SZÉCHENYI EGYETEM
UNIVERSITY OF GYŐR

Nagy András Lajos

Oil degradation and engine wear due to alternative fuels

Thesis booklet

Supervisor
Dr. Zsoldos Ibolya

Department of Materials Science and Technology
Széchenyi István Egyetem

2022

Doctoral School of Multidisciplinary Engineering Sciences

Contents

1 Introduction

This thesis summarizes the results of independent and joint research activities in the field of internal combustion engine tribology. The main focus of the presented research activities is engine oil aging in conjunction with fuel dilution. Most research activities – including friction and wear experiments, artificial engine oil aging, data analysis and post-processing – were carried out at the Department of Internal Combustion Engines and Propulsion Technology of Széchenyi István University (University of Győr). Preliminary oil aging experiments and oil analysis were performed by MOL-Lub Kft. In-depth oil analysis was carried out by the Austrian Competence Centre for Tribology (AC2T GmbH).

1.1 Motivation

The widespread utilization of alternative fuels and hybridisation can present new challenges to automotive lubricant development. Previously absent species of combustion by-products and fuel components could affect oil aging and induce increased wear on the contact pairs and bearing surfaces of an internal combustion engine. For a successful introduction of carbon-neutral biogenic and synthetic fuels, their compatibility with the existing vehicle fleet in terms of chemical and physical properties has to be assured. Biofuels and synthetic fuels, which require little to no modifications to in-use vehicles can be considered as drop-in alternatives. The thermodynamic behaviour, emissions, cost of production and effect on the fuel system of such non-fossil fuels are a vital part of their assessment. Long-term effects of alternative fuels on the internal combustion engine as a complex tribosystem must be considered as well.

1.2 Goal and hypotheses

The goal of my PhD research was to establish a methodology to evaluate the long-term effect of alternative fuels on engine oil aging and the consequent alteration in friction and wear. This main goal was divided into the following sub-goals, tasks and hypothesis:

- Evaluating the state-of-the-art through literature review,
- Conducting an exploratory study of artificial engine oil aging,
- Developing a controlled procedure and apparatus for artificial aging,
- Validating the artificial aging procedure through a field study.

Hypothesis #1: Alternative fuels can contribute to an accelerated degradation of engine oils, which will have an effect on friction and wear of engine bearings and load bearing surfaces.

Hypothesis #2: An artificial aging method can be used to simulate in-use engine oil aging and produce aged samples with comparable physical and chemical properties to real-life used oil.

Hypothesis #3: Engine oil aging is heavily influenced by vehicle use, which, in some way, can be traced back to the recurrence of severe operating conditions.

2 Materials and methods

This section presents the utilised materials and methods in general to establish a basic understanding of the workflow and instrumentation used for measurements and experiments discussed in the thesis.

2.1 Tribometrology

In order to investigate numerous variations of the system with a constrained budget, an Optimol Instruments SRV5 tribometer (Figure 1) was used as a basis of experiments related to this thesis. An SRV5 tribometer enables the user to apply a vast number of test sample types in a variety of experimental setups. In the initial exploratory research phase, a ball-on-disc setup was selected for friction and wear measurements. A standardised ball and disc sample complying with the requirements set in ISO 19291:2016 was used for the ball-on-disc experiments.

a) Optimol SRV5 oscillation system

b) Test chamber of the SRV5 with ball and disc

Figure 1. Optimol Instruments SRV5 tribometer for friction and wear testing of diverse materials, surfaces and lubricants (courtesy of Optimol Instruments Prüftechnik GmbH)

2.2 Samples, samples preparation and post-processing

Standardized friction and wear measurement samples for the ball-on-disc experiments were acquired from Optimol Instruments GmbH. An alternating head engraving machine was utilized to apply an alphanumeric identifier to the samples. Samples are stored in engine oil until further use. Every sample goes through a cleaning procedure before surface analysis, and friction and wear measurement. Samples are spayed with an organic solvent, then placed individually in 50 – 100 ml borosilicate glass beakers and covered with a 1:1 mixture of isopropyl alcohol and acetone. The samples are agitated in an ultrasonic cleaner at 50°C for 10 minutes. Cleaned samples are dried with compressed air, and placed into a desiccator cabinet until utilization.

Before each friction and wear test on the tribometer the initial surface topology of the samples is recorded. High resolution photographs and microscope images are taken of the surface for visual comparison. Surface topography is determined with a Leica DCM3D measuring microscope equipped with a 50x / 0.8 Leica HC PL Fluotar lens. The collected 3D dataset is post-processed in MountainsMap. Results are either exported manually, or batch processed for selected measurement series, and saved in a spreadsheet.

