Katriina Sirviö

Issues of various alternative fuel blends for off-road, marine and power plant diesel engines

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ACTA WASAENSIA 400

Vaasan yliopisto
UNIVERSITY OF VAASA

ACADEMIC DISSERTATION

To be presented, with the permission of the Board of the School of Technology and Innovations of the University of Vaasa, for public dissertation in Auditorium Kurtén (C203) on the 15th of June, 2018, at noon.

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Julkaisija
Vaasan yliopisto

Julkaisupäivämäärä
Kesäkuu 2018

Tekijä(t)
Katriina Sirviö

Julkaisun tyyppi
Artikkeliväitöskirja

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Julkaisusarjan nimi, osan numero
Acta Wasaensia, 400

Yhteystiedot
Vaasan yliopisto
Tekniikan ja innovaatiojohtamisen yksikkö
Energiatekniikka
PL 700
FI-65101 VAASA

ISBN
978-952-476-804-7 (painettu)
978-952-476-805-4 (verkkoaineisto)

ISSN
0355-2667 (Acta Wasaensia 400, painettu)
2323-9123 (Acta Wasaensia 400, verkkoaineisto)

Sivumäärä
138

Kieli
Englanti

Julkaisun nimike
Työkone-, laiva- ja voimaladieselmoottorien vaihtoehtoisista polttoaineseoksista ja niiden käytettävyydestä

Tiivistelmä

Energiapoliittisena tavoitteena on lisätä uusiutuvan energian osuus Euroopassa 27 prosenttiin energian kokonaiskulutuksesta vuoteen 2030 mennessä. Osana tavoitteen toteuttamista tässä väitöskirjassa tutkittiin nestemäisiä vaihtoehtoisia polttoaineita ja niiden ominaisuuksia. Sekä uusiutuvat että kierrätyspolttoaineet ja niiden seokset fossiilisen polttoaineen kanssa soveltuvat voimala-, laiva- ja työkonemoottoreihin.

Tutkimuksessa perehdyttiin polttoaineiden säilyvyyteen, yhteensopivuuteen ja varastointiominaisuuksiin teoriatasolla. Lisäksi analysoitiin näihin tekijöihin liittyviä ominaisuuksia. Sekä uusiutuvia että kierrätyspolttoaineita tutkittiin. Tulokset, jotka perustuvat laboratorioanalyyseihin, on esitetty kuudessa tutkimusartikkelissa. Työkone-, laiva- ja voimalamoottoreihin on saatavilla useita soveltuvia vaihtoehtoisia polttoaineita. Tämän tutkimuksen yhtenä tuloksena todettiin, että täysin uusi ja 100 % uusiutuva vaihtoehtoinen polttoaineseos, uusiutuvan naftan ja rypsipohjaisen biodieselin seos, on soveltuva dieselmoottoreihin. Päätös polttoaineiden seostamisesta tulee tehdä tapauskohtaisesti riippuen siitä, mihin tarkoitukseen polttoainetta tarvitaan ja mitkä ovat polttoaineseoksen ominaisuudet. Tämän takia tieto erilaisista seoksista ja niiden analyysituloksista on erittäin tärkeää. Tuloksina todettiin myös, että metyyliesterit tarvitsevat antioksidantteja säilyäkseen hyvin, mutta polttoaineiden säilyvyyteen vaikuttavat voimakkaasti myös varastointiolosuhteet. Polttoaineen 20 tilavuusprosentin bio-osuus ei huonontanut voiteluöljyn laatua pitkäaikaisessa moottoritutkimuksessa. Fossiilisten ja uusiutuvien polttoaineiden seoksilla korkea rikkipitoisuus paransi seoksen hapettumisenkestoa. Seostaminen on myös hyödyllistä ympäristön kannalta, jos ainoa vaihtoehto fossiiliseksi polttoaineeksi on korkearikkinen. Polttoainevaihtoehtojen laaja valikoima on vaativaa moottorien kehitystyön kannalta, mutta sellaisenaan käyttökelpoisia vaihtoehtoja on jo nyt useita. Uusiutuvien polttoaineiden seostaminen perinteisiin nopeuttaa teknistä siirtymävaihetta energiantuotannon murroksessa.

Asiasanat
vaihtoehtoiset polttoaineet, dieselmoottori, uusiutuva polttoaine, polttoaineiden seostaminen, polttoaineiden säilyvyys

Publisher
Vaasan yliopisto

Date of publication
June 2018

Author(s)
Katriina Sirviö

Type of publication
Doctoral thesis by publication

Orcid ID
orcid.org/0000-0002-0859-1832

Name and number of series
Acta Wasaensia, 400

Contact information
University of Vaasa
School of Technology and Innovations
Energy Technology
P.O. Box 700
FI-65101 Vaasa
Finland

ISBN
978-952-476-804-7 (print)
978-952-476-805-4 (online)

ISSN
0355-2667 (Acta Wasaensia 400, print)
2323-9123 (Acta Wasaensia 400, online)

Number of pages
138

Language
English

Title of publication
Issues of various alternative fuel blends for off-road, marine and power plant diesel engines

Abstract

The share of renewable energy needs to increase. The target is to have an at least 27% share for renewables in the energy consumption in Europe by 2030. This dissertation contributes to achieving said target by concentrating on phenomena and properties related to alternative liquid fuels for different diesel engines. Both renewable and recycled fuels as well as their blends are used for power generation in power plants and marine and off-road engine applications. There are several fuel options for non-road engines. The theory and properties of a number of options were examined in terms of stability, compatibility and storage behavior. Both renewable and recycled fuels were studied. The research was implemented as a series of six studies with laboratory analyses. As one result of this dissertation, the blend of renewable naphtha and rapeseed methyl ester constitutes a completely novel 100% renewable fuel option for all kinds of diesel engines. The fuel blending and decisions as to which fuels should be used are case-specific and dependent on the application the fuel is used in and the fuel options for blending. That is why all the information about different blends and their properties is extremely important. The results showed that FAMEs need antioxidants as additives to be stabilized but the storage conditions play an important role in storage stability. Fuel blending up to a biodiesel content of 20 vol-% was compatible with lubricating oil quality in long-term engine experiments. In case the only option for the fossil blending component is high-sulphur fuel, fuel blending is beneficial for both blend stability and the environment. The diversity of alternative fuels is demanding for engine development. There are, however, several straightforward fuel options for medium-speed and other diesel engines. Blending new renewable fuels with conventional ones facilitates the technical transition period of the power production revolution.

Keywords
alternative fuels, diesel engine, renewable fuel, fuel blending, fuel stability

ACKNOWLEDGEMENT

The research work presented in this thesis was done in the Energy Technology unit in the University of Vaasa. Nowadays, the Faculty of Technology no longer exists and our research group, "Renewable Energy" is under the School of Technology and Innovations. The research work has been done within several years. The work started in 12th April in 2010, which was my first working day in the University of Vaasa. The knowledge used for this thesis has been collected ever since. The decision to start the PhD -studies is much younger and was made in the autumn 2015. After a few years of work as a chemist, it was a really good decision. Learning new is always inspiring and the studies gave variety to my work. The projects I have been involved during the research work used for this study were FCEP, Flexe and Hercules-2.

I wish to express my deepest gratitude to Professor Seppo Niemi, my supervisor, for his faith on me and support through hard times. Professor Niemi has probably more on faith on me than I do. He is the best possible mentor and role model for younger researchers.

I am sincerely grateful for my other supervisor, research manager Dr. Erkki Hiltunen for seeing my potential to become a member of his research team in 2010. Dr. Hiltunen has a good nose of employees and he is also incredibly talented as a teacher. I hope his expertise is still available for young scientists in his emeritus times.

In addition to the great supervisors, I wish to thank my wonderful colleagues, present and former. Dr. Jukka Kiijärvi I wish to thank for proofreading my studies every now and then, Mrs. Sonja Heikkilä, Ms. Saana Hautala and Mrs. Kirsi Spoof-Tuomi for their support at daily work, and Mrs. Anne Mäkiranta for a great conference and traveling company. Mrs. Michaela Hissa, Mr. Teemu Ovaska, Mr. Olav Nilsson, Dr. Carolin Nuortila, Ms. Maria Tuuri, Mr. Janne Suomela, Mr. Antti Niemi, Mr. Antti Kiikeri, Dr. Petri Välisuo, Mrs. Elena Wikberg, Mrs. Riikka Help, Ms. Nelli Vanhala, Mr. Antti Savola, Ms. Annika Svahn, Mr. Ville Vauhkonen, and the whole Levón institute's energy team deserve to be mentioned. The coffee breaks and discussions with you have been full of life. My special thanks also to Mrs. Maikki Niemi for her kind hospitality during my studies in Turku.

I am thankful for my employer, the University of Vaasa, for the opportunity to write my dissertation partly within the daily work. I wish to thank several people from AGCO Power, Wärtsilä, Neste and UPM for sharing their knowledge with

me during these years. During my studies, I got funding from Henry Fordin Säätiö and Kauppias Gustaf Svanljungin Lahjoitusrahaston Säätiö. I am grateful for their financial support.

To my friends I want to say thank you for being there for me. Without my friends, there wouldn't be me.

As my mother Marjaana is no longer with us, I am not able to express my gratitude to her. My comfort is that I know she would be proud of me. My father Juha I wish to thank for all the advices and showing the best places for picking berries. My sister Eveliina I am grateful for being my partner in crime in our common hobby harness racing and my brother Heikki for being a good role model as an ambitious researcher. Heikki's family, Tiina, Eino and Väinö, I wish to thank for cheering up my life. My hearty thanks also to Pirjo and Jouko, and Seija for their help whenever it is needed. Last but not least I want to thank Juhani for his love and support.

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Abbreviations

AFME	Animal Fat Based Methyl Ester
AN	Acid number
ASTM	American Society for Testing and Materials
B20	20 V-% Biodiesel-80 V-% Fossil Diesel Fuel Blend
B30	30 V-% Biodiesel-70 V-% Fossil Diesel Fuel Blend
BTL	Biomass To Liquid
Cxx/C_{xx}	Carbon Number
CFPP	Cold Filter Plugging Point
CI	Compression Ignition
CO	Carbon Monoxide
Cr(VI)	Chromium (VI)
DCN	Derived cetane number
DFO	Diesel Fuel Oil
DTBHQ	2, 5-di-tert-butylhydroquinone
EN	European Standards
EU	European Union
FAME	Fatty Acid Methyl Ester
GHG	Greenhouse Gas
GTL	Gas To Liquid
HC	Hydrocarbon
H_2SO_4	Sulphuric acid
HVO	Hydrotreated Vegetable Oil
ICE	Internal Combustion Engine
ICP	Inductively Coupled Plasma
ICP OES	Inductively Coupled Plasma Optical Emission Spectrometer
IQT	Ignition Quality Tester
ISO	International Organization for Standardization
JOAP	Joint Oil Analysis Program
KV	Kinematic viscosity
MTBHQ	Mono t-butyl hydroquinone
LFO	Light Fuel Oil
MGO	Marine Gas Oil

NOx	Nitrogen Oxides
OSI	Oxidation Stability Index
RME	Rapeseed Methyl Ester
RSD	Relative Standard Deviation
SME	Soy bean oil Methyl Ester
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TAN	Total Acid Number
TBN	Total Base Number
UV	University of Vaasa

Formulas

Publications

This doctoral dissertation consists of a summary of the following six publications, which are referred to in the text by their numerals:

I. Sirviö, Katriina; Niemi, Seppo; Vauhkonen, Ville; Hiltunen, Erkki. 2014. Antioxidant studies for animal-based fat methyl ester. Agronomy Research, issue 2, pages 407-416. ISSN: 1406-894X.[1]

II. Sirviö, Katriina; Niemi, Seppo; Hiltunen, Erkki. 2015. Storage stability studies with commercially available soy bean methyl ester. EUBCE 2015. 23rd European Biomass Conference & Exhibition Proceedings, pages 1305 – 1308. ISSN: 2282-5819. ISBN: 978-88-89407-516. doi: 10.5071/23rdEUBCE2015-3DV.2.7[2]

III. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Hiltunen, Erkki. 2016. The effect of sulphur content on B20 fuel stability. Agronomy Research, issue 1, pages 244-250. ISSN: 1406-894X. [3]

IV. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Hiltunen, Erkki. 2017. Effects of sulphur on the storage stability of the bio and fossil fuel blends. Agronomy Research, issue Special Issue 1, pages 1232-1241. ISSN: 1406-894X. [4]

V. Sirviö, Katriina; Niemi, Seppo; Katila, Tapani; Ovaska, Teemu; Nilsson, Olav; Hiltunen, Erkki. 2016. B20 fuel effects on engine lubricating oil properties. CIMAC Congress 2016. CIMAC paper number 025. [5]

VI. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Kiijärvi, Jukka; Hissa, Michaela; Hiltunen, Erkki. 2018. Feasibility of new liquid fuel blends for medium-speed engines. *Article submitted to Fuel. Under revision.*

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Author’s contribution

Paper I: Sirviö is the main author. Sirviö designed the study and implemented the laboratory analyses. Sirviö wrote the paper together with Niemi. Vauhkonen and Hiltunen provided comments on the paper.

Paper II: Sirviö is the main author. Sirviö proposed the research topic and designed the laboratory experiments. She wrote the paper together with Niemi. Hiltunen provided comments on the paper.

Paper III: Sirviö is the main author. Sirviö designed the study, implemented the laboratory analyses, and wrote the paper together with Niemi. Heikkilä and Hiltunen provided comments on the paper.

Paper IV: Sirviö is the main author. Sirviö proposed the research topic and designed the study. Sirviö and Heikkilä implemented the laboratory analyses. Sirviö and Niemi wrote the paper. Hiltunen provided comments on the paper.

Paper V: Sirviö is the main author. The research was implemented within a wider context of engine experiments designed by Katila and Niemi. Nilsson, Ovaska and Sirviö implemented the engine experiments. Sirviö, Niemi and Katila wrote the paper. Hiltunen provided comments on the paper.

Paper VI: Sirviö is the main author. Sirviö proposed the research topic and designed the study together with Niemi. Sirviö and Heikkilä implemented the laboratory analyses. Hissa assisted with the procurement of the studied fuels. Sirviö, Niemi and Heikkilä wrote the paper. Kiijärvi was responsible for the layout of the paper and Hiltunen provided comments on the paper.

1 INTRODUCTION

1.1 Background

Energy demand is increasing, especially in developing countries where the population and living standards are growing. According to predictions, the global energy demand will rise by 25% and commercial transportation by 50% by the year 2040. Still, emissions are prognosticated to decline after 2030 leading to a situation where they globally rise by only 10%. This is possible due to enhanced energy efficiency in buildings and transportation as well as increasing power plant efficiencies. Coincidentally, less carbon-intensive energy sources, such as natural gas, nuclear energy and gaseous, liquid and solid renewables are becoming more frequent. Natural gas in its various forms is at the moment said to replace coal-based energy resources. (ExxonMobile, 2017) It has been predicted that fossil oil itself will dominate as a major transportation fuel for 50 years (Zhao, 2017). This prediction implies that liquid fuels will also be utilized in power production for at least an equivalent time frame.

These predictions are taken into account in the EU. The European Parliament has proposed three key targets to increase the use of cleaner energy and enhance energy efficiency by the year 2030. The first one is to improve energy efficiency by 35%. The second target is to have an at least 35% share for renewables in energy consumption, versus the current target of 27%. The third one is to achieve an at least 12% share of energy from renewable sources in transportation. (European Parliament, 2018; Climate Action, 2018)

To reach these targets and enable a universal increase in living standards, much research work is needed. Despite the gas revolution in power generation, liquid fuels will still be used to fulfil the energy demand for a long time. One reason is the existing prime mover technology; for example, the useful life of a ship is approximately 15 to 30 years. The energy density of liquid fuels is also superior to most energy carriers. Despite the fact that the number of gas applications is increasing heavily in power generation, heavy-duty transportation and marine prime movers are presumed to continue utilizing liquid fuels for the next few decades. In these applications, the compression ignition (CI) engine is most likely to remain the main prime mover. The fuel conversion efficiency of a CI engine is the best of all stand-alone prime movers within an output range of approximately 100 kW to 100 MW.

