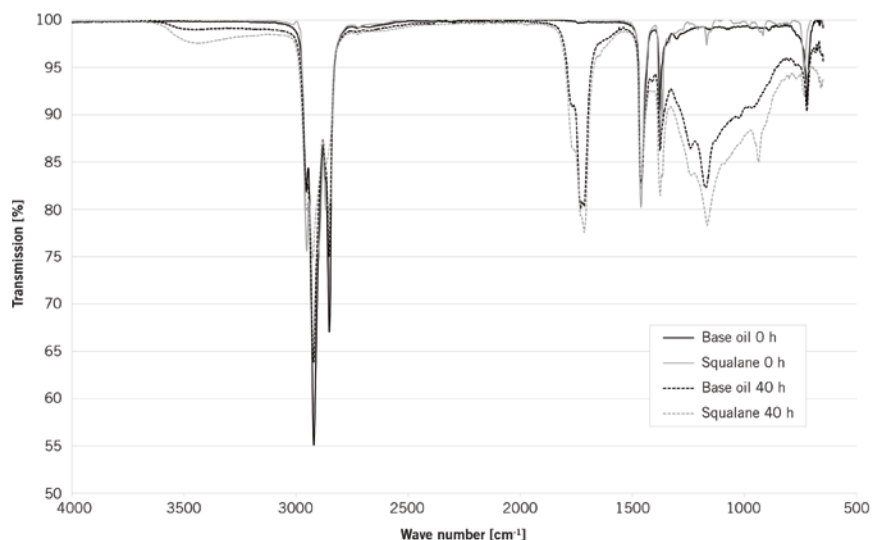


FIGURE 2 FTIR spectrum of base oil and squalane before and after aging (© Coburg University)

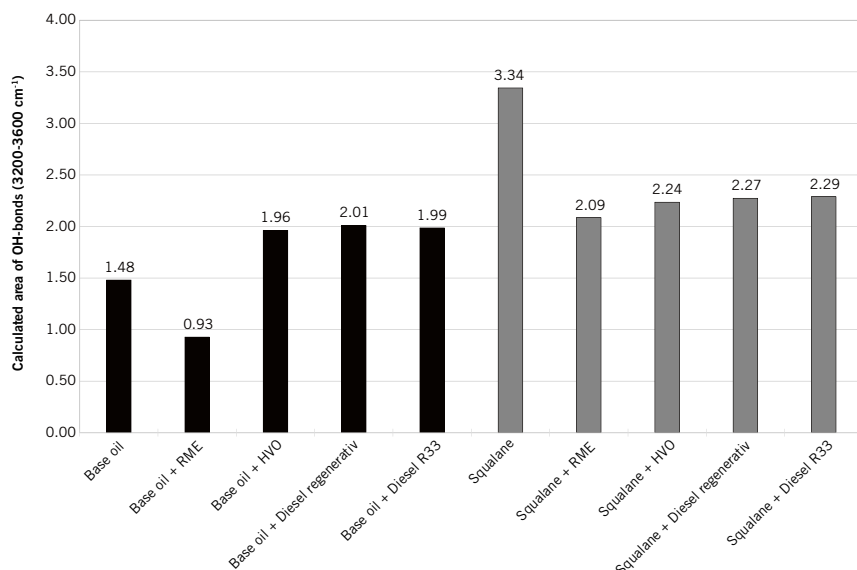


FIGURE 3 Calculated OH-bond areas of the FTIR spectrum of the aged substances (© Coburg University)