2.3 Engine oil analytics

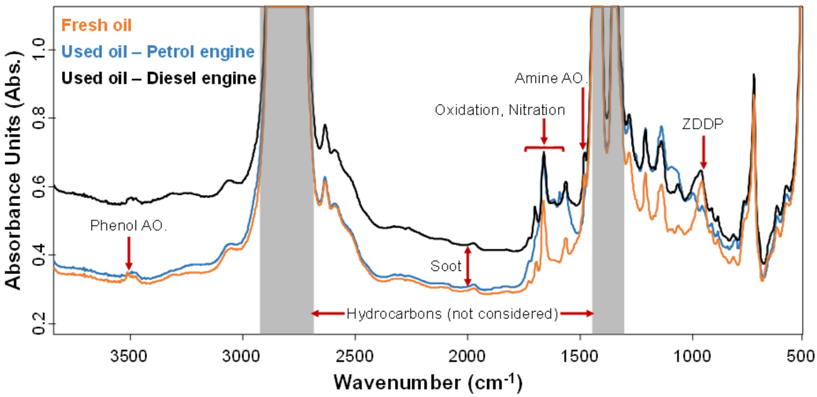

Figure 2. FTIR spectrum of used petrol and diesel engine oil samples compared to fresh engine oil {8}.

Physical and chemical analysis of the lubricant is a fundamental step in tribology research. The properties presented in this section were determined by the Austrian Excellence Centre for Tribology. Based on the source of the analysed sample a different set of analytical investigation steps were taken. For in-use engine oil samples, the verification of wear metal content can provide vital information regarding the health of the engine. However, no meaningful result can be derived from this assessment in case of the artificially aged samples studied in this thesis, since no mechanical aging was considered in the degradation process. Hence, the methodology of external analytics is grouped into three depth levels:

- General physical and chemical properties – e.g. oxidation, additive reserves, kinematic viscosity, total base number – through FT-IR spectroscopy (Figure 2), Stabinger viscosimetry and potentiometric titration.

- Conventional engine oil analysis through FT-IR, Karl-Fischer titration, and inductively coupled plasma optical emission spectroscopy for nitration, sulfation, soot content, water content, and wear metal content.
- Advanced analysis through gas chromatography mass spectroscopy for gasoline and diesel content assessment.

2.4 Thermo-oxidative engine oil aging

In order to reduce cost and time needed for investigating several oil formulations with diverse fuel samples regarding thermal and oxidation stability a laboratory procedure was established based on Singer et al. The chosen method simulates the conditions of high temperature and constant gas flow inside the internal combustion engine with a cyclic load structure similar to real-life vehicle use in order to induce chemical alterations of the lubricant. A thermal-cycling rig (Figure 3) was designed with 6 individual heater stations for the simultaneous aging of different samples. The unit is based on a FALC BE-6 6-station laboratory heater originally designed for Soxhlet extraction. The heater stations are able to accept flasks up to 500 ml and utilize a ceramic mantle for direct heat transfer. Each mantle is connected to an individual power regulator circuit and has a maximum power throughput of 180 W.

Temperature control is realized through six power width modulated (PWM) bidirectional triode thyristor (AC dimmer) circuits. These circuits communicate via SPI (Serial Peripheral Interface) on a two-wire bus with the Arduino MEGA control board, which dictates heating and accumulation times. K-type thermocouples are connected through six MAX31850 thermocouple amplifiers for closed-loop control. The control software of the aging rig is implemented in the Arduino language, a programming language similar to C. Temperature and electrical output values are logged to an SDcard for diagnostic purposes. Air flow rate is controlled through individual rotameters, which are connected to a compressed air supply line.

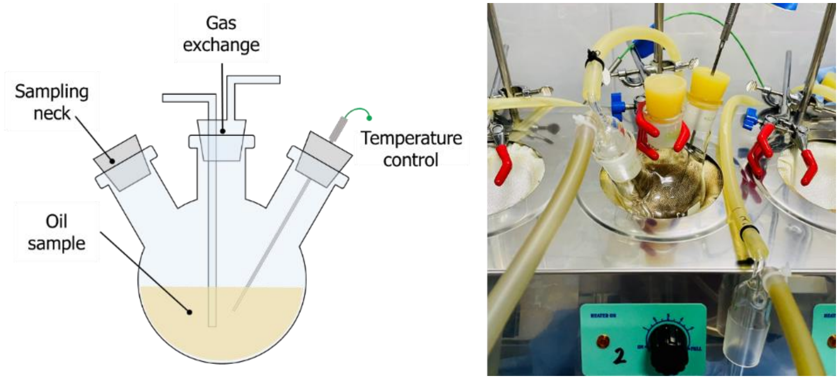

Figure 3. Revised thermal-cycling rig for controlled engine oil aging experiments, with three-neck round bottom flasks and improved control system

Apart from the type of the investigated lubricant, the system allows for a variation of sample volume, setpoint temperature, aging duration and air flow rate independently. A number of experiments were conducted with various parameter sets to identify the best suiting boundary conditions for artificial engine oil aging.