Since greenhouse gas emissions are to be markedly reduced, however, the share of gaseous and renewable liquid fuels will be increasing rapidly in the near future. The exhaust pollutant emissions of CI engines are rigorously regulated. The strictest standards concern on-road engines but even the off-road and power plant engine legislation is very strict. The emission standards in maritime transport will be tightened; nitrogen oxides and sulphur are already restricted. For the EU inland waterways, even particulate matter will be limited strongly in the near future. (DieselNet, 2017) The development of the emissions legislation guides engine development and simultaneously directs the transfer from fossil fuels to more sustainable alternative fuels.

1.2 Need for new liquid fuels

So far, the price of the alternative fuel options has not been competitive with cheap fossil fuels. Still, alternative, local and cost-effective fuels are needed in many regions around the world to increase the self-sufficiency of energy generation. Independence from imported energy will be emphasized during the coming decades. The production of renewable electricity, e.g., wind or solar power, increases globally, but its weakness is that it is highly intermittent. Engine-driven power plants, especially ones run on gas, will be needed for peaking power to keep the electricity grids stable. They are extremely suitable for this purpose because the plants can be started, loaded and stopped very quickly. (Franck & Hägglund, 2013) The availability of gas, however, varies, and in some areas it may even be limited. Biogas is of course one option but the production needs to be substantial to suffice for power plants, for example. As a whole, thus, various liquid fuel options will in the future still play an important role both in flexible power generation and in marine and heavy-duty applications.

The range of alternative, renewable fuels is at the moment quite narrow. The amount of renewables in all liquid fuels is at present less than 2%. One realistic way to increase the amount of renewables to fulfil the 27% target set in the EU climate & energy framework is to blend renewables with fossil fuels. The blends with biodiesel, fatty acid methyl esters (FAMEs), are already standardized. FAMEs have been studied for a long time and apparently, despite some problems they may have, are still of great interest. That said, FAMEs are not the only option in the category of alternatives. In the last decade, HVO (Hydrotreated Vegetable Oil) fuels have been developed. They are high qualified fuels, probably even too qualified and expensive for the applications dealt with in this dissertation. HVO fuels are suitable for automotive usage. The fuels studied in this dissertation are not sufficiently homogeneous for automotive engines. An important addition to the category of alternatives are fuels produced from e.g. oil wastes, that is, recycled fuels. They are not renewable, but recycling of potential energy raw materials is still one step forward in increasing the use of suitable and more sustainable options.

At the moment, the quality of fuels is ensured by standardization. The quality standards are fit for their purpose and each application category has its own standards. The purpose of retail fuel standardization is to protect the customer. There should be a correlation between the fuel that fulfils the requirements set in the standard and the operability and reliability of the power generation application concerned. As regards FAME type fuels, their cold properties and oxidation and storage stability have constituted the fuel quality bottleneck. The quality parameters for new fuels which have not yet been introduced to the market cannot be specified accurately. In this dissertation the properties of several renewable and fossil fuel blends for medium- and high-speed non-road engines are investigated. The work produces a large amount of new information about the feasibility of these liquid fuel options.

1.3 Objective and outline of dissertation

The research strategy in this dissertation is one of experimental research. The research was designed to widely examine the properties of renewable alternative fuels. The properties were measured by means of quantitative chemical analyses. The aims of this dissertation were to increase knowledge of the fuels' stability and to produce novel information about the feasibility and compatibility of different fuel blends. In particular, this dissertation answers the following research questions:

1) How much antioxidant is needed to improve the stability of waste animal fat based FAME? (Paper I)

2) How long can SME (soy bean methyl ester) be stored in clean laboratory conditions? (Paper II)

3) Does the vessel material or temperature affect the storage time of SME? (Paper II)

4) Does the sulphur content affect the fuel blend stability? (Papers III, IV)

5) What effects does the B20 fuel blend have on the quality of lubricating oil in long-term engine operation? (Paper V)

6) What are the properties of the blend of renewable naphtha and RME (rapeseed methyl ester)? Is the blend suitable for medium-speed engine applications? (Paper VI)

7) What are the properties of the blend consisting of the circular economy product marine gas oil (MGO) and RME? Is it suitable for medium-speed engine applications? (Paper VI)

The dissertation proceeds from additive and stability studies (Papers I-IV) to the compatibility of the renewable alternative fuels (Papers II and V), and Paper VI presents novel alternative blends and their properties.

In Paper I, "*Antioxidant Studies for Animal-Based Fat Methyl Ester*", the study indicated that antioxidants are needed to reach decent oxidation stability. The FAME studied in Paper I was a local animal fat-based biodiesel and the results published were unique.

The oxidation phenomenon of FAMEs is complex. In Paper II, "*Storage stability studies with commercially available soy bean methyl ester*"**,** the storage stability of soy bean methyl ester (SME) was followed for one year. The fuel quality did not decline much in proper conditions.

Paper III was entitled "*The effect of sulphur content on B20 fuel stability*", and IV "*Effects of sulphur on the storage stability of the bio and fossil fuel blends*". The obtained results indicated that the amount of sulphur in fuel blends with 20 V-% of FAME and 80 V-% of sulphur-containing light fuel oil (LFO) might correlate with the oxidation stability of the blend. Adding FAME type biodiesel to high-sulphur fossil fuel brings double benefit; it is favourable for the fuel stability and beneficial for the environment as the amount of sulphur emissions is decreased.

Nevertheless, there is also need to research other renewable alternatives than FAMEs. In Paper VI, "*Feasibility of new liquid fuel blends for medium-speed engines*", several fuel blends and their properties were analysed. Rapeseed methyl ester was blended with renewable naphtha, kerosene, marine gas oil (MGO), and LFO. In addition, a blend of LFO and renewable naphtha was studied. All blends were found to be feasible in compression-ignition engines.

Along with the feasibility and availability of the fuel, its compatibility with the whole engine system must be taken into account. Paper V, "*B20 fuel effects on engine lubricating oil properties",* describes the effect of B20 fuel on the engine lubricating oil properties which were not threatened in a 500-hour engine experiment run on B20 fuel.

2 ISSUES OF NOVEL FUEL OPTIONS

An alternative fuel must fulfil the quality assurance and standardization requirements to secure acceptance by consumers. The US and EU standards are the most used standards, and other biofuel utilizing nations often follow them. (Hassan & Kalam, 2013) In terms of FAMEs, the most challenging properties have been their oxidation and storage stabilities. Partly due to stability, the compatibility with, e.g., lubricating oil is also an important issue. Surprisingly, fuel sulphur has seemed to improve the stability of fuel blends. The theory of these issues is discussed in the following sections.

2.1 Fuel blending

Various sustainable liquid fuel alternatives are needed for different CI engine applications to reduce GHG emissions and ensure proper primary energy sources for the engines. The decrease of fossil reserves together with the concern related to emissions has furthered the research of alternative fuels in internal combustion engines (ICEs). Theoretically, alternative fuels are able to reduce the emissions and several profitable results have already been obtained in practice. To ensure positive progress in energy security and sustainability, alternative fuels need to be increasingly accessible.

For CI engine applications, one reasonable solution is to use various blends of renewable and fossil liquid fuels until the availability of renewable fuels reaches a sufficient extent. Blending facilitates the technical transitional period while the availability of renewable fuels is limited. Together with special renewable fuels, fuel options originating from circular economy can also be blended with conventional fuels. For instance in Finland, the government strives to promote circular economy, which in fuel production means that waste greases and lubricating oils can be used as fuel raw material. Blending studies have been reported in many articles which mainly cover FAMEs and light fuel oil (LFO) blends (Giuliano Albo et al., 2017; Hasan Altaie et al., 2017).

In Europe, the maximum FAME content in diesel fuel is 7 V-% according to EN 590:2013 (SFS-EN 590:2013, 2013) but higher percentages are also achievable and targeted around the world. For example in the United States, the 20 V-% blend fraction is becoming more common as the targets set for increasing renewable energy are aspired after. B20 and B30 fuels even have their own standard, EN 16709, which specifies the quality of fuels with a high biodiesel content (SFS-EN 16709:2015, 2015). The limits for FAME do not apply to other renewable fuels, such as HVO, GTL (Gas To Liquid) or BTL (Biomass To Liquid) fuels. These fuels may be added in any proportions provided that the properties of the blend comply with the limitations set in EN 16709. However, new fuels cannot be standardized as the quality parameters for fuels which have not yet been introduced to the market can impossibly be specified accurately.

Fuel blending may inflict operating complications. The fuel blend needs to be stable and compatible with engine, lubricant and other fuels. Several studies have been conducted to determine how biodiesels and their blends affect the lifetime of engines. A review of short-run tests reports that biofuels can replace conventional diesel fuel but a long-run analysis is needed for the assessment of engine lifetime. In CI engines, fuel blending may cause, e.g., carbon deposition, lubricating oil dilution, piston ring sticking, and injector nozzle choking (Patel et al., 2016). Accelerated ageing of exhaust after-treatment systems may also occur if FAME contains a substantial amount of alkaline metals. Some studies indicate that catalyst systems are at a high risk of damage even with FAME quality in compliance with proper standards. Therefore, B20 blend is not recommended for state-of-the-art heavy-duty engines unless the limit values of EN14214 for alkali and earth alkaline metals are revised (Aakko-Saksa et al., 2014).

2.2 Studied fuel blend properties

The variety of all kinds of blends and alternative fuels, used for applications other than automotive use, is diverse, which is why not all possible blends can be regulated by their own standard. Not all cheap and local fuels will necessarily meet all the requirements set in the relevant standards but the resulting properties of available fuels are still useful for engine design. However, the standards provide good information about the quality target which the alternative liquid fuels even for medium-speed applications should aim at. In the following sections, the most important properties of blends are described briefly.

2.2.1 Cetane number, oxidation stability and acid number

The cetane number (CN, also derived cetane number, DCN) represents the ignition quality of the fuel. In CN determination, both chemical and physical properties are taken into account. CN determination provides important information if it is to be decided whether alternative fuel is suitable for use in CI engines. One way to measure cetane number is to employ the ignition quality tester, IQT. In this instrument, the fuel is injected into a heated chamber filled with compressed air. The ignition delay of the fuel is measured and the CN is calculated based on the result. (Kalghatgi, 2014; Neste Oil, 2007)

Oxidation stability (OSI) is one of the most important properties of alternative fuels, especially biofuels. FAME and bio-oils oxidize more readily than other renewable and petroleum diesel fuels. (Neste Oil, 2007; Guibet, 1999) Oxidation resistance is determined by a procedure where the change of the inherent stability is measured under accelerated oxidizing conditions. The methods for analysing the oxidation stability of the fuels provide a basis for the estimation of their storage stability.

Acidity may restrict the prevalence of alternative fuels, especially bio-oils. Acid number is measured by a titrimetric method where the free fatty acids present in the sample are neutralized with alkali (EN 14104, 2003).

2.2.2 Cold properties

The cold flow performance of a diesel fuel is determined by its composition. It is represented by different critical temperatures based on the formation of wax crystals as the fuel is cooled during the test. Paraffins with chain lengths typically ranging from 10 to 30 carbon atoms have limited solubility in the fuel. When the fuel is cooled, paraffins heavier than C_{15} will form wax. The wax can block fuel lines and filters and cause malfunction at low temperatures. (Kalghatgi, 2014) Nevertheless, paraffins are profitable for the cetane number and other combustion properties and not all paraffins can be removed from the fuel (Neste Oil, 2007). The cold flow properties are measured by three different methods: cloud point, pour point, and cold filter plugging point (CFPP).

The cloud point is the temperature at which the wax first becomes visible when the fuel is cooled in a test procedure. It is a subjective measurement because the wax formation is estimated by the human eye. The pour point is the temperature below which the wax crystals grow and form gel which stops flowing. The CFPP is the lowest temperature at which 20 ml of fuel still passes through a fine wire mesh screen of 45-micrometre nominal openings in less than 60 seconds. The fuel is cooled and checked at 1°C intervals. This is the most recognized method of the three. (Guibet, 1999)

2.2.3 Distillation curve

The distillation curve describes the temperature range where the mixture of hydrocarbons vaporizes when the mixture, in this case fuel, is heated slowly and steadily at atmospheric pressure (Neste Oil, 2007). The light fraction of the fuel is distilled first and is, thus, more volatile than the heavy fraction. The volatility affects the combustion process. The heavy fraction may not be too broad because the fuel atomization into fine droplets is important for the progress of the combustion, which is reduced if the heavy fraction is too large. The heavy fraction content also affects emissions by increasing soot, hydrocarbon (HC), and carbon monoxide (CO) emissions. (Kalghatgi, 2014)

2.2.4 Density and kinematic viscosity

Density is controlled within a narrow range for the following reasons. The air-fuel mass ratio is the determining value in the combustion chamber. Variation in fuel density affects the mass of the injected fuel because the injection is usually controlled by setting the injection system to deliver a predetermined volume of fuel. A minimum value for the fuel density is given to ensure decent maximal power from an engine with volume-based fuel flow control. Density also affects the volumetric fuel consumption and emissions. A lower content of heavy aromatics usually means lower fuel density, which may contribute to reducing HC, CO and particulate emissions. A maximum value of density is given so as to better avoid smoke formation at full load. The smoke results from growth in the average equivalence ratio in the combustion chamber as smoke is formed by incomplete combustion. The density is dependent on the temperature. (Kalghatgi, 2014; Guibet, 1999)

The kinematic viscosity of the fuel depends on the fuel density while factors influencing the fuel viscosity are identical to those affecting the density. Changes in viscosity cause instant changes in engine operation. Excessive fuel viscosity increases pumping losses in the injection system and the injection pressure at the pump end may increase when conventional in-line pumps are adopted. All this may cause disruptions in the combustion process. On the other hand, insufficient viscosity may cause the injection pump to seize. Insufficient viscosity may also produce leakage at the injection pump and injector tips. This affects the pressure and delivered volume at the injector and may cause fuel leakage into the cylinder late during the expansion phase. (Kalghatgi, 2014; Guibet, 1999)

2.2.5 Flash point and lubricity

The flash point is the lowest temperature at which the fuel can vaporize to form an ignitable mixture in air. It has no direct effect on engine performance but it is used to quantify the flammability hazard of the fuel during storage and distribution. (Kalghatgi, 2014; Guibet, 1999)

Diesel fuel needs to have adequate lubricity to ensure the integrity of the fuel system. Naturally, low concentrations of polar compounds exist in the diesel fuel and these compounds lubricate the engine high-pressure fuel pumps by forming a protective layer on the metal surfaces. The lubricity is measured by the size of the wear scar in a high-frequency reciprocating rig (HFRR) test. A hardened steel ball vibrates in loaded contact with a hardened steel plate immersed in the fuel tested. (Kalghatgi, 2014)

2.3 Effect of fuel blend on lubricating oil

Lubricating oil serves several functions in an engine. Modern lubricant oils protect the engine and extend engine lifetime. Other basic functions of lubricant oil are to improve fuel economy and assist in sustaining a low level of emissions. Engine lifetime may be shortened by alternative fuels or fuel blends, which emphasizes the importance of the lubricant.

For the most part, engine durability is protected by inhibiting wear. Lubricant oil also inhibits deposit formation by combustion products. Piston skirt and ring groove deposits are often reported in neat biodiesel engines. (Sem, 2004) Lubricant oil ages over time and may become acidic. Acidity may also increase through contamination caused by unburnt fuel or combustion gases, both of which may cause corrosion in engine parts. The lubricant oil should act against acidification.