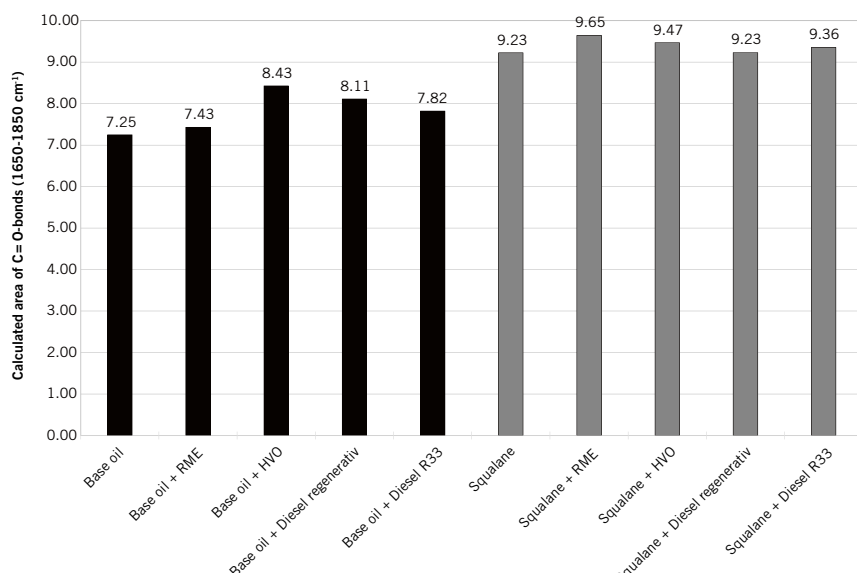


FIGURE 4 Calculated C=O-bonds areas of the FTIR spectrum of the aged substances (© Coburg University)

Variations in hydroxyl vibrations are presented in **FIGURE 3**. Mixtures with RME showed a smaller formation of long chain acids or alcohols after the aging compared to the other mixtures in the same sample series. After the aging process, the differences in the built up of OH-bonds between base oil and squalane with fuels including HVO were negligible though.

The differences in the C=O-bonds are shown in **FIGURE 4**. By comparison of the aged base oil and the squalane mixtures at the carbonyl vibrations (1650-1850 cm^{-1}), squalane and its mixtures showed higher C=O-vibrations. It can be recognized that the mixtures with all fuels showed slightly increased carbonyl vibration bonds compared to the pure base oil as well as the pure squalane.

FIGURE 5 shows the increase of the TAN. It can be observed that the building of acids is higher with squalane mixtures than with base oil mixtures. This observation agrees with the results of the shown areas from the FTIR spectra in **FIGURE 3**. In comparison of RME with HVO, Diesel regenerativ and Diesel R33 a higher TAN could be registered. The reason for this effect is the faster aging of isoalkanes in HVO which are relevant chemicals in the fuels Diesel regenerativ and Diesel R33 [3]. However, it was not expected that a mixture of squalane with RME shows a lower TAN than the pure squalane sample. Furthermore, this sample shows the highest error indicators (34 % higher than the second highest value). Further analysis need to be pursued on the identification of this effect.

The analysis with SEC in **FIGURE 6** presents a higher molar mass for the aged base oil and aged squalane. This building of oligomers could be observed because of the autoxidation of pure substances including isoalkanes and the associated formation of radicals [15].

FIGURE 7 shows the most important area (2000 to 21,000 g/mol) of the chromatogram of SEC of the aged substances. The biggest molecules could only be measured up to a relative molar mass of 21,000 g/mol because of the calibration standards. Higher molecules could not be measured. For better clarity the fuels in **FIGURE 7** are portrayed with markings (RME: X; HVO: squares; Diesel regenerativ: triangles; Diesel

R33: dots). The marks are made at three hundred measuring point intervals as a guide for the eye.

For comparison of base oil with squalane, bigger molecules with the base oil as well as with its mixtures were built. A look at the different fuels, mixtures with RME showed much bigger molecules than mixtures with the other fuels. Because of unsaturated esters in RME and the consequently increased autoxidation reaction oligomers were formed. The formation of almost the same molar masses can be observed for squalane mixtures with HVO, Diesel regenerativ and Diesel R33. The mixtures with base oil and HVO, Diesel regenerativ and Diesel R33 showed a small difference. The smaller the amount of HVO in the mixtures, the bigger the molecules which were built. A reason for this effect are the short isoalkane molecules in HVO which possibly lead to the building of smaller polymers [15, 16].

Like the formation of bigger molecules which were detected with SEC, the measurements of viscosity, **FIGURE 8**, showed the same effect. The viscosity of the base oil mixtures is higher than the squalane mixtures. In comparison of HVO, Diesel regenerativ and Diesel R33, the viscosity of RME mixtures is higher. The mixtures of squalane and HVO, Diesel regenerativ and Diesel R33 shows nearly the same viscosity.