2.5 Oil aging field study on a vehicle fleet

To investigate oil degradation in the field, a study was conducted on a passenger car fleet composed of 12 vehicles (compacts, sedans, estates and SUVs) with 2-liter four-cylinder turbocharged gasoline (9) and diesel (3) engines ranging between 130 kW and 221 kW. Vehicles were filled with a VW 504.00/507.00 compliant SAE 0W-30 grade fully synthetic engine oil. A subset of the fleet was designated as short-range vehicle. Short-range vehicles were confined to a controlled speed zone of 50 km/h, meant to represent city traffic. Long-range vehicles were operated without limitations. An intended sampling period of 1 month and 2 500 km was defined for short and long-range vehicles, respectively. A total of 47 in-use engine oil samples were collected throughout a 6-month time period. Oil sampling was carried out through the dipstick tube of each vehicle. Each engine was operated at idle for at least 5 minutes before sampling in order to stir the lubricant. 10-12 ml of engine oil was extracted at a time, to avoid the need for oil refill. Used engine oil samples were labelled with vehicle identifier, sampling date and vehicle mileage values.

2.6 Data analysis through Principal Component Analysis

It is common in the field of engineering, that an experimental design considers numerous influencing factors, while monitoring the behaviour of multiple features over an extended number of observations and elongated amount of time. Such holistic approaches can yield an immense amount of data with high dimensionality, which requires advanced analysis methods. One approach of dimension reduction is Principal Component Analysis (PCA). PCA takes a dataset of m observations along n features as its input and computes the projection of each feature to a new coordinate system (loadings), as well as the position of each observation in the new coordinate system (scores). Figure 4 depicts a visual representation of the resulting scores of a PCA, which was calculated from 19 quantitative oil properties (features) of 47 oil samples (observations), equalling to 893 individual values. This example also shows how additional information, like utilization and fuel type can be used to gain insight into the data. These parameters are not included in the PCA itself, but used for colouring objects during visualization. The score plot on Figure 4 presents a clear separation of short-range gasoline samples, suggesting a significant difference in the chemistry of oils originating from these vehicles.

PCA was applied to the gathered data using Python 3.8 with scikit-learn 0.23.2.

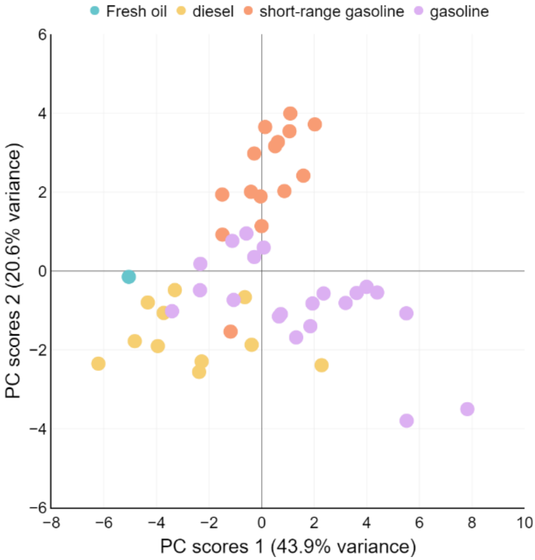

Figure 4. Visualization of PCA results from quantitative oil properties. Objects are coloured by fuel type and utilization

3 New scientific results

This section summarizes new scientific results, which were discovered during the research.

Thesis 1 – Friction and wear with alternative fuel contaminated oils

I have demonstrated the effect of OME3-5 on the degradation of a modern fully synthetic multi-grade engine oil through friction and wear testing on a model system with artificially aged engine oil samples. Experiments according to ISO 19291 on a ball-on-disc setup have shown, that adding 7 wt% OME3-5 to a commercially available SAE 0W-20 engine oil during artificial aging results in increased wear and an alteration in the dominant wear process on 100Cr6 bearing steel test samples compared to regular diesel fuel. Surface analysis results after friction and wear testing with a 96 hour old artificially aged sample including 7 wt% EN 590 regular diesel fuel have shown predominantly abrasive wear marks. In contrast, surfaces after testing with a 96 hour old artificially aged sample containing identical amounts of OME3-5 exhibit an increased amount of fatigue wear. In addition to the apparently distinct wear mode, OME3-5 as a contaminant contributed to ~6% increase in the averaged wear scar diameter.