The use of renewable fuels and their blends may cause problems for lubricant technology because it needs to be ensured that the fuel is compatible with the lubricant. It has been assumed that new fuels, especially FAME type biodiesels, may affect lubricating oils in a different way from conventional fossil fuels. Biodiesel is less stable and less volatile than traditional diesel. Especially in diesel fuel blend, the lower volatility may cause the biodiesel to accumulate in higher concentrations in the oil than mineral diesel. This is claimed to be the main reason for problems in vehicle operation when using biodiesel. Fuel dilution may increase acidity and make the oil thicker, producing a higher total acid number and kinematic viscosity, and leading to, e.g., oil degradation and further to corrosion of engine parts, piston deposits, sludge, or wear. All this shortens the oil change intervals. (Howard, 2014; Thornton et al. 2009)

2.4 Stability and storage stability

Storage stability is one of the main quality parameters related to FAMEs. The declining of biofuel properties during storage is more serious than with conventional fuels. The oxidative stability of biodiesel is threatened primarily during lengthened storage. Generally, factors such as the presence of air, elevated temperatures or presence of metals promote the oxidation process (Knothe, 2007). The storage time of FAMEs is regrettably short, at the moment said to be 6-12 months. Improving oxidation and storage stability is an important issue for commercializing biodiesels irrespective of the applications they are used for. (Bouaid et al., 2007) The storage stability of FAMEs has been studied in many earlier studies (Serrano et al., 2013; Das et.al, 2009) but the storage time in these studies was only 6 months.

The materials used for storage containers or barrels of fuels are, e.g., high density polyethylene or steel. Methyl esters have a tendency to develop acidic material during storage. Acidity may cause corrosion on metal surfaces. The acid number (acid value) describes the development of acidic materials during oxidation. Insoluble gums and organic acids (e.g. formic acid) may be formed. (Lacoste & Lagardere, 2003; Bouaid et al. 2007; Yamane et al. 2007) Engine fuel filters and injectors may become choked if polymerization or acid formation occurs, while acids also provide a corrosive environment for the fuel injection equipment. Polymerization caused by oxidation increases the viscosity of the sample, thereby causing injector blockage. Therefore, kinematic viscosity is one of the physical properties most commonly measured. Moreover, undesirable oxidation products may affect the function of fuel pumps and injectors due to increased wear. (Waynick, 2005; Pullen & Saeed, 2014)

Unsaturated fatty acids are the most reactive compounds in biodiesels and therefore prone to autoxidation (Yaakob et al. 2014; Shahabuddin et al. 2012). Antioxidants inhibit the autoxidation process and can be used as additives to extend the storage time of biofuels (Knothe, 2007). This autoxidation cycle where radicals are formed needs to be hindered at an early stage to sufficiently slow down the autoxidation process. There are distinctions between antioxidants and their impact on a certain biodiesel (Tang et al., 2008; Xin et al., 2008; Xin et al. 2009). This means that to ensure efficient stability of the biodiesel, the antioxidant has to be selected according to the feedstock used. Several articles have been published related to biodiesel antioxidants and relatively high concentrations of antioxidants are needed to meet the requirements set for fuel stability (Yang et al., 2017; Das et al., 2009).

2.5 Effects of sulphur content

In the past few decades, the sulphur content of liquid engine fuels has drastically decreased to reduce exhaust sulphur compounds that are harmful both environmentally and for people. Fuel sulphur increases particulate matter and soot emissions in the exhaust of all kinds of internal combustion engines. The reasons for fuel sulphur limitations are also technical, i.e., sulphur causes corrosion and has a deleterious effect on advanced catalytic systems used for CO, HC, NOx and particulate reduction (Kalghatgi, 2014; Zhao et al., 2016). Moreover, the fuel sulphur has adverse effects on engine components. This aspect renders desulphurization important. However, refining processes which remove sulphur from the fuel simultaneously reduce fuel lubricity.

On the other hand, some studies indicate that higher sulphur contents may benefit the oxidation stability of fuel blends (McCormick & Westbrook, 2007) or neat fossil diesel (Kalitchin et al., 1992). Sulphur is known as an essential compound for living organisms. Several studies (Meister & Anderson, 1983; Roxas et al., 1997; Madhulika et al., 2017) imply that an example of the antioxidative effect of sulphur compounds can be found from biochemistry. Organic sulphuric compounds, such as glutathione, are well known for being capable of protecting cells from free radicals and reactive oxygen compounds (Meister & Anderson, 1983). It has also been shown that glutathione can reduce the lipid peroxidation caused by reactive oxygen radicals (Roxas et al., 1997). Singh et al. (2017) have studied the involvement of sulphur assimilating enzymes and sulphur containing non-enzymatic antioxidants in the regulation of metal (in this case Cr(VI)) toxicity in eggplant seedlings. They found that an elevated level of sulphur-containing non-enzymatic antioxidants such as cysteine, glutathione and non-protein thios decreases oxidative stress in eggplant seedlings. In other words, high sulphur protects seedlings against Cr(VI) toxicity. (Singh et al. 2017) Also, for a long time, sulphur dioxide has been used as an antioxidant in winemaking to prevent alterations of the wine (Vanne, 2012; Salaha et al., 2008).

Selenium, Se, belongs to the same group of elements in the periodic table as sulphur. In mammals, selenoproteins act as cellular antioxidants. (Tapiero et al, 2003) There is a similarity in their chemical characteristics as they both have six valence electrons. In their study on prevention of metal-mediated DNA damage with sulphur and selenium, Zimmerman et al. (2015) propose that sulphur and selenium antioxidant mechanisms occur via metal. (Zimmerman et al. 2015)

Biodiesel oxidation is a complex process of radical chain reactions. Hydroperoxides are first formed during degradation and react further to form secondary oxidation products (Fattah et al., 2014). In living organisms and fuel blends, the reaction environments and reaction chains differ and it cannot be stated that the phenomenon is the same. Nonetheless, there is interesting similarity. However, the possible beneficial effects of sulphur on the fuel oxidation stability are an important issue in cases where high-sulphur fossil fuels, such as marine bunker oils or MGO, are blended with biofuels or renewable fuels. The latter reduce the absolute sulphur content of the blends while the decreased sulphur content still improves the storage properties of the blend.

3 METHODS

In this dissertation, each paper is based on its own research plan and approach in the laboratory. The aim was to create extensive novel information about the most important properties of alternative fuels. Each laboratory study was planned and carried out separately, an exception being the studies discussed in Papers III and IV, of which the latter was conducted to improve the conclusions presented in Paper III.

3.1 Oxidation stability measurements

The aim of the study in Paper I was to determine the optimal concentration of an antioxidant, BioSineox, for local animal-based fat methyl ester, AFME, in the fuel production process. The fuel was treated with antioxidant to meet the six-hour oxidation stability requirement as set in Standard EN 14214:2010 (since 2012, eight-hour) (EN 14214, 2012). In Paper I, the experimental research plan was developed throughout the measurements and via discussions with the fuel producer, as the aim was to find out which is the lowest amount of antioxidant needed.

The fuel was an ester-type biodiesel produced using a two-stage process combining acid-catalyzed esterification and alkali-based transesterification. The product is mainly used as heating fuel and as fuel in non-road engines (Bengts, 2010). The tested antioxidant was BioSineoxTM Liquid. It is a synergistic blend of hindered phenolic compounds with a chemical name of mixed butylated hydroquinones, the major components being MTBHQ (mono t-butyl hydroquinone) and DTBHQ (2,5-di-tert-butylhydroquinone) (AAFC, 2009).

The oxidation stability index was measured by a Biodiesel Rancimat 873 instrument. The method describes the fastened oxidation stability of biodiesel. The sample is heated and air flow is conducted through it. Vaporizing compounds of the sample drift with air into water and the conductivity of the water is measured. The end point is achieved when the conductivity increase is at its highest. The method is described in Standard EN 14112 (EN 14112, 2003). For AFME, several sets of measurements were performed with various concentrations of the antioxidant. The measurements were repeated for all of the samples and the presented results show the mean values of the two parallel measurements.

The research was started by analyzing the oxidation stability of samples of known antioxidant concentrations (0, 100, 250 and 500 ppm) prepared in the laboratory. The targeted six-hour limit was reached in laboratory conditions when 500 ppm of antioxidant was added. After that, the same was studied in the manufacturing process; how much antioxidant is needed in the process to reach the six-hour limit in a Rancimat experiment. Several studies were conducted and it was found that in the process the needed amount of antioxidant is higher than it was for the laboratory samples.

3.2 Studies of storage conditions

In the investigation of Paper II, commercial soy bean methyl ester (SME) samples were stored in two high-density polyethylene bottles produced for chemicals and in two tin-plated steel cans produced for paints. All the containers had a volume of 1 litre. The containers were filled up with the samples with a couple of centimeters of airspace when the experiment started. The vessels were closed with corks for the duration of the storage period. The airspace volume increased during the experiment because of sampling but the increase was not determined precisely. One plastic bottle and one can were stored at 20°C in a dark cupboard. Another plastic bottle and another can were stored in a refrigerator which was set at a temperature of 4°C. The samples were stored for 12 months. When starting the study, the monitored properties (ester content, kinematic viscosity, oxidation stability and acid number) were measured by the SME supplier at the end of the year 2012. The metal contents (Al, Cu, Fe, Mn, Si, V, Zn) were measured at the University of Vaasa (UV) at the beginning of 2013. All these properties were remeasured after 12 months of storage time at UV. The methods described below in the methods section are those used by UV.

The concentrations of metal elements were measured with a Perkin Elmer ICP OES spectrometer 7000DV. In this method, a weighted sample is diluted with kerosene in a weight ratio of 1:1. The solution is injected into the spectrometer plasma. Calibration was performed with the known concentrations of multi-standards. The elements measured by this method were Al, Cu, Fe, Mn, Si, V and Zn. In the method, the defined emission intensities at known concentrations and the presence and concentration of the element are evaluated by comparing the intensity of the light against these standards. The analyses were performed by an in-house method based on Standards EN 14538 and EN 14107, as well as according to the manufacturer’s advice. (EN 14538, 2007; EN 14107, 2003)

The acid number was analysed with a Metrohm Titrando 888 titrator. The method is a potentiometric titration method. The sample is diluted with iso-propanol and titrated with potassium hydroxide. The acid number, AN, is reported according to Equation 1

$$AN = \frac{56.1 \times V \times c}{m} \tag{1}$$

where

V is the volume of the standard volumetric potassium hydroxide solution used (ml);

c is the exact concentration of the standard volumetric potassium hydroxide solution used (mol/l);

m is the mass of the sample (g); and

56.1 is the molecular mass of potassium hydroxide.

Results are expressed as mg KOH/g.

The measurement was performed according to Standard EN 14104 (EN 14104, 2003).

The oxidation stability index was measured by a Biodiesel Rancimat 873 instrument and the principle of the method is described above (3.1 Oxidation stability measurements).

The kinematic viscosity was measured with a Stabinger SVM 3000 rotational viscometer. The measurement is based on torque and speed measurements. The device calculates the dynamic viscosity, η (mPas), from the rotor speed by Equation 2

$$\eta = \frac{K}{(n_2 / n_1 - 1)} \tag{2}$$

where

K is constant;

n_1 is the speed of the measuring rotor (mm/s); and

n_2 is the speed of the measuring tube (mm/s).

The device also has a density measuring cell that employs the oscillating U-tube principle. The kinematic viscosity, KV (mm^2/s), was calculated automatically based on these measurements according to Equation 3

$$KV = \frac{\eta}{\rho} \qquad (3)$$

where

η is dynamic viscosity (mPas); and

ρ is density (g/cm^3). (Novotny-Farkas et al. 2010)

The ester content was measured with a Perkin Elmer Clarus 580 gas chromatograph. Methyl heptadecanoate is used as an internal standard for this method. It is suitable for biodiesels containing methyl esters between C14 and C24, and when the ester content is higher than 90 m-%. The ester content, C (m-%), is calculated in compliance with Equation 4

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \qquad (4)$$

where

$\sum A$ is the total peak area from the methyl ester in C_{14} to that in $C_{24:1}$;

A_{EI} is the peak area corresponding to methyl heptadecanoate;

C_{EI} is the concentration of the methyl heptadecanoate solution (mg/ml);

V_{EI} is the volume of the methyl heptadecanoate solution (ml); and

m is the mass of the sample (mg).

The method is described in Standard EN 14103 (EN 14103, 2003).

3.3 Storage stability measurements

In Paper III, the parameters correlating with the storage stability of the fuel blends were compared in two B20 fuel samples consisting of 20 V-% biodiesel and 80 V-% fossil diesel. One of the samples was mixed with commercial rapeseed methyl ester (RME) and distillate fuel oil (DFO) containing 6.6 mg/kg sulphur [below: B20 (6.6 mg/kg S)]. The other was mixed using the same RME but with DFO containing 186 mg/kg sulphur [below: B20 (186 mg/kg S)]. The fuel containing 6.6 mg/kg sulphur did not contain any biocomponent before being mixed with RME. Information about the added biodiesel for the DFO containing 186 mg/kg sulphur was not available. The supplier assumed it did not contain any biodiesel before it was mixed with RME. The DFOs originated from different continents. Most likely, the crude oils used for their manufacturing also differed. The chemical compositions of the fossil fuels were not analysed. The difference of the composition may have had an unknown effect on the results. The RME had been produced three years before this study and delivered to the UV in 2012. Even so, it fulfilled the requirements of Standard EN 14214:2012 in terms of the properties measured in this study (EN 14214, 2012). Information about the added antioxidant was unavailable.

The analyses carried out for these two samples were oxidation stability, acid number, and kinematic viscosity. The samples were analysed immediately after mixing, after 4 weeks, and finally, after 9 weeks of storage. The storage conditions were not specified in great detail but the samples were similarly placed in a dark cupboard at room temperature (around 20°C). The mentioned properties (oxidation stability, acid number, kinematic viscosity) of neat RME were also measured before mixing it with DFOs.

The acid number was again analysed with the Metrohm Titrando 888 titrator, the method having been described in 3.2 above, Studies of storage conditions.

Even though the standard methods for biodiesel and blend differ slightly, oxidation stability was measured with a Biodiesel Rancimat 873. The operating principle of the instrument was described earlier in this chapter (3.1 Oxidation stability measurements) and it also applies to the fuel blend method described in Standard EN 15751. (EN 15751, 2014)

Kinematic viscosity was measured with a Stabinger SVM 3000 rotational viscometer, the method principle having been described above (3.2 Studies of storage conditions).

3.4 Stability improvement by sulphur addition

The study discussed in Paper IV was implemented to confirm the conclusions presented in Paper III. In the Paper IV study, the parameters correlating with the storage stability of the fuel blends were investigated. Four B20 fuel samples were compared consisting of 20 V-% biodiesel and 80 V-% fossil diesel. All samples were prepared by mixing commercial rapeseed methyl ester (RME), diesel fuel oil (DFO) containing 6.6 mg/kg sulphur, and high-sulphur diesel solvent. Different amounts of sulphuric diesel solvent were added into the B20 samples. The obtained sulphur contents were 6 mg/kg (B20 1), 76 mg/kg (B20 2), 149 mg/kg (B20 3), and 226 mg/kg (B20 4). The aim was to determine how the storage stability of fuel blends having various S contents changed as a function of time when the samples were stored in stable conditions (in the dark, at 20°C) for 12 weeks.

The fuel samples were prepared by mixing three different compounds; RME, DFO, and ICP diesel solvent containing 1000 mg/kg sulphur. The RME had been produced three years prior to this study and delivered to the UV in 2012. This notwithstanding, the RME fulfilled the requirements of EN 14214:2012 in terms of the properties measured in this study (EN 14214, 2012). The ester content of the RME was not measured. No information concerning the most likely added antioxidant in the RME was available.

The analyses performed on these four samples were oxidation stability, acid number, and kinematic viscosity. The samples were analysed immediately after mixing and after 4, 8 and 12 weeks of storage. The storage conditions were a dark cupboard at room temperature (approximately 20°C). The oxidation stability, acid number and kinematic viscosity of both RME and DFO were determined before mixing them together and adding high-sulphuric diesel solvent. For the prepared sulphur-containing B20 samples, the sulphur contents were measured immediately after mixing.