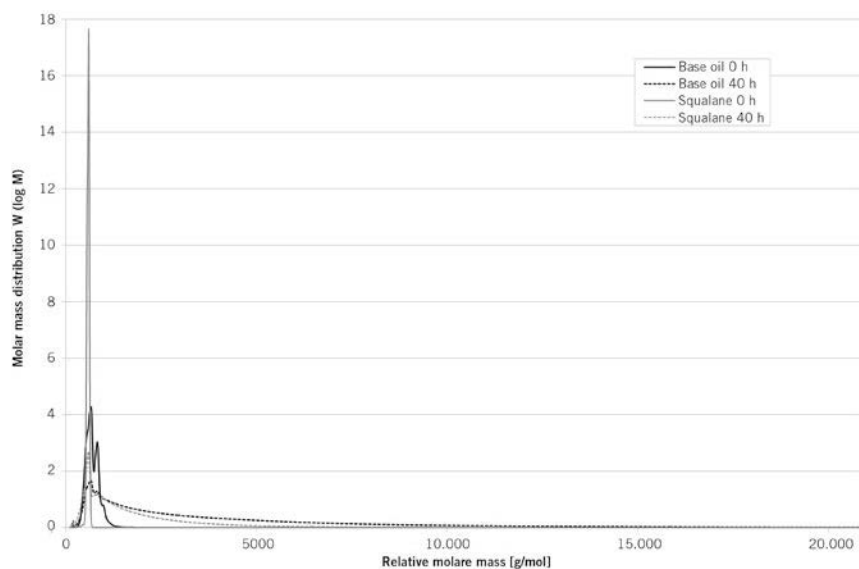


FIGURE 6 Chromatogram of the SEC of base oil and squalane before and after the aging (© Coburg University)

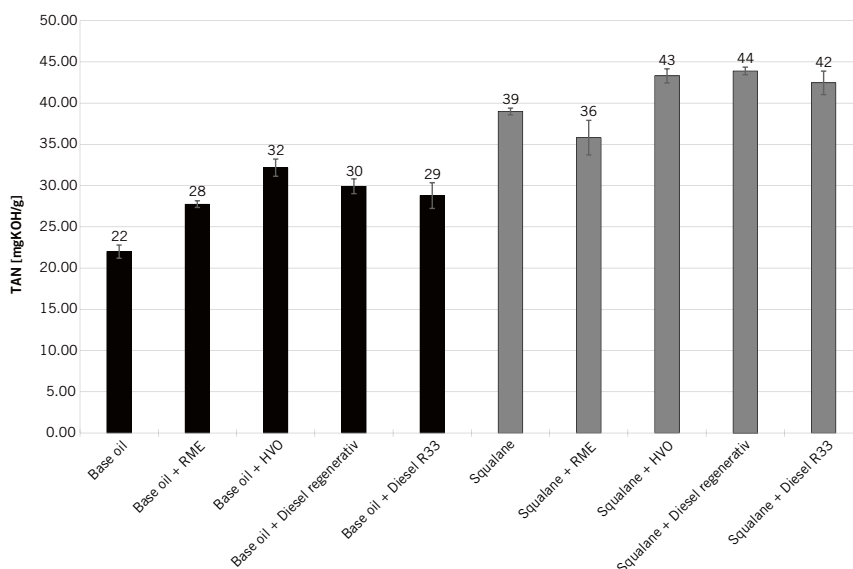


FIGURE 5 Increase of the total acid number of the aged substances (© Coburg University)

CONCLUSION

Up to 20 % fuel in engine oil is realistically reported for diesel fuel powered passenger cars with diesel particulate filter [11]. Under operating conditions, the engine oil degrades and finally has to be changed. For clarification of the aging process in detail and to understand the impact of fuel, neat base oil without additives and squalane as a model substance were used [4, 10]. Squalane represents the isoalkanes in base oil.

Comparative aging experiments using neat base oil and squalane showed an increased formation of organic acids. A reason for this could be the tendency of isoalkanes taking part in autoxidation reaction [15, 16]. Aged base oil showed a higher formation of undesired macromolecules for base oil than for squalane. Base oil molecules can have more than twice the mass of squalane molecules and so the oligomers from base oil can have a higher mass than those from squalane. This could explain the formation of bigger molecules in unaged base oil than in unaged squalane.