Related personal publications: {1}, {2}, {3}; related chapters: 5

Thesis 2 – Artificial oil aging without contamination

I have demonstrated that thermo-oxidative aging for 96-hours at 160°C with 1 l/min air throughput has a significant effect on the antioxidant and antiwear additive reserves of the investigated engine oil. 150 ml SAE 0W-20 samples exhibited a 17% drop in aminic and phenolic antioxidant content on average, due to the thermal load and reactions with O2 from the constant agitated airflow during the procedure, which is quantifiable through a 4.1 A/cm average oxidation. An average 89.2% decrease in ZDDP antiwear additive content was also established as a result of the thermal degradation of ZDDP.

Related personal publications: {4}, {5}, {7}; related chapters 4.4, Appendix A

Thesis 3 – Artificial aging with alternative fuel contamination

I have concluded in a follow-up aging experiment on Shell Helix 0W-30 engine oil, that the previously experienced transition in wear processes can be explained with the change in engine oil chemistry due to an increased oxidation in the presence of OME3-5, which is quantifiable through the decrease of aminic antioxidants in the aged sample.

Related personal publications: {4}, {5}, {7}; related chapters 4.4, Appendix A

Thesis 4 – Engine oil aging under real-life conditions

I have demonstrated through principal component analysis of experimental data, that in a vehicle fleet comprising of a selection of passenger cars with various performance classes of the same base motorization, the physical and chemical deterioration of the lubricant is mainly dependent on the attributes of vehicle usage. A strong correlation was found between the number of cold starts and the severity of engine oil degradation as a result of real-life short-range utilization of identical passenger cars. A relatively high number of ~290 cold starts under a low mileage of ~1700 km contributed to quantifiable increase in acidity based on the neutralisation number from 1.6 to 2.2 mgKOH/g and a significant drop in kinematic viscosity from 58 mm^2/s to 39 mm^2/s. This phenomenon can be attributed to a 3.7% dilution of the engine oil with fuel. No strong correlation can be found between the differences in engine performance and the physical and chemical properties of the used engine oils in a test fleet.

Related personal publications: {6}, {8}; related chapters: 7

3.1 Summary

Results suggest, that the proposed method is suitable for artificial oil aging in order to simulate in-use phenomena. The process and apparatus can serve as a basis for follow-up research on lubricant degradation in the presence of alternative fuels. Various additional scenarios, e.g. commercial and heavy-duty vehicles, or hybrid powertrains can be taken into account. Furthermore, extending artificial aging and oil analysis with advanced friction and wear measurements on a piston ring – cylinder liner experimental model could provide valuable data regarding boundary layer formation and wear.

Additionally, the presented correlative analysis of fleet data and engine oil condition could be implemented by fleet operators or OEMs to continuously monitor both oil and powertrain fitness and effectively preserve a good operating condition without unnecessary, or late oil changes.

4 Personal publications

{1} **A. L. Nagy**, J. Knaup and I. Zsoldos, ”A Review on the Effect of Alternative Fuels on the Friction and Wear of Internal Combustion Engines,” *In: Jármai, K., Bolló, B., Eds.; Vehicle and Automotive Engineering 2,* pp. 42–55, 2018

{2} **A. L. Nagy**, J. Knaup and I. Zsoldos, ”A friction and wear study of laboratory aged engine oil in the presence of diesel fuel and oxymethylene ether,” *Tribology-Materials, Surfaces & Interfaces*, vol. 13 (1), pp. 20-30, 2019, doi: 10.1080/17515831.2018.1558026, **Citations: 6, SJR Q2**

{3} **A. L. Nagy**, J. Knaup and I. Zsoldos, ”Investigation of Used Engine Oil Lubricating Performance Through Oil Analysis and Friction and Wear Measurements,” *Acta Technica Jaurinensis*, vol. 12, no. 3, pp. 237-251, 2019, doi: 10.14513/actatechjaur.v12.n3.495, **Citations: 2**

{4} **A. L. Nagy**, ”Development of an artificial aging process for automotive lubricants,” *Spring Wind 2019*, pp. 771–775, 2019