The acid number of the blends was analysed with a Metrohm Titrando 888 titrator. The viscosities were measured with a Stabinger SVM 3000 rotational viscometer. These methods were described above in 3.2, Studies of storage conditions. The oxidation stability was measured with the Biodiesel Rancimat 873 instrument. The method is described above in 3.1, Oxidation stability measurements.

The sulphur contents were measured with a Thermo Scientific, iCAP 6500 duo instrument. In this method, microwave (Milestone UltraWAVE) assisted acid digestion was used to decompose the organic structure of the samples into a water-soluble form. The solution was injected into the spectrometer plasma. The instrument was calibrated with the known concentrations of the standards. The defined standards (emission intensities in known concentrations) and the presence and concentration of the element were evaluated by comparing the intensity of the light to these standards. The sample pretreatment and ICP analyses were performed by an in-house method based on the US EPA methods and the manufacturer's advice.

3.5 Study on effects of fuel blend on lubricating oil

The main objective of the study in Paper V was to determine how long-term use of high-quality B20 fuel affects the engine lubricating oil. In this study, B20 fuel (20 V-% soy bean methyl ester and 80 V-% light fuel oil, LFO) was used in an endurance engine experiment, and the lubricating oil sample was analysed fresh and after 207, 357 and 553 hours of engine operation.

The total running period was 553 hours. The aging run was carried out with B20 as fuel. The engine was equipped with a common-rail injection system and complied with the EU Stage 3B/US Tier 4 interim emissions legislation. The average power during the 553-hour test cycle was 41 kW which is 40% of the rated power.

Table 1. Methods used in the oil analyses

Property	Method
Kinematic viscosity, 40°C	ASTM D445, DIN 51562
Kinematic viscosity, 100°C	ASTM D445, DIN 51562
Viscosity index	ASTM D2270, ISO 2909
TBN	ASTM D664
TAN	ASTM D664
Oxidation	JOAP
Nitration	JOAP
Additives ICP	ASTM D5185, in-house
Corroding metals ICP	ASTM D5185, in-house
Contaminants ICP	ASTM D5185, in-house
Water content	ASTM D6304 C
Fuel dilution	DIN 51451, JOAP
Biodiesel content	DIN 51451

The lubricant used during the engine operation was commercially available, as was the LFO. The biodiesel fuel, soy bean methyl ester, was also commercially available and met the requirements of Standard EN 14214 except for the iodine value which for this fuel was 131 when it should be below 120 g Iodine/100 g (EN 14214, 2012). The experimental engine was a high-speed, turbocharged, intercooled non-road engine.

B20 fuel was produced by weighing and mixing at UV. The condition of the lubricating oil was monitored at 0, 207, 357 and 553 operating hours. The total volume of the samples taken was 1 litre. The samples were analysed in the laboratory of Fluidlab Oy, Turku, Finland. The methods used in the oil analyses are provided in Table 1. These standards are not mentioned as references in this dissertation.

Based on the results of the analyses, the lubricating oil was not changed during the 553-hour run. The temperature of the lubricating system was not monitored for scientific accuracy during the experiment. The total volume of the lubricating oil in the system was 8 litres. New oil was added to the system after 189, 256, 357, and 464 hours, 1 litre at a time. The oil consumption was 0.12 g/(kWh) during the experiment. This is a normal value for heavy-duty diesel engines.

3.6 Feasibility of new fuel blends

The main aim of the study in Paper VI was to determine the most important properties of certain blends to obtain fundamental knowledge about their suitability for, in particular, medium-speed CI engines. The fuels used for blending were RME, renewable naphtha, LFO, MGO, and kerosene. The rapeseed methyl ester RME fulfilled the requirements of EN 14214:2012 (EN 14214, 2012). The naphtha was a residue of the manufacturing process for renewable diesel based on wood and forest residues through tall oil. The light fuel oil was sulphur-free and winter-grade and fulfilled the requirements of Standard EN 590: 2013 (EN 590, 2013). The MGO was a marine fuel produced from recycled lubricating oils, and the kerosene was produced in Finland.

Table 2 shows the studied fuel blends and their blending ratios.

Table 2. Fuel blends and their blending ratios

Fuels	Blending ratio (V-%)
LFO+RME	80:20
Kerosene+RME	80:20
MGO+RME	80:20
RME+Naphtha	80:20
LFO+Naphtha	80:20

For the selected fuel blends, several properties were determined to assess how suitable the blends are for CI engines. Below, the analysis methods of the properties are described.

The cetane number describes the ignition quality of the fuel. In Paper VI, the cetane numbers were analysed by the IQT according to Standard EN15195. In this analysis, the ignition delay, ID, is measured. The derived cetane number, DCN, is calculated based on Equation 5

$$DCN = 4.460 + 186.6 / ID \tag{5}$$

where

ID is ignition delay (ms)

(SFS EN 15195:2014).

The oxidation stability was measured with a Biodiesel Rancimat 873 instrument. The method is described in Standard EN 15751:2014. According to this standard, the maximum induction period is 48 hours (SFS-EN 15751, 2014). The OSI was not measured for the LFO + naphtha blend.

The cold flow properties were evaluated by three different methods: cloud point (according to ASTMD7689), pour point (ASTMD7346), and cold filter plugging point (CFPP) (EN116) (ASTMD7689, 2011; ASTMD7346, 2015; EN116, 2015).

The distillation curve was produced in compliance with Standard EN ISO 3405 (EN ISO 3405, 2011).

The densities and viscosities were measured with a Stabinger SVM 3000 rotational viscometer according to Standard ASTM D7042 (Anton Paar, 2012).

The flash points were measured according to Standard ASTM D93-A (ASTM D93, 2002).

The lubricity of especially neat naphtha is, most probably, excessively high (i.e., poor) for engines, and it may be assumed to cause problems in the entire engine fuel system. When using naphtha as CI engine fuel, additives or blending would be the means to reduce lubrication problems. The viscosity of neat naphtha may also be too low. Therefore, naphtha was investigated as blended particularly to avoid possible problems due to poor lubricity and low viscosity. The lubricity was measured according to Standard EN ISO 12156-1 (EN ISO 12156-1, 2016).

3.7 Method quality assurance

The results measured at UV are the arithmetic means of two replicate measurements. The analysis methods had been previously validated in the laboratory. Using validation samples, the relative standard deviations, RSD, of the analysis methods were calculated in compliance with Equations 6 and 7

$$s = \sqrt{\frac{\sum_{i}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} \qquad (6)$$

$$RSD = \frac{s}{\bar{x}} \times 100\% \qquad (7)$$

where

s is the standard deviation;

n is the number of measurements;

x_i is the measured value;

$\bar{x}$ is the mean value of all the measurements, and

RSD is the relative standard deviation

(Jaarinen & Niiranen, 2002).

The relative standard deviations were the following: ester content <1%, kinematic viscosity <1%, oxidation stability 4.5%, acid number 7.9%, density <1%, and flash point 3.0%. The detection limit for ICP OES used for analyzing metal contents was not measured. An internal standard method and blank sample were used in ICP OES analyses for quality assurance. The detection limit for ICP OES used for sulphur content analyses in Paper IV was not known but the measured concentrations were the same as the calculated concentrations.

The method for analyzing biodiesel content in Paper V was an unvalidated in-house method based on fuel density. The relative standard deviation for the density measurement was <1%.

The relative standard deviations of the analysis methods of other laboratories were not known. These analyses were cetane number, cold flow properties, distillation and lubricity for the fuels. Similarly, the relative standard deviations of all the analyses for the lubricant were unknown.

4 RESULTS

4.1 Oxidation stability improvement of AFME

In Paper I, the aim was to determine how much antioxidant is needed to improve the stability of waste animal fat based FAME. The experimental procedure showed that the lowest concentration of BioSineox antioxidant in the AFME manufacturing process was 2000 ppm in order to achieve the six-hour limit oxidation stability. For a sample prepared in the laboratory, the lowest concentration of BioSineox antioxidant was 500 ppm.

4.2 Storage stability of SME

In Paper II, the aim was to figure out how long SME can be stored in clean laboratory conditions and whether the vessel material or temperature affects the storage time. The fuel properties monitored for 12 months were ester content, kinematic viscosity, oxidation stability, acid number, and metal content (Al, Cu, Fe, Mn, Si, V, Zn). The measured results are listed in Table 3.

It can be seen in Table 3 and Fig. 1 that fresh SME fulfilled the requirements of Standard EN 14214 with regard to the properties measured in this study. No significant changes were found in samples that were stored at two different temperatures, 4°C and 20°C, and in two different storage vessel materials, plastic and steel. All other properties of all the samples fulfilled the requirements of Standard EN 14214 for the entire storage time except for the oxidation stability index, which was at the desired level (above 8 hours) only for the sample stored at 4°C in a steel can. The biggest deterioration in percentage terms, 50%, was in the acid number for SME stored in a plastic bottle at 20°C. However, the result (0.18 mg KOH/g) clearly met the requirements of Standard EN 14214. The materials of the storage vessels did not affect the quality of the fuel. Metals did not dissolve from the steel cans into the fuel as the metal contents remained close to zero level for all the samples (Table 3).

Table 3. Results measured for fresh SME and SME samples stored for 12 months

Property	SME fresh	SME, 20˚C plastic	SME, 4˚C plastic	SME, 20˚C steel	SME, 4˚C steel
Ester content (m-%)	99.5	98.6	98.5	98.9	98.9
Kinematic viscosity, 40˚C (mm^2/s)	4.1	4.1	4.1	4.1	4.1
Oxidation stability, 110˚C (hours)	9.2	6.9	7.8	7.3	8.1
Acid number (mgKOH/g)	0.12	0.18	0.16	0.17	0.15
Al (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
Cu (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
Fe (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
Mg (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
Si (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
V (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5
Zn (mg/kg)	<0.5	<0.5	<0.5	<0.5	<0.5

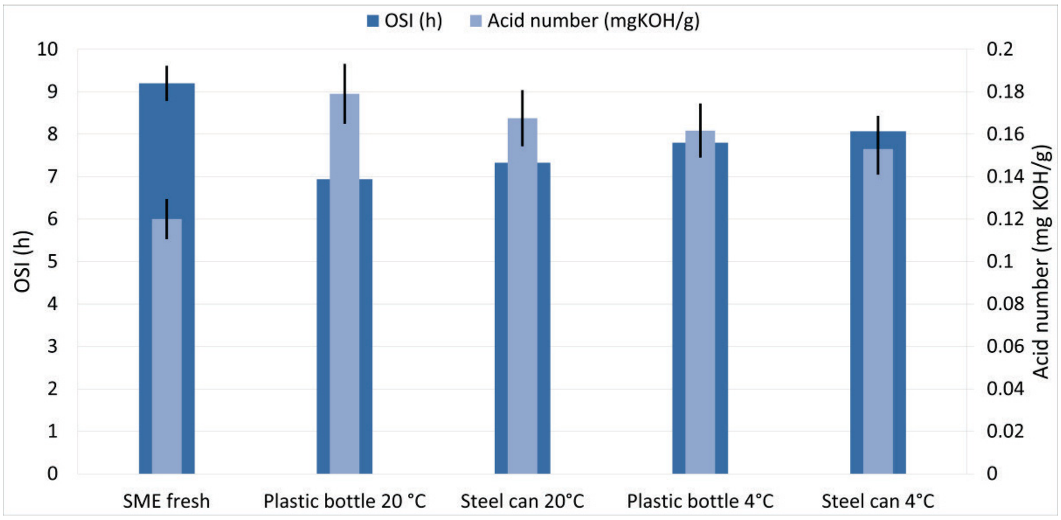

Figure 1. Oxidation stability index and acid number results of fresh SME samples and samples stored for 12 months

Fig. 1 shows that after the storage time, the sample which had the highest oxidation stability index had the lowest acid number, and the sample which had the lowest oxidation stability index had the highest acid number. Even though the differences were minor, this was to be expected. It is commonly known that an increase in oxidation causes an increase in the acid number (Yaakob et al., 2014).

4.3 Effect of sulphur content on fuel blend stability

In Paper III, the objective was to determine how the sulphur content affects the stability of the fuel blend. The results obtained for neat RME and B20 fuel blends are shown in Table 4 and Figure 2 where the low-sulphur blend is denoted by B20 (6.6 mg/kg S) and the high-sulphur one by B20 (186 mg/kg S).

The kinematic viscosity of both blend samples remained constant during the 9-week period (Fig.2). During the entire duration of the study, the viscosity of the sample B20 (6.6 mg/kg S), 3.7 mm^2/s, was higher than that of B20 (186 mg/kg S), 3.4 mm^2/s.

In fresh samples, the acid number of the sample B20 (186 mg/kg S) was higher than that of B20 (6.6 mg/kg S) (Fig. 2). The result of the sample B20 (186 mg/kg S) seemed to increase from 0.08 to 0.09 mg KOH/g. For the B20 (6.6 mg/kg S), the result seemed at first to decrease from 0.07 to 0.06 mg KOH/g but increased back to a level of 0.07 mg KOH/g after 9 weeks of storage. This phenomenon for both B20 samples probably occurred due to measurement precision.

Table 4. Analysis results for studied B20 fuels

Property	B20 (6.6 mg/kg S)	B20 (186 mg/kg S)	RME
Kinematic viscosity, 40°C (mm^2/s)			
Fresh	3.7	3.4	4.5
4 weeks	3.7	3.4	
9 weeks	3.7	3.4	
Acid number (mg KOH/g)			
Fresh	0.07	0.08	0.19
4 weeks	0.06	0.09	
9 weeks	0.07	0.09	
Oxidation stability (h)			
Fresh	36	29	9.5
4 weeks	34	29	
9 weeks	33	28	

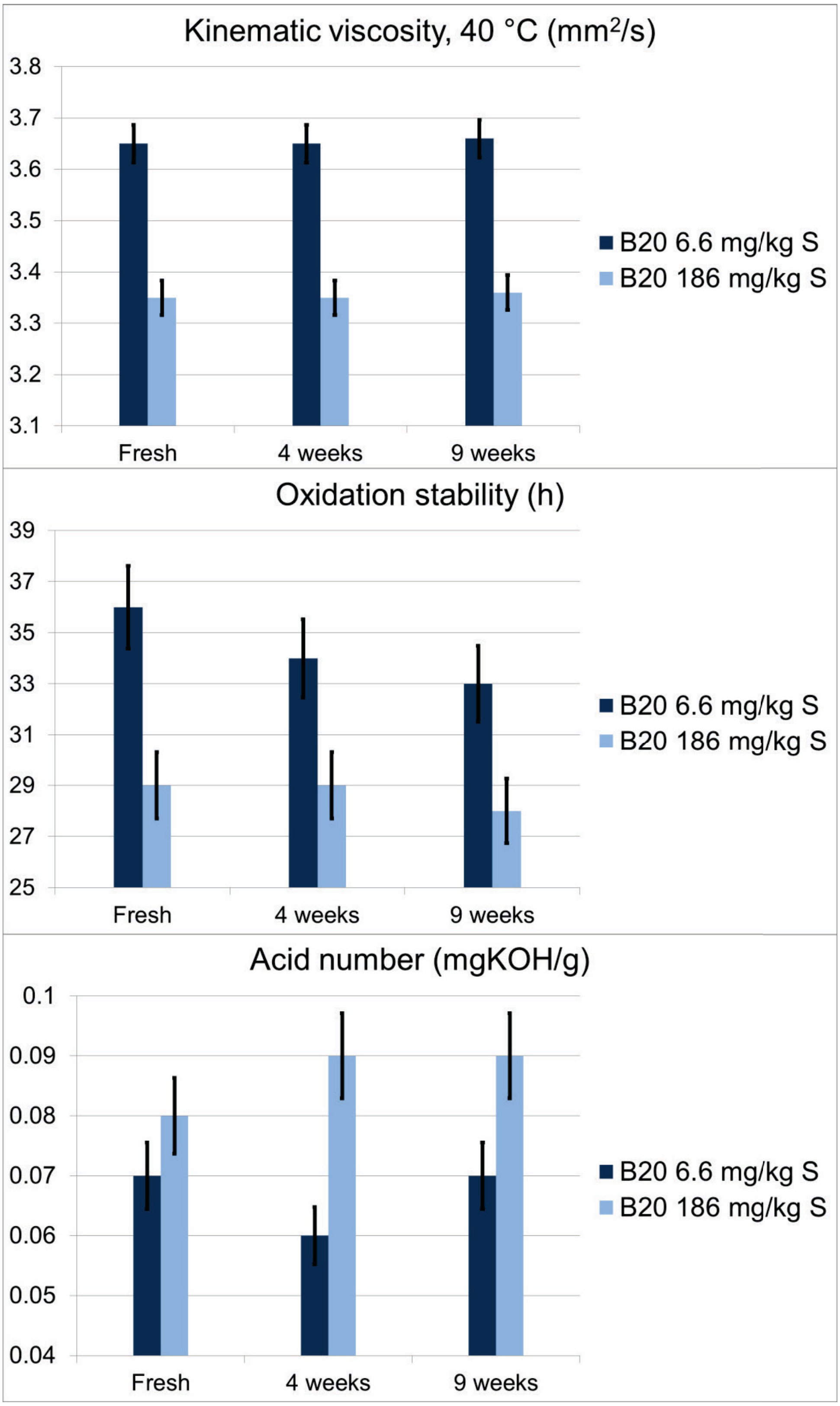

Figure 2. Kinematic viscosity, oxidation stability and acid number for fresh and stored (4 and 9 weeks) blends with different sulphur contents

Fig. 2 shows that the oxidation stability of the sample B20 (6.6 mg/kg S) (36, 34, 33 hours) was higher during the whole study than it was for the sample B20 (186 mg/kg S) (29, 29, 28 hours). However, the decrease in OSI was 8% for the sample B20 (6.6 mg/kg S) while it was only 3% for the sample B20 (186 mg/kg S). The oxidation process usually accelerates with an increase in time. In terms of the sample B20 (186 mg/kg S), the oxidation process did not accelerate. The higher S content seemed, thus, to curb the decline in OSI.