The viscosity showed different effects. Aged squalane obtained a higher viscosity increase than base oil after the aging. The reason for this is currently under investigation.

Additionally four fuels (RME, HVO, Diesel regenerativ and Diesel R33) of 20 % amounts were investigated with regard to their engine oil degradation potency. The result for the formation of acids and alcohols in the RME mixtures were smaller than with HVO, Diesel regenerativ and Diesel R33. These results are a consequence of the evaporation of short-chain and highly volatile compounds which were formed during the aging. With HVO, Diesel regenerativ and Diesel R33 the values of acids and alcohols were in the same range. The viscosity as well as the molecular size showed similar trends.

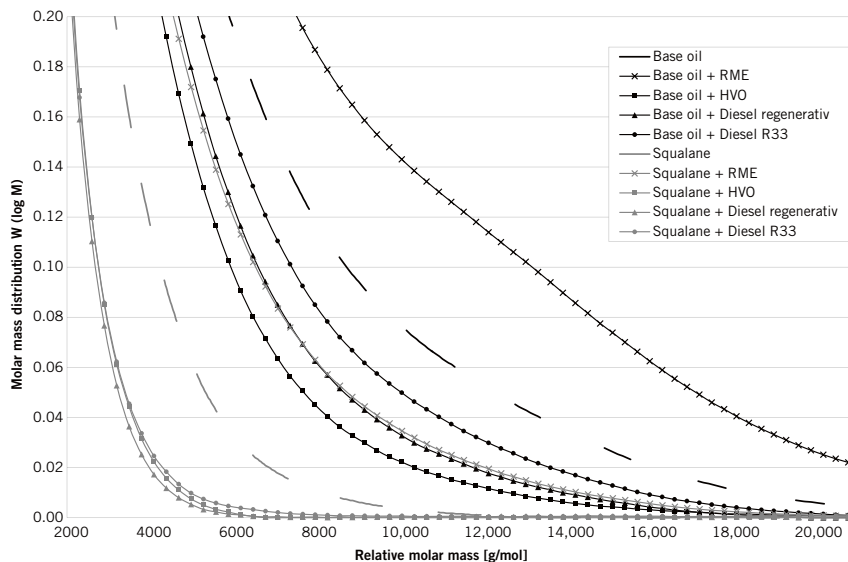


FIGURE 7 Zoom in the most important area of the chromatogram of SEC of the aged substances (© Coburg University)

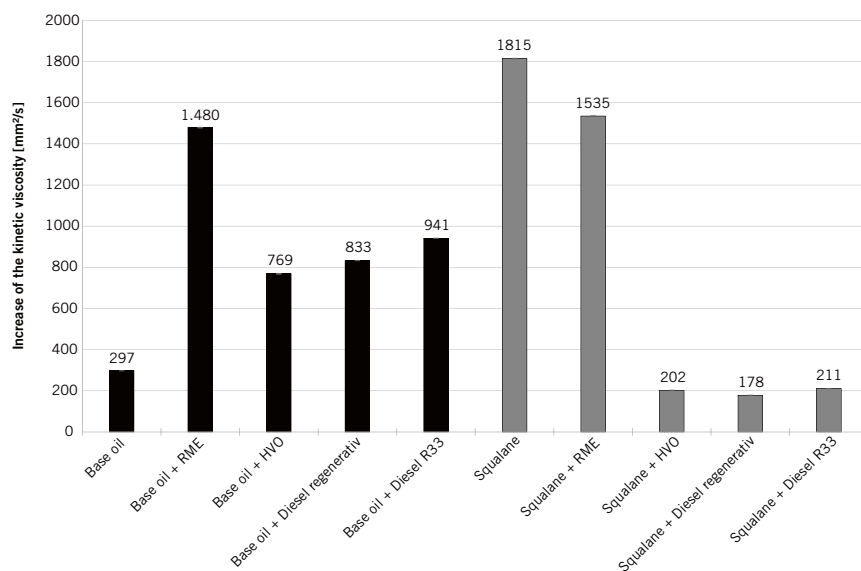


FIGURE 8 Increase of viscosity of the aged substances (© Coburg University)

Finally, it can be stated that diesel fuels with 7% RME content such as Diesel regenerativ and Diesel R33 did not lead to a significantly higher formation of oligomers in base oil or squalane relative to neat HVO.