{5} **A. L. Nagy** and I. Zsoldos, ”Artificial Aging of Ultra-low Viscosity Lubricant Samples on a Programmable Oil Aging Rig,” *VAE 2020: Vehicle and Automotive Engineering 3*; pp. 139–147, 2021, doi: 10.1007/978-981-15-9529-5_12

{6} A. Agocs, **A. L. Nagy**, Z. Tabakov, J. Perger, J. Rohde-Brandenburger, M. Schandl, C. Besser and N. Dörr, ”Comprehensive assessment of oil degradation patterns in petrol and diesel engines observed in a field test with passenger cars—Conventional oil analysis and fuel dilution,”

Tribology International, 2021, doi: 10.1016/j.triboint.2021.107079. ,
Citations: 1, SJR Q1 / D1

{7} **A. L. Nagy**, J. Rohde-Brandenburger, I. Zsoldos, “Artificial Aging Experiments of Neat and Contaminated Engine Oil Samples,” *Lubricants*, vol. 9, no. 63, 2021, doi: 10.3390/lubricants9060063,
SJR Q2

{8} **A. L. Nagy**, A. Agocs et al, “Rapid Fleet Condition Analysis through Correlating Basic Vehicle Tracking Data with Engine Oil FT-IR Spectra,“ Lubricants, vol. 9, no. 12, 2021, doi: 10.3390/lubricants9120114
SJR Q2

Independent citations according to Scopus and MTMT.

Personal publications,

that are not related to, or referenced in the dissertation.

{A} I. Hatos, I. Fekete, T. Ibriksz, B. Kocsis, **A. L. Nagy**, H. Hargitai, "Effect of locally increased melted layer thickness on the mechanical properties of laser sintered tool steel parts," *IOP CONFERENCE SERIES: MATERIALS SCIENCE AND ENGINEERING*, pp. 426-433, 2018, doi: 10.1088/1757-899X/426/1/012014,
Citations: 1

{B} **A. L. Nagy**, "The impact of RME biodiesel on base oil aging – a friction and wear study," *In: Dörr, N.; Gachot, C.; Franek, F.; Kalin, M.; Ciulli, E.; Crockett, R. - ECOTRIB 2019 Book of Abstracts,* pp. 55-56, 2019

{C} A. Agocs, **A. L. Nagy**, Z. Tabakov, J. Perger, J. Rohde-Brandenburger, B. Ronai, C. Besser and N. Dörr, „Feldstudie über die Motorölalterung in Personenkraftwagen," *TRIBOLOGIE UND SCHMIERUNGSTECHNIK,* vol. 5-6, no. 67, pp. 78-79, 2020, **SJR Q4**

{D} **A. L. Nagy**, "Wear Analysis and Measurement on Friction and Wear Test Samples," *In: Adrienn, Dernóczy-Polyák Kutatási jelentés 2. - Research Report*, pp. 324-332, 2020

{E} T. Markovits, L. Borbás, L. Molnár, **A. L. Nagy**, D. Fülöp, "Lézersugárral felületkezelt acél minták ball-on-disk típusú koptató vizsgálata," *ACTA PERIODICA (EDUTUS)*, vol. 20, pp. 51-63, 2020, doi: 10.47273/AP.2020.20.51-63

{F} **A. L. Nagy**, "Tribológiai modellvizsgálatok kopásmeghatározási módszereinek összehasonlítása," *In: Dernóczy-Polyák, Adrienn Kutatási jelentés 3*, pp. 407-416, 2020

Thesis booklet

Throughout my PhD research I have been studying engine oil degradation from the perspective of a mechanical engineer. Oil aging can be crucial in the wake of alternative fuel technologies, as fuelling affects physical, and chemical properties, as well as the longevity of the lubricant. Ensuring fuel-oil-compatibility is an essential factor for successful bridge technologies towards a carbon-neutral future.

My research has led me to the following new scientific results:

- I have found evidence, that the presence of oxymethylene ether (OME), a proposed alternative fuel affects engine oil aging under laboratory conditions, resulting in elevated wear rate and a transition in the dominant wear phenomenon from abrasion to pitting in a ball-on-disc model study.
- I demonstrated the applicability of my aging apparatus and methodology to produce artificially aged engine oil samples with comparable chemical properties to an in-use sample from a gasoline engine after 7 000 km of mixed utilization.
- I correlated vehicle utilization properties e.g. use patterns and the number of cold starts to oil degradation mechanism e.g. oxidation and fuel dilution in a fleet with similar motorisation.

SZÉCHENYI EGYETEM
UNIVERSITY OF GYŐR

2022