4.4 Further studies on effect of sulphur content on stability

The study of Paper IV continued to investigate how the sulphur in fuel blends affects the changes in the properties of the blends over time. The properties were now also determined for DFO (partly) and four blends, the S contents of the blends being 6, 76, 149 and 226 mg/kg, respectively. The total follow-up period lasted 12 weeks. The analysis results presented in Paper IV are shown below. The results related to storage stability are provided in Table 5. The oxidation stability, acid number and kinematic viscosity results are also depicted in Figure 3.

For the OSI results above 48 hours, the reproducibility is approximately 9.5 hours. The OSI results above 48 hours should be announced as >48 hours according to Standard EN 15751.

Fig. 3 shows how the oxidation stability of the samples changed during 12 weeks:

- B20 1, decreased 5% (from 46 to 42 h)
- B20 2, remained almost constant (varied between 47 and 48 h)
- B20 3, increased 12% (from 47 to 53 h)
- B20 4, increased 10% (from 51 to 56 hours).

As mentioned earlier, the OSI results of above 48 hours should be announced as >48 hours. In this study, the difference between the samples was so clearly seen above the range of 48 hours that the actually measured values were reported. It should also be noted that, as fresh, the greater the sulphur content, the higher the OSI value, though the increase was not linear.

Fig. 3 also shows that the acid numbers of all the samples remained within the range of 0.06-0.08 mg KOH/g during the entire study. There were no significant differences between the samples, nor did the results change during the storage. Thus, the sulphur content did not seem to affect the acid number.

Table 5. Storage stability analysis results for DFO, RME and B20 fuels

Property	DFO	RME	B20 1	B20 2	B20 3	B20 4
Oxidation stability (h)						
Fresh	72*	11	45	47	47	51
4 weeks			44	47	51	54
8 weeks			42	48	52	55
12 weeks		10	42	47	53	56
Acid number (mgKOH/g)						
Fresh		0.19	0.07	0.06	0.06	0.07
4 weeks			0.06	0.06	0.06	0.06
8 weeks			0.07	0.06	0.08	0.07
12 weeks			0.07	0.07	0.07	0.07
Kinematic viscosity, 40°C (mm^2/s)						
Fresh	3.5	4.5	3.6	3.4	3.2	3.1
4 weeks			3.6	3.4	3.2	3.1
8 weeks			3.6	3.4	3.2	3.1
12 weeks			3.7	3.4	3.2	3.1

*The measurement was stopped after 72 hours.

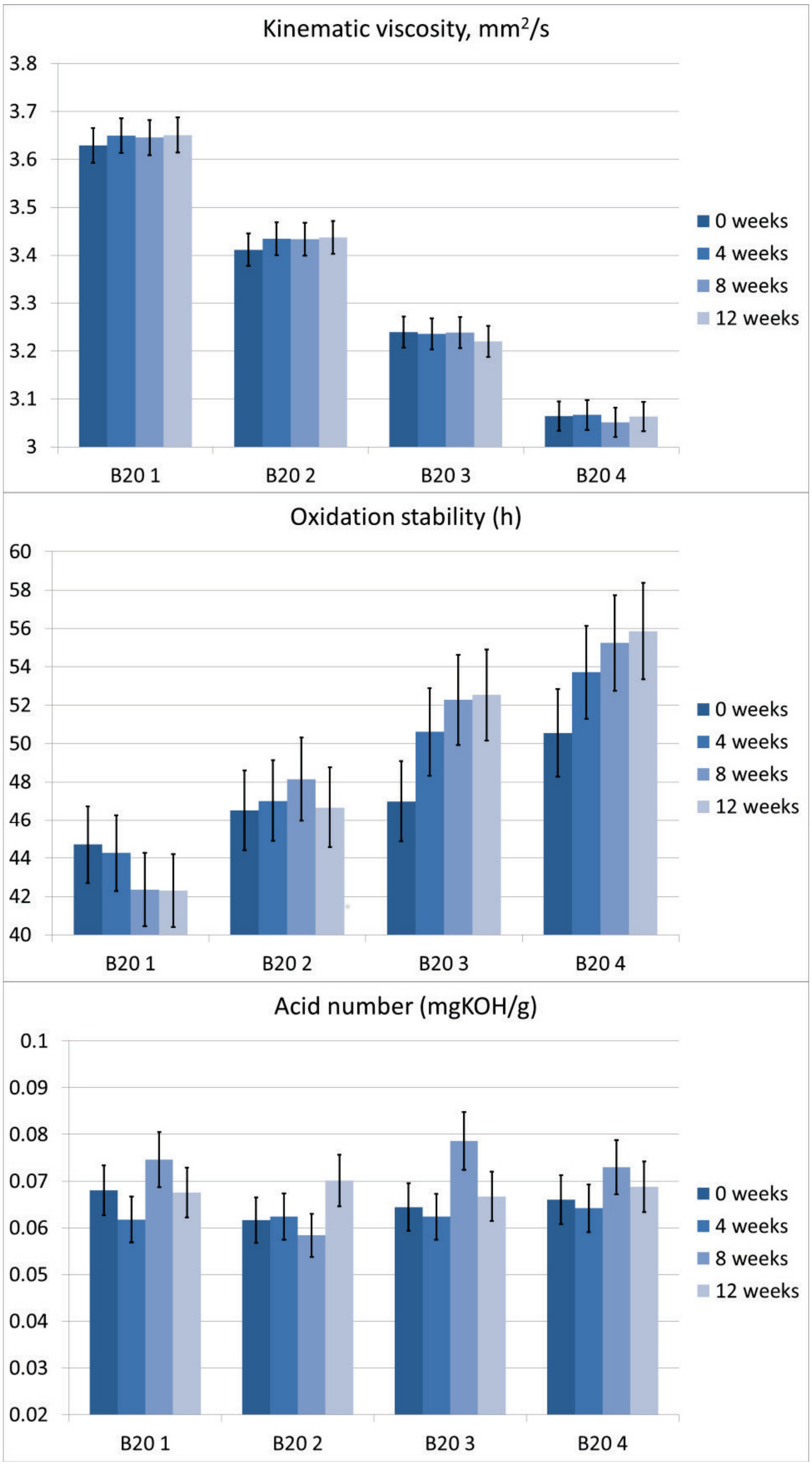

Figure 3. Kinematic viscosities, oxidation stabilities and acid numbers of blends, monitored for 12 weeks. The sulphur concentrations were 6 mg/kg (B20 1), 76 mg/kg (B20 2), 149 mg/kg (B20 3), and 226 mg/kg (B20 4), respectively.

Similarly, the kinematic viscosities remained quite constant during the storage time of 12 weeks for all the samples. The differences between the samples were due to different mixing ratios. For the samples B20 2, 3 and 4, the diesel solvent containing sulphur lowered the kinematic viscosity in relation to its mixing ratio.

4.5 Effect of B20 fuel on lubricant oil quality in long-term engine experiment

The research question in Paper V was how the B20 fuel blend affects the quality of lubricating oil in long-term engine operation. First, the results of the fuel analyses are presented in Table 6. The lubricating oil analysis results are presented in Tables 7-10 and Figures 4 and 5. The analyses were carried out in the oil analysis laboratory Fluidlab, in Turku, Finland. The properties that are known to indicate deterioration of the oil or that exhibited notable change during the endurance experiment are described in the text and presented in more detail in the figures after the tables.

The analysis results of the B20 fuel shown in Table 6 were quite typical of mixed fuel containing 20 V-% of biodiesel. Several batches of B20 fuels were prepared. The properties did not vary.

Table 6. B20 fuel specification

B20 (SME)	
Property and unit	Result
Biodiesel content (V-%)	19.1
Acid number (mg KOH/g)	0.06
Na, K (mg/kg)	2
Mg, Ca (mg/kg)	2
P (mg/kg)	1
Zn (mg/kg)	<1
Cu (mg/kg)	<1
Pb (mg/kg)	<1
OSI (h)	29

Table 7. Results of oil analyses

Property	Operating hours			
	0	207	357	553
Kinematic viscosity, 40°C (mm^2/s)	93	82	83	85
Kinematic viscosity, 100°C (mm^2/s)	14	12	12	12
Viscosity index	151	145	144	143
TBN (mg KOH/g)	10.1	9.49	9.49	8.49
TAN (mg KOH/g)	2.14	2.74	2.88	4.50
Oxidation A/cm	1	3	4	2
Nitration A/cm	0	0	0	0
Water content (ppm)	140	30	70	30
Fuel dilution (%)	1.18	0.38	<0.30	<0.30
Biodiesel content (%)	<0.30	<0.30	<0.30	<0.30
Soot content (%)	<0.1	<0.1	<0.1	<0.1

The viscosity of the lubricating oil declined slightly during the 553 engine running hours (Fig.4.). However, the decline was reasonable, being 8.6% (from 93 to 85 mm^2/s) at the measuring temperature of 40°C and 14% (from 14 to 12) at 100°C. The total base number decreased by 15.9% (from 10.1 to 8.49 mg KOH/g) but the value after 553 hours remained quite high: values from 6 to 9 mg KOH/g are at an acceptable level even for fresh engine oil (Clean Oil Services, 2015). The total acid number increased by 52% (from 2.14 to 4.50 mg KOH/g). Some references recommend changing the oil if the total acid number is over 2.50 mg KOH/g (Atlas, 2008). In this study, this limit would have been reached approximately after 200 hours. However, the starting value of the total acid number was relatively high and at the end of the experiment the remaining TBN-TAN was still about 4 mg KOH/g. It is generally accepted that the oil is usable when TBN-TAN has a positive value (Katila, 2015).

Table 8. Results of oil analyses, additives

Additives ICP (ppm)	Operating hours			
	0	207	357	553
Calcium	2108	2308	2542	2760
Magnesium	4	4	7	12
Boron	16	10	8	7
Zinc	1090	1064	1169	1240
Phosphorus	934	865	937	966
Barium	0	1	1	1
Sulphur	3259	3712	3835	3844

Table 9. Results of oil analyses, corroding metals.

Corroding metals, ICP (ppm)	Operating hours			
	0	207	357	553
Iron	1	11	17	22
Chromium	0	0	1	1
Tin	0	0	0	1
Aluminium	0	1	2	2
Nickel	0	0	0	0
Copper	0	13	49	420
Lead	0	5	5	6
Molybdenum	0	0	0	0

Table 10. Results of oil analyses, contaminants

Contaminants, ICP (ppm)	Operating hours			
	0	207	357	553
Silicon	12	34	36	35
Potassium	3	6	8	9
Sodium	0	4	10	19

The fuel dilution, FAME content and soot levels (Fig.4) remained at a relatively low level during the engine running hours. Of all the corroding wear metals, only the copper and iron contents increased, that of copper significantly. The copper content of the oil was high (420 ppm) at the end of the experiment, Fig.4. The magnesium, sodium, silica and potassium contents increased slightly during the experiment. Magnesium is an additive whereas the others are contaminants. The fuel contained small quantities of Mg, Na and K, and it can be assumed that some of the increase in these elements in the oil came from the fuel. Sulphur, calcium, zinc and phosphorus are all lubricant oil additive metals. The contents of sulphur and calcium had notably increased after 553 hours. The contents of zinc and phosphorus remained nearly constant during the experiment.

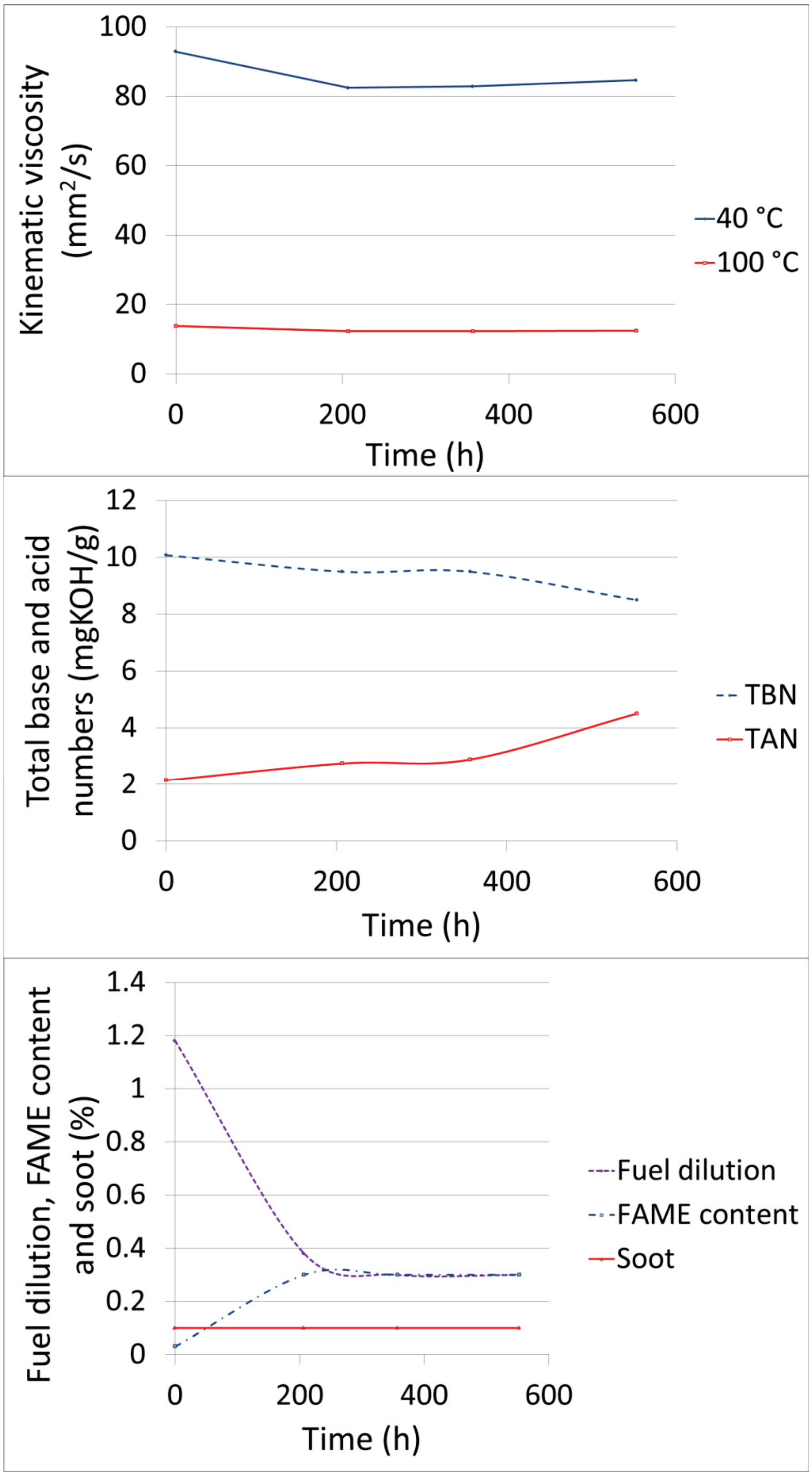

Figure 4. Results of oil analyses. Kinematic viscosities, TBN, TAN, fuel dilution, FAME content and soot as functions of time.

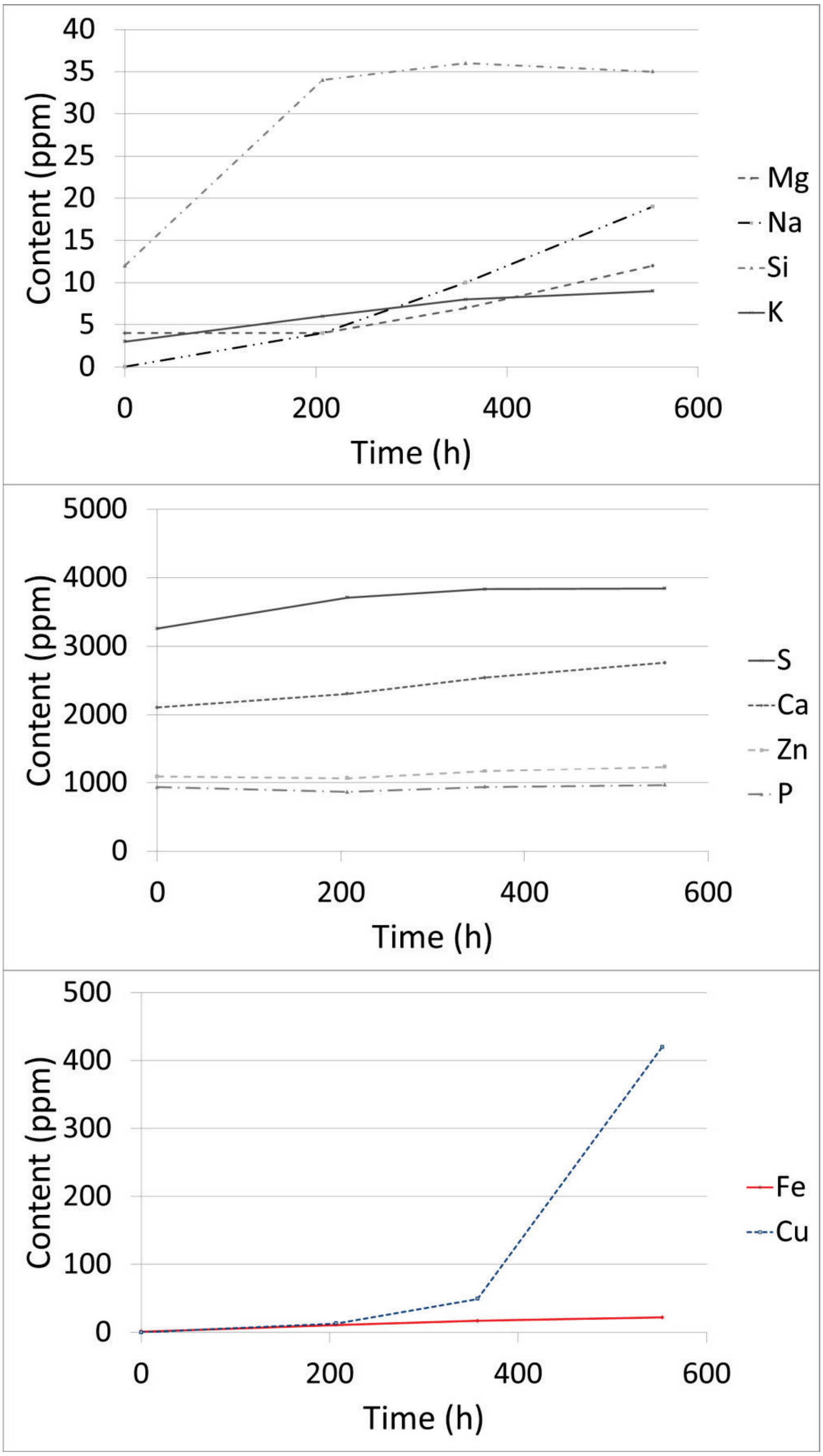

Figure 5. Results of oil analyses. Mg, Na, Si, K, S, Ca, Zn, P, Fe and Cu contents as functions of time.

4.6 Feasibility of novel fuel blends for medium-speed engine applications

In Paper VI, the aim was to determine what the properties of several renewable fuel blends are and to determine whether the blends are suitable for medium-speed engine applications.

The results of the analyses of Paper VI are presented in Table 11 and Figures 6 and 7. The information about the cold properties of naphtha was provided by the fuel supplier.

Table 11. Properties of blends, neat rapeseed methyl ester and neat naphtha

		Flash point, °C	OSI, h	Density, kg/m^3 (15°C)	Kinematic viscosity, mm^2/s (40°C)	CFPP, °C	Cloud point, °C	Pour point, °C	Cetane number	Lubricity, HFRR, µm/60 °C
Sample	Blending ratio	ASTM D93- A or C	EN 15751	ASTM D7042	ASTM D7042	EN116	ASTMD 7689	ASTMD 7346	EN 15195	ENISO 12156-1
RME+Naphtha	80:20	20	15	850	2.8	-19	-9	-18	52	174
LFO+Naphtha	80:20	20	-	805	1.4	-32	-29	-50	51	391
LFO+RME	80:20	67	42	837	2.2	-29	-21	-39	53	171
Kerosene+RME	80:20	43	69	807	1.3	-29	-30	-72	44	170
MGO+RME	80:20	125	42	853	6.8	-8	-5	-18	64	169
RME		170	13	883	4.5	-14	-5	-15	54	196
Naphtha		20	-	722	0.5	-	<-50	<-20	34	-

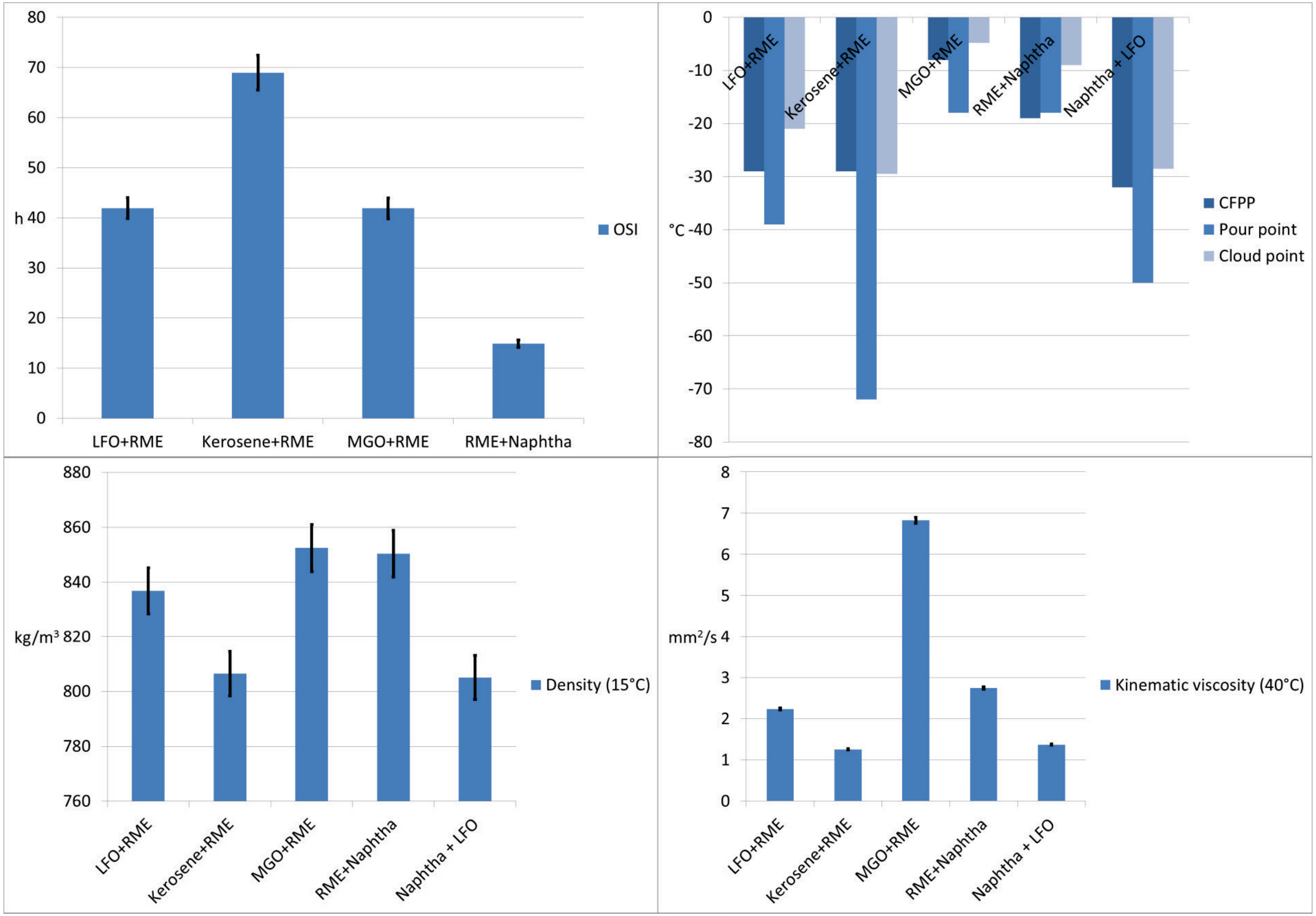

Figure 6. Analyses results of blends: oxidation stability index, cold flow properties, density and kinematic viscosity.

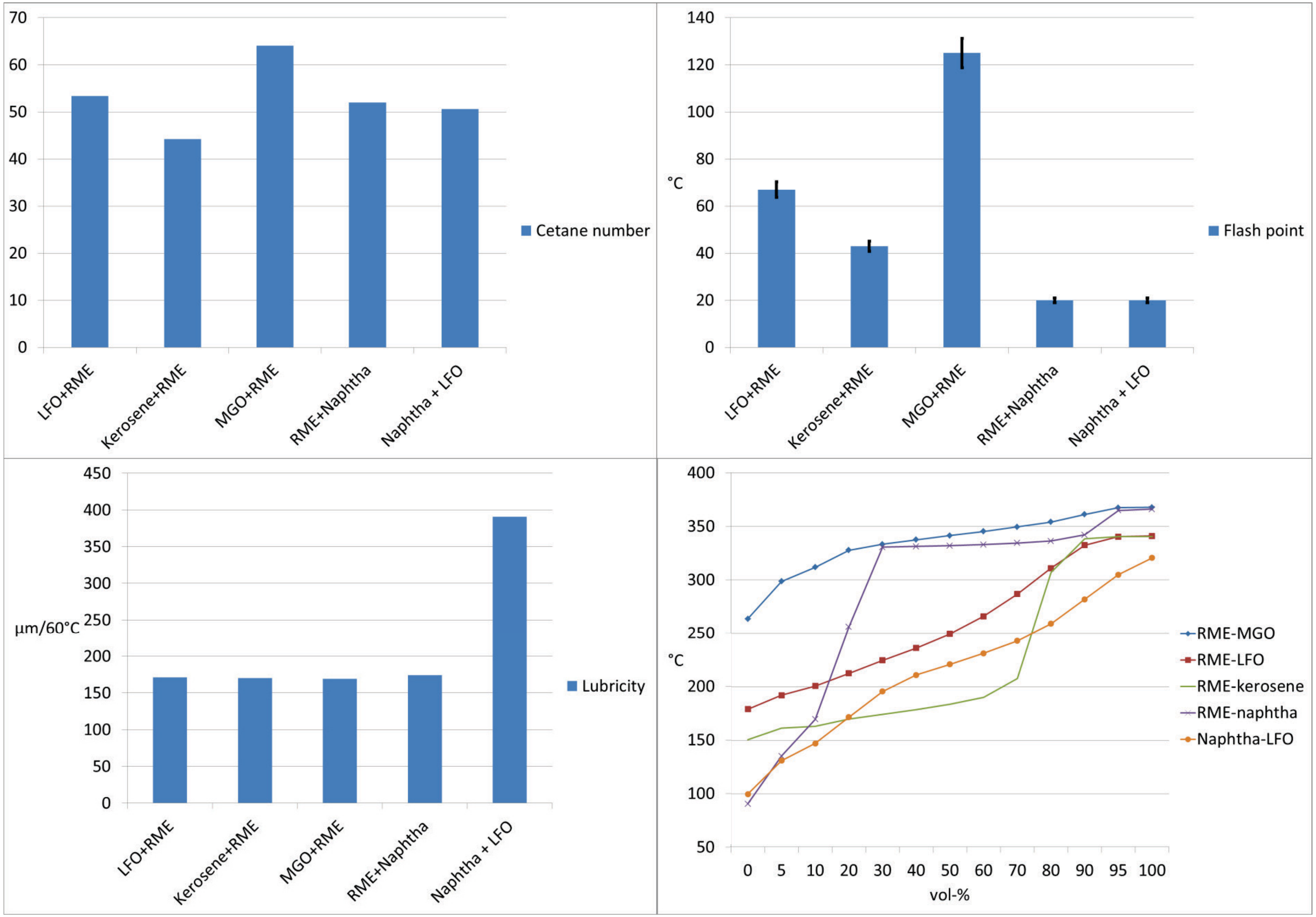

Figure 7. Analyses results of blends: cetane number, flash point, lubricity and distillation curve.

4.6.1 Blend of naphtha and RME

The distillation of the RME-naphtha blend started at below 100°C (Fig.7). For this blend, it can be clearly seen that the fractions of naphtha (20 V-%) distill first at below 350°C and the rest are heavier fractions of RME. The lubricity of neat naphtha is, most probably, excessively high (i.e., poor) for engines, and it may be assumed to cause problems in the entire engine fuel system. Still, this RME-naphtha blend exhibited good lubricity with 174 µm at 60°C. When using naphtha as CI engine fuel, additives or blending are the means to reduce lubrication problems.

While RME improved the lubricity of the blend, adding 20 V-% naphtha into the RME enhanced the cold properties (e.g. the CFPP of the blend was -19°C while it was -14°C for neat RME) and the OSI (from 13 h to 15 h) of the blend compared to neat RME. The cetane number remained quite high at 52 and the density and viscosity (850 kg/m^3 and 2.8 mm^2/s) were at an acceptable level even though the viscosity was still relatively low. However, the volatility of naphtha lowered the flash point to a value under the detection limit of the method, approximately 20°C. The safety properties of naphtha are, thus, relatively poor and its storage and distribution may require special measures. If these measures are taken, the blend of naphtha and RME is suitable for medium-speed engines.

4.6.2 Blend of naphtha and LFO

The distillation of the LFO-naphtha blend started at below 100°C (Fig.7). The curve for naphtha-LFO is more even than it is for naphtha-RME, most probably due to the lighter fractions of LFO compared to fractions of RME. Despite the poor lubricity of neat naphtha, the lubricity of this blend was at an acceptable level with 391 µm/60°C. The cold properties of the LFO-naphtha sample were good with a CFPP of -32°C, the lowest of all the samples measured. The OSI was not measured for this sample. The cetane number remained quite high at 51 and the density and viscosity (805 kg/m^3 and 1.4 mm^2/s) were relatively low. This may cause power losses, if the engine has volume-based fuel flow control, and leakages in the injection system. Similarly to the other naphtha blend, another frailty of this fuel was its low flash point (20°C) and its storage and distribution may require special measures. Despite its frailties, the blend of naphtha and LFO seems to be feasible in medium-speed engines.

4.6.3 Blend of MGO and RME

The blend of MGO and RME started to distill at the relatively high temperature of 264°C (Fig.7). The distillation ended at 368°C. This blend showed good lubricity with 169 µm at 60°C. The cold properties of the MGO-RME sample were rather poor; its CFPP was -8°C which was the highest of all the samples measured. The OSI was, instead, at a decent level with 42 hours. The blend also exhibited a high cetane number, 64. The density was 853 kg/m^3 and viscosity 6.8 mm^2/s. The density was at a decent level, as the marine standard sets a maximum limit of 890 kg/m^3 for the lightest MGO quality but according to the standard, the viscosity should not exceed 6.0 mm^2/s. The MGO-RME blend seems to be safe to handle as its flash point was as high as 125°C. According to these results, the blend of MGO and RME is usable in medium-speed engines.

4.6.4 Blend of kerosene and RME

The blend of kerosene and RME started to distill at a rather low temperature, 150°C, and the end point was at 201°C (Fig.7). The lubricity of this blend was 170 µm/60°C. The blend's cold properties were, however, relatively favourable even for northern areas since its CFPP was -29°C. The blend also exhibited relatively good oxidation stability as the OSI result was 69 hours, or clearly above the highest detection value (48 hours) set in Standard EN 15751. The kerosene contained 0.1 m-% (1000 ppm) of sulphur, which may enhance its oxidation stability. This phenomenon is described in the results sections of Papers III and IV. The cetane number was the lowest of all the blends, being 44. The density was 807 kg/m^3 and viscosity 1.3 mm^2/s. The flash point was rather low, 43°C.

These measured properties were quite typical of neat kerosene even though the blend also contained RME. The blend of kerosene and RME is suitable while not optimal for medium-speed engines. For CI engine applications, the challenging properties of the kerosene-RME blend are its flash point, density, viscosity and cetane number.

4.6.5 Blend of LFO and RME

The distillation of the LFO-RME sample started at 179°C (Fig.5). The curve rose evenly, and the distillation ended at 341°C. The lubricity of FAME blends is usually at a decent level, which was the case also in this study, with 171 µm/60°C. The cold properties were at an acceptable level, e.g., the CFPP was -29°C. The oxidation stability index, which often hampers the commercialization of FAMEs and their blends, was at a good level with 42 hours. The cetane number (53) was appropriate. The density was 837 kg/m^3 and viscosity 2.2 mm^2/s. The rather high flash point (67°C) indicated that the fuel is safe to use. The blend of LFO and RME is suitable for medium-speed engines. The properties of the LFO-RME blend fulfilled all the requirements set in Standard EN 590, which is the diesel standard for automotive applications.

5 DISCUSSION

The research question in Paper I was how much antioxidant is needed to improve the stability of waste animal fat based FAME or AFME (RQ 1). Based on the experiments, the answer was 2000 ppm. The amount of needed antioxidant in laboratory conditions was 500 ppm but further analyses indicated that in the manufacturing process, the needed amount would be much higher, 2000 ppm. The main antioxidants are phenolic compounds (Fattah et al., 2014; Verma et al., 2015), which was also the case in Paper I. The major compounds in this antioxidant were MTBHQ (mono t-butyl hydroquinone) and DTBHQ (2,5-di-tert-butylhydroquinone). However, Chen & Luo have reported that hydroquinones have not proven to be the most efficient antioxidants for biodiesel synthesized from free fatty acids (Chen & Luo, 2011).

The fatty acid composition of the studied AFME was measured in later studies although it was not published in Paper I. The sample was different but the biodiesel was manufactured by the same manufacturer using the same raw material. The content of oleic acid (18:1 cis) was 48%, that of linoleic acid (18:2 n-6 cis) 9.7%, and that of linolenic acid (18:3 n-3 cis) 1.2%. These are the most common unsaturated acids present in oils or fats and consequently in biodiesel. The oxidation stability of biodiesel decreases with an increasing unsaturation level in the fatty acid chain. (Yaakob et al. 2014; Shahabuddin et al. 2012) The total content of unsaturated acids in AFME was 71.2%, which was relatively high. Compared to one studied rapeseed methyl ester, which had a content of unsaturated acids of 92.6%, it was lower, however. Probably both the rather high unsaturation level and the inefficient antioxidant led to a high required concentration of antioxidant.

Optimizing the antioxidant concentration in the manner described is fairly suitable if the biodiesel producer is able to expend resources on several Rancimat measurements. Currently, there is also available another method, PetroOxy, for analysing the oxidation stability of biodiesel and their blends. What needs to be taken into account is that samples prepared in the laboratory are easier to handle and give more positive analysis results than samples taken from the real process. This was also noticed in this study, as it first seemed that smaller amounts of antioxidants were needed than what the final result actually proved necessary. In Paper I, the studied AFME is a moderate option for engine applications. There are no published results related to the stability of this AFME fuel on record. It is a locally produced fuel, which is an advantage in terms of decentralized energy production as well as energy autonomy. The quality constraints, mainly concerning oxidation stability, are well known and equally true for AFME fuel as for other biodiesels. Additives are needed to improve the oxidation stability of biodiesels and need to be studied individually for each biodiesel raw material to find the optimal antioxidant and its concentration.

In Paper II, the research questions were how long SME can be stored in clean laboratory conditions (RQ 2) and whether the vessel material (steel or high-density plastic) or the temperature (4 or 20°C) affects the storage time of SME (RQ 3). SME was stored in four different conditions. The results were promising, and the answer to the second research question is that the fuels maintained their quality during the 12 months of storage. Real-life storage conditions may not be as clean as they were for the laboratory samples. Still, based on the results of this study, biodiesels should be stored at a lower than 20°C temperature. As vessel materials, steel and high-density plastic are suitable for storing biodiesel when the relative air humidity is low and no water is present. To answer the third research question, it can be said that the temperature and material had no effect on the fuel quality. The results obtained in Paper II were also promising in that chemically, the biodiesels were not particularly reactive. Some oxidation reactions occurred as the oxidation stabilities of all the samples decreased. The effect of the reversible transesterification reaction was not significant. The most notable decrease in ester content was from 99.5 m-% to 98.5 m-% (plastic vessel, at 4°C) which is still clearly above the minimum limit (96.5 m-%) set in the automotive standard for biodiesels. The transesterification process is well known to be reversible (Pullen & Saeed, 2015). In the studied conditions, no significant reversion occurred, neither did any oxidation reaction, i.e., the chemistry of biodiesels may be stable for some time. The storage stability in terms of oxidation has been studied widely but there are no other results on record about storage stability research based on ester content. In real life storage the reasons for impaired quality are related to storage conditions, such as high temperature and sunlight. The oxidation reaction is faster when storage temperatures are high. (Fu et al., 2017) The tendency of biodiesels to oxidize is strong but proper conditions may enable the fuel to preserve properly.

The effect of sulphur on the storage stability of the fuel blends was studied in Papers III and IV, the research question being whether the sulphur content affects fuel blend stability (RQ 4). The answer to this question is that an increasing concentration of sulphur enhances the oxidation stability of fuel blends. In Paper III, one sample was prepared from Brazilian high-sulphur DFO and RME. Another sample was prepared from very clean low-sulphur DFO containing no additives and no RME. The high-sulphur fuel blend retained its stability better than the low-sulphur blend. Still, the first measurement results presented in Paper III were suggestive as the compositions of the DFOs used for the samples were not analysed. The DFOs had been produced on different continents and most probably from different kinds of crude oil. This most likely had effects on the fuel quality and the difference in the composition had an unknown effect on the results. Kalitchin et al. (1992) stated that sulphuric compounds at a concentration of 900-3600 ppm reduce the formation of carboxylic acids in fossil diesel fuels (Kalitchin et al., 1992). The amount of sulphur in Brazilian fuel was significantly lower than that (186 ppm) but sulphur content may still explain the results discussed in Paper III. The study of Paper III led to a more detailed study in Paper IV. In Paper IV, the research plan was designed more carefully to properly represent the phenomenon. The DFO in all the samples was the same but the amount of high-sulphur diesel solvent varied. Nevertheless, the research plan was successful and the results stated the same as in Paper III. However, explaining how sulphur works as stabilizer would require more research work and detailed analyses of the chemical structure of these fuels.

On record, there are no other studies on the effects of sulphur as detailed as this one. That said, Karavalakis et al. (2010) have studied the stability of diesel-biodiesel blends. They state that higher refining to lower sulphur content in the fossil diesel decreases the oxidation stability of the final blend with biodiesel. Their result was parallel to the result of the Paper IV study. It might be that the composition and oxidation stability of the fossil component plays a greater role in the stability of the blend than the biocomponent. The issue is, however, still contradictory. The amount of sulphur should be decreased in all kinds of fuels and diverse measures are being taken to reach the target of reducing sulphur emissions (Lahtinen, 2016; Cuff, 2016). Nevertheless, if renewable fuel use is to be increased through biodiesel blending and the only option is high-sulphur fossil fuel, sulphur is indeed beneficial for the blend’s stability as is blending for the environment.

In Paper V, the research question concerned the effects B20 fuel has on the quality of lubricating oil in long-term engine operation (RQ 5). The experiment was a long-term engine endurance experiment. Apparently, as an answer to the fifth research question, it can be stated that although biodiesels and their blends may cause many kinds of problems such as lubricating oil dilution, a high-technology engine will safely tolerate B20 fuels in terms of lubricant quality. An oil sample was taken four times during the experiment. What needs to be taken account is that although the lubricant system is not threatened of B20 blend, B20 is not recommended to use with state-of-the-art heavy-duty engines. The most of the catalyzing after treatment systems used together with diesel engines does not fully work together with B20 fuels (Coda Zabetta, et al. 2006; He, 2016; Schobing et al., 2018).

In Paper VI, several fuel blends for medium-speed engines were studied. The blends studied here were pioneering. There are no other published studies on either a renewable naphtha and RME blend nor a naphtha and LFO blend. The objective was to answer research questions concerning the properties of the blend of renewable naphtha and RME, and whether the blend is suitable for medium-speed engine applications (RQ 6), what properties a blend consisting of circular economy product MGO and RME has, and whether it is suitable for medium-speed engine applications (RQ 7). Based on the results, both blends can be used as alternative fuels. In terms of the measured properties, these blends may be feasible in marine, power plant and off-road applications when the targeted 27% share of renewable fuels of total energy consumption must be reached. The sixth research question was about the naphtha and RME blend which was an interesting addition to the biofuel genre as it was 100% renewable. RME had a positive effect on the viscosity of naphtha, as the viscosity of neat naphtha was 0.5 mm^2/s whereas for this blend it was 2.8 mm^2/s. RME also raised the lubricity to an acceptable level.

For both naphtha blends, naphtha-RME and naphtha-LFO, which was also studied, the cold properties of neat biodiesel and LFO were enhanced when naphtha was added. The cetane number of neat naphtha was only 34, but for both naphtha blends, the cetane number was above 50. These blends have really low flash points, which requires safe storage and usage.

As an answer to the seventh research question, the MGO-RME blend appeared to be a beneficial option as a marine fuel in large regions globally apart from arctic areas. In arctic regions, the limited cold properties may restrict the usability of the blend. MGO is a high-quality fuel for reducing sulphur emissions in ships. The studied circular economy MGO contained less than 100 ppm of sulphur. For the sake of comparison, the heavy fuel oil in Finland is allowed to have a maximum sulphur content of 1.00 m-% which is equal to 10 000 ppm (Finlex 413/2014, 2014). Adding non-sulphur RME to MGO decreases the blend's sulphur content even further. Moreover, used lubricating oil is a reasonable raw material for marine fuel.

The RME-kerosene blend, which was also studied, exhibited extremely good oxidation stability. Accordingly, kerosene could perhaps be used to enhance the oxidation stability of FAMEs. This should, however, be studied in more detail. The neat kerosene contained 1000 ppm of sulphur. Based on the blending ratio, the sulphur content of the blend was approximately 800 ppm. According to the results obtained in Papers III and IV, the high sulphur content may have improved the oxidation stability of the kerosene-RME blend.

Regarding alternative fuels, the diversity constitutes a complication. When the properties of the renewable blending components are known, some conclusions of the blend properties can be drawn. When the fuels are new and have previously not been studied, there is a need for a detailed study of certain properties to estimate their suitability for CI engines. In this study, RME could not be considered a new fuel, nor could the RME-LFO blend. The kerosene-RME blend had also been studied before (Bayındır et al., 2017) as had neat waste-oil based marine diesel (Gabiña et al., 2016; Wang & Ni, 2017) but the results concerning naphtha and MGO blends were pioneering. Thus, the results of the study of Paper VI create valuable fundamental new knowledge and knowhow even for engine research and development.

Blending new renewable fuels with more conventional ones facilitates the technical transitional period as long as the availability of renewable fuels is limited. The fuel blending and decisions on which fuels are to be used need to be case-specific. The main parameters are in which application the fuel is used and what the fuel options for blending are. That is why all information about different blends and their properties is important. The diversity of alternative fuels is great and makes engine development demanding but there are also several straightforward options for medium-speed engine fuels.

6 CONCLUSIONS

According to the results obtained from the studies of Papers I-VI, the following conclusions can be drawn:

1) High amounts of antioxidants, in this case 2000 ppm, are needed to sufficiently enhance the stability of fatty acid methyl esters.

2) In clean laboratory conditions, the chemistry of fatty acid methyl esters may remain constant for one year. The reversion of the transesterification reaction is of minor significance in proper storage conditions.

3) Biodiesel should be stored at temperatures between 4 and 20°C to ensure stability. Steel and high-density plastic are suitable vessel materials when no visible water is present.

4) If fatty acid methyl ester and high-sulphur fossil light fuel oil are blended to increase the use of renewable fuels, environmental advantages are achieved by a reduced fuel sulphur content.

5) Sulphur improves the storage stability of the blend of fatty acid methyl ester and fossil diesel fuel.

6) In a state-of-the-art off-road diesel engine, a high-content fatty acid methyl ester blend of B20 did not cause any problems in terms of lubricating oil quality during 500 hours of engine operation.

7) The blend of renewable naphtha and RME forms a completely novel 100% renewable fuel option for all kinds of CI engines.

8) Blending renewable naphtha with RME enhances the cold properties and oxidation stability of the RME and the cetane number and kinematic viscosity of the naphtha.

9) The blend of the circular economy product MGO and RME is a beneficial and sustainable marine fuel option. It exhibits a high cetane number and good lubricity. It is also safe to use since it has a high flash point.

10) For arctic areas, the cold properties of the blend of MGO and RME must be improved.

11) Kerosene blended with RME significantly enhances the oxidation stability and cold properties of RME.

12) The fuel blending and decisions on which fuels should be used are case-specific; factors affecting the decision are, e.g., application where the fuel is used, fuel blendability, effects of fuel on the blend, and fuel availability.

13) The diversity of alternative fuels complicates engine development but there are several feasible fuel options for medium-speed engines. Blending new fuels with conventional ones facilitates the technical transitional period.

The limited availability of some of these fuels may restrict their use in marine and power plant applications, which merely emphasizes the importance of various novel fuel blends. At the same time, engines must be developed to enable the use of said sustainable blends. In the near future, additional results should be obtained concerning the combustion behaviour of all kinds of blends. Forthcoming studies should include ignition research and more detailed injection studies, particularly for low-viscosity fuels such as those containing naphtha and kerosene.

7 SUMMARY

This dissertation concentrates on phenomena and properties related to liquid alternative fuels used for power generation in power plants and in marine and non-road engine applications. The properties of the alternative fuels were comprehensively examined within six research studies. The aims of the dissertation were to further the knowledge about the storage stability of the fuels and to produce novel scientific information about the properties, usage and compatibility of different new fuel blends. The various fuels and their blends were assessed based on how suitable they would be for different compression-ignited engine applications.

The scientific theory for the research was collected during several years. Each paper was based on its own research plan and approach in the fuel laboratory. Each laboratory study was planned and carried out separately. Papers III and IV form the only exception since the latter was implemented to improve the conclusions of Paper III. Several laboratory instruments and standardized methods were used for obtaining the fuel analysis results.

The results showed, first, that a high concentration of additives, such as antioxidants, is needed to enhance the oxidation stability of animal fat based methyl ester. The additive concentration must also be determined based on fuel samples directly from the production process. In laboratory conditions, favourable stability was already achieved with clearly lower additive quantities.

Second, storage conditions play an important role in fuel stability. In proper conditions, biodiesel can be stored for one year. The chemistry of fatty acid methyl esters may remain constant for that time and the reversion of the transesterification reaction is of minor significance. Both steel and plastic vessels are suitable for long-term storage, but the fuel temperature should be kept low enough, at below 20°C if possible, and the vessels must be protected against sunlight.

Fuel blending is beneficial for both blend stability and the environment in case the only option for the fossil blending component is high-sulphur fuel. Sulphur improves the stability of the blend considerably, and the use of a renewable blend component reduces the engine sulphur emissions.

When a fatty acid methyl ester blend is used as fuel, the lubricating oil quality remains at an acceptable level for a long period in a high-technology engine. No notable deterioration of the lubricant was observed during an endurance test of more than 500 hours when B20 fuel was used in a low-emission non-road diesel engine.

FAMEs are the most studied group of renewable alternative fuels but there are several other appropriate renewable options available even for medium-speed engines. In this dissertation, renewable naphtha, circular economy based marine gas oil and fossil kerosene were also studied and evaluated along with renewable RME and fossil low-sulphur LFO. Different blends of these fuels were also prepared and investigated. Of these blends, the naphtha-RME one was 100% renewable.

In the blend, the renewable naphtha improved those properties of RME that are poor, namely oxidation stability and cold properties. Correspondingly, RME increased the blend viscosity and lubricity to an acceptable level. The MGO-RME blend appeared to be a beneficial option as a marine fuel in large regions globally apart from arctic areas where its limited cold properties may restrict its usability. Adding non-sulphur RME to moderate-sulphur MGO decreases the blend's sulphur content, which is desirable in maritime fuels.

The fuel blending and decisions on which fuels should be used are case-specific and depend on in which application the fuel is used and what the fuel options for blending are. That is why all the information about different blends and their properties is extremely important. The diversity of alternative fuels is demanding for engine development work but there are several feasible and straightforward options for medium-speed and other CI engine fuels. The mere blending of new renewable fuels with conventional ones facilitates the technical transitional period as long as the availability of renewable fuels is limited.

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Publications

This doctoral dissertation consists of a summary of the following six publications, which are referred to in the text by their numerals:

I. Sirviö, Katriina; Niemi, Seppo; Vauhkonen, Ville; Hiltunen, Erkki. 2014. Antioxidant studies for animal-based fat methyl ester. Agronomy Research, issue 2, pages 407-416. ISSN: 1406-894X.

II. Sirviö, Katriina; Niemi, Seppo; Hiltunen, Erkki. 2015. Storage stability studies with commercially available soy bean methyl ester. EUBCE 2015. 23rd European Biomass Conference & Exhibition Proceedings, pages 1305 – 1308. ISSN: 2282-5819. ISBN: 978-88-89407-516. doi: 10.5071/23rdEUBCE2015-3DV.2.7

III. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Hiltunen, Erkki. 2016. The effect of sulphur content on B20 fuel stability. Agronomy Research, issue 1, pages 244-250. ISSN: 1406-894X.

IV. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Hiltunen, Erkki. 2017. Effects of sulphur on the storage stability of the bio and fossil fuel blends. Agronomy Research, issue Special Issue 1, pages 1232-1241. ISSN: 1406-894X.

V. Sirviö, Katriina; Niemi, Seppo; Katila, Tapani; Ovaska, Teemu; Nilsson, Olav; Hiltunen, Erkki. 2016. B20 fuel effects on engine lubricating oil properties. CIMAC Congress 2016. CIMAC Congress paper number 025.

VI. Sirviö, Katriina; Niemi, Seppo; Heikkilä, Sonja; Kiijärvi, Jukka; Hissa, Michaela; Hiltunen, Erkki. 2018. Feasibility of new liquid fuel blends for medium-speed engines. *Article submitted to Fuel. Under revision.*

Author’s contribution

Paper I: Sirviö is the main author. Sirviö designed the study and implemented the laboratory analyses. Sirviö wrote the paper together with Niemi. Vauhkonen and Hiltunen provided comments on the paper.

Paper II: Sirviö is the main author. Sirviö proposed the research topic and designed laboratory experiments. She wrote the paper together with Niemi. Hiltunen provided comments on the paper.

Paper III: Sirviö is the main author. Sirviö designed the study, implemented the laboratory analyses and wrote the paper together with Niemi. Heikkilä and Hiltunen provided comments on the paper.

Paper IV: Sirviö is the main author. Sirviö proposed the research topic and designed the study. Sirviö and Heikkilä implemented the laboratory analyses. Sirviö and Niemi wrote the paper. Hiltunen provided comments on the paper.

Paper V: Sirviö is the main author. The research was implemented within a wider context of engine experiments designed by Katila and Niemi. Nilsson, Ovaska and Sirviö implemented the engine experiments. Sirviö, Niemi and Katila wrote the paper. Hiltunen provided comments on the paper.

Paper VI: Sirviö is the main author. Sirviö proposed the research topic and designed the study together with Niemi. Sirviö and Heikkilä implemented the laboratory analyses. Hissa assisted with the procurement of the studied fuels. Sirviö, Niemi and Heikkilä wrote the paper. Kiijärvi answered for the layout of the paper and Hiltunen provided comments on the paper.

Contents

Publication I

Antioxidant Studies for Animal-Based Fat Methyl Ester

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Abstract. The aim of this study was to test an antioxidant, BioSineox, for animal-based fat methyl ester, AFME, in order to determine the optimal concentration of this antioxidant for meeting the six-hour oxidation stability requirement as set in the EN 14214:2010 standard. Oxidation stability was measured using a Biodiesel Rancimat 873, which meets the requirements of the EN 14112 standard. The variety of raw materials used in the production of methyl esters, i.e. biodiesels, renders a variety of fatty acid profiles. Consequently, the reaction of biodiesels with various antioxidants must be individually tested for each combination. Before the antioxidant is added during the manufacturing process, it must be tested in laboratory conditions. As the main result of this study it can be stated that the process requires a relatively high (2000 ppm) BioSineox concentration in order for the biodiesel to meet the six-hour oxidation stability requirement. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum. To reach this target, the concentration of the antioxidant must be further increased.

Keywords: Antioxidant, biodiesel, methyl ester, oxidation stability, Rancimat.

Introduction

The interest in biofuels as engine fuels is increasing in both developing and industrialized countries. The trend covers many engine applications from transport to agricultural mechanization and electricity production. The growing interest in biofuels correlates to increasing energy consumption, a decline in crude oil resources and hence the obligation to replace fossil fuel products, the obligation to reduce greenhouse gas (GHG) emissions, and the desire to improve energy self-sufficiency by utilizing waste-derived feedstock in distributed energy production – often managed by minor local companies (Sidibé et al, 2010).

Accordingly, in the year 2007 the EU set an ambitious target for increasing the use of renewable energy sources to 20 % of the total energy consumption, as well as for increasing the energy efficiency to 20 % in comparison with the baseline scenario under development in the EU by 2020. Also, the share of biofuels in transportation shall be increased to 10 % (The EU Climate and Energy Package, 2011). In 2014, the EU's framework 2030 presents even more ambitious targets; the greenhouse gas emissions should be decreased 40 % below the 1990 level and the renewable energy consumption should increase up to 27 % of the total energy consumption by 2030 (The European Commission, 2014).

To achieve this target, even smaller-scale production of biofuels requires further attention and development. Biodiesels produced from oils and fats through the transesterification reaction with alcohol is one of the smaller-scale alternatives needed on a national level to maximize overall energy production and efficiency. The optimal raw material for the production of biodiesel is waste or non-edible oil.

In Finland, biodiesel production is focused on certain raw materials, such as rapeseed oil, animal fat and spent edible frying oil. In particular, increasing attention has been placed on the manufacture of waste-derived fuels in order not to compete with food production when promoting biofuel launching.

In the Ostrobothnia region of Finland, in the surroundings of the city of Vaasa, animal fat containing waste is widely used as feedstock for biofuels. The production of animal-based fat methyl ester, AFME, studied in the current project, does not compete with food production. Much to the contrary, the utilization of waste feedstock for fuels reduces environmental loading, since the uncontrolled decomposition of wastes in landfills is avoided (Lagus, 2010). According to Cooper (Cooper, 2010) the CO_2 production per megajoule is very low for waste animal oil biodiesel.

In many respects, biodiesel is similar to fossil diesel fuel, which poses a great advantage. Its potential as an alternative fuel for compression ignition engines is significant. The production and processing of biodiesel is, however, not always sufficiently controlled, and thus the fuel's chemical and physical properties may vary depending on the adopted feedstock and thermal parameters, as well as on the chemical components applied to develop the final product. The various processes involving oils and fats produce fuels with varying compositions and properties (Knothe, 2010; Varde & Veeramachineni, 2011).

In order to replace fossil fuel consumption by biodiesel, the latter must be of good quality and meet the requirements set in the EN 14214 standard. The oxidation stability limit has proven to be one of the most difficult requirements to fulfill and is thus an obstacle for the widespread commercialization of biodiesels. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum.

Several studies have indicated that even the six-hour oxidation stability could not be reached without the addition of an antioxidant (Chen et al, 2011; Karavalakis et al, 2011; Vauhkonen et al, 2011). The increase of the six-hour requirement to a minimum of eight hours aims to ensure the usability of biodiesel as a blending component in fossil diesel grades, a part of paraffinic diesel fuels, as well as pure diesel fuel even after prolonged storage times (AGQM, 2010; AGQM 2011).

Resulting from the wide variety of biofuel origins and manufacturing processes, the properties and suitability of each fuel have to be studied individually. The paucity of data on animal fat based fuels also calls for examining such new fuel options that may be of importance in promoting distributed energy production and self-sufficiency of farms, local communities, and factories.

In this study, the oxidation stability of AFME was determined in dependence on antioxidant concentration. Several measurements were conducted. The main targets were to further the work of a local biodiesel producer and to gather additional general information about biodiesel antioxidants. Antioxidant concentrations are usually relatively high which increases the overall costs of biodiesel production. Testing several antioxidants aims at finding an antioxidant that would improve oxidation stability to the desired level in the smallest possible concentration. The results presented in this paper were measured in the end of the year 2011 and in the beginning of 2012. At the time, the desirable oxidation stability level for biodiesel was still 6 hours and it was therefore used as the target when the optimum antioxidant concentration was determined.

Material and methods

Samples

The examined animal-based fat methyl ester was produced by Feora Ltd in Nykarleby, Finland. Feora Ltd is a Finnish animal feed company that commenced biodiesel production in 2010. Feora produces ester-type biodiesel using a two-stage process that combines acid-catalyzed esterification and alkali-based transesterification. The product is mainly used as heating fuel and as fuel in non-road engines (Bengts, 2010).

Antioxidants

The tested antioxidant was BioSineox™ Liquid, a product of Antioxidant Aromas and Fine Chemicals Ltd, KZN, South Africa. It is a synergistic blend of hindered phenolic compounds with a chemical name of mixed butylated hydroquinones (Fig. 1). The major components are MTBHQ (mono t-butyl hydroquinone) and DTBHQ (2.5-di-tert-butylhydroquinone) (AAFC, 2009).

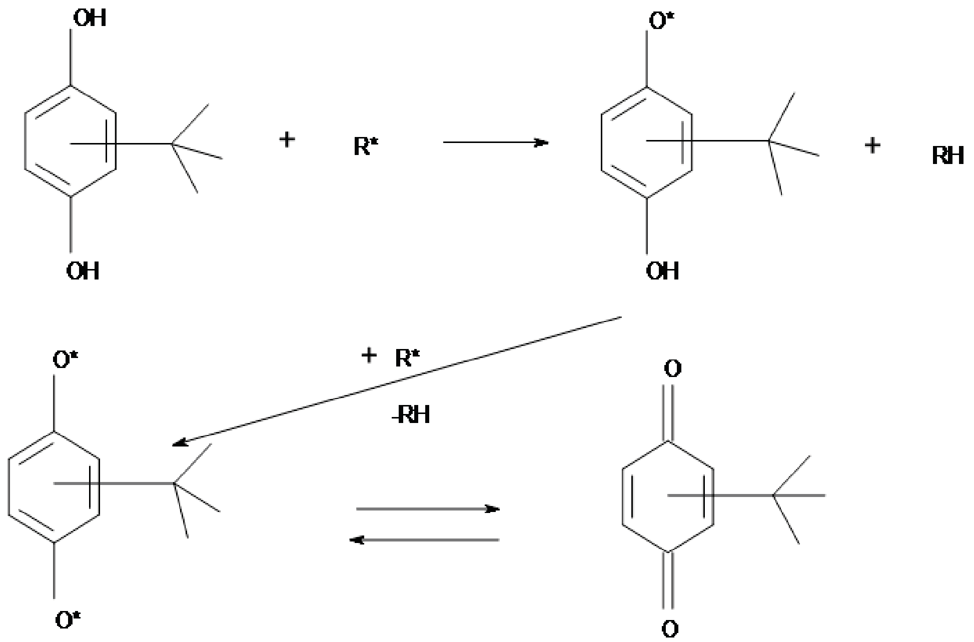

Fig. 1. Tert-Butylated hydroquinones form a stable electron structure by donating two H atoms. Forming resonance stabilizes the structure (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

In general, hindered phenols work best in biodiesels produced from any kind of raw material, and butylated hydroquinones are said to work best in biodiesels produced from vegetable feedstock. Biodiesel is prone to oxidation depending on the raw material it has been produced from. Various raw materials have a variety of fatty acid profiles. The higher the unsaturation level is, the more reactive and unstable the resulting biodiesel becomes, thus requiring a higher antioxidant concentration in order to be stabilized. (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

Feora previously used the Ionol BF 1000 antioxidant, a product of Degussa Sant Celoni, S.A., Spain, in the production of biodiesel. Ionol BF 1000 contains a blend of butylated phenolic compounds (Oxiris Chemicals S.A., 2009). The concentration of this antioxidant in production was rather high, 2000 ppm. The new BioSineox™ Liquid antioxidant was tested to determine whether a smaller dosage would prove sufficient for biodiesel to reach the six-hour limit in a Rancimat test.

Experimental

Two types of samples were sent to the University of Vaasa (UV) by Feora Ltd, i.e. biodiesel samples containing the antioxidant and samples without the antioxidant, both obtained directly from the production process. In the following text, the term 'blank sample' is used to refer to samples that were obtained before the addition of the antioxidant. The term 'process sample' refers to samples obtained directly after the addition of the antioxidant during the production process (Fig. 2). Moreover, in the laboratory at UV, 'laboratory samples' were prepared by adding various amounts of the antioxidant into the blank or process samples provided by Feora Ltd. The preparation of the laboratory samples began with the blending of