REFERENCES

- [1] BioKraftQuG: Gesetz zur Einführung einer Bio-Kraftstoffquote durch Änderung des Bundes-Immissionsschutzgesetzes und zur Änderung energie- und stromsteuerrechtlicher Vorschriften. Bundesgesetz, BT-Drs 16/2709, 2006.
 [2] Krahl, J.; Zimon, A.; Schröder, O.; Fey, B.; Bockey, D.: Diesel regenerativ. Fuels Joint Research Group, Band 2, Cuvillier-Verlag, Göttingen, 2012

- [3] Bhardwaj, O.; Lüers, B.; Holderbaum, B.; Koerfer, T.; Pischinger, S.; Honkanen, M.: Utilization of HVO fuel properties in a high efficiency combustion system: Part 2: Relationship of soot characteristics with its oxidation behavior in DPF. SAE Technical Paper 2014-01-2846, 2014
 [4] Singer, A.; Schröder, O.; Pabst, C.; Munack, A.; Bünger, J.; Ruck, W.; Krahl, J.: Aging studies of biodiesel and HVO and their testing as neat fuel and blends for exhaust emissions in heavy-duty engines and passenger cars. In: Fuel 153 (2015), pp. 595-603
 [5] Kuronen M.; Mikkonen S.: Hydrotreated vegetable oil as fuel for heavy duty diesel engines. SAE Technical Paper 2007-01-4031, (2007)
 [6] DIN EN 590:2013 + AC:2014: Automotive fuels – Diesel – Requirements and test methods

- [7] Götz, K.; Krahl, J.: Diesel R33. Fuels Joint Research Group, Band 15, Cuvillier-Verlag, Göttingen, 2015
 [8] Dugmore, T. I. J.: The autoxidation of biodiesel and its effects on engine lubricants. University of York, Dissertation, 2011
 [9] Dugmore, T. I. J.; Stark, M. S.: Effect of biodiesel on the autoxidation of lubricant base fluids. In: Fuel 124 (2014), pp. 91-96
 [10] Knorr, M.: Untersuchungen zur Verwendung von Squalan als Modellschubstanz für Grundöl. Tagungsband zum 6. Biokraftstoffsymposium am 27. und 28. Februar 2014, Fuels Joint Research Group, Band 11, Cuvillier-Verlag, Göttingen 2015
 [11] Schumacher, S.: Untersuchungen zum Einfluss verschiedener Diesel- und Biodiesel-Komponenten auf den Mechanismus der Ölschlammbildung im Motorenöl. Otto-von-Guericke-Universität Magdeburg, Dissertation, 2013
 [12] Munack, A.; Petchatnikov, M.; Schmidt, L.; Krahl, J.: Spektroskopische Untersuchungen zur Ergründung der Wechselwirkungen zwischen Biodiesel und Dieseldieselkraftstoff bei Blends. Forschungsvorhaben des Verbands der deutschen Biokraftstoffindustrie, Projektnummer 7-TA-VDB, 2009
 [13] DIN EN 15751:2014: Automotive fuels – Fatty acid methyl ester (FAME) fuel and blends with diesel fuel – Determination of oxidation stability by accelerated oxidation method
 [14] Singer, A.; Ruck, W.; Krahl, J.: Influence of different biogenic fuels on base oil aging. SAE Technical Paper 2014-01-2788, 2014
 [15] Breitmaier, E.; Jung, G.: Organische Chemie: Grundlagen, Stoffklassen, Reaktionen, Konzepte, Molekülstruktur. 5. überarbeitete Auflage, Georg-Thieme-Verlag, Stuttgart, Germany, chapter: Autoxidation, 2005
 [16] Buddrus, J.; Schmidt, B.: Grundlagen der organischen Chemie. 4. überarbeitete und aktualisierte Auflage, de-Gruyter-Verlag, Berlin, chapter: Alkane, radikalische Substitution, 2011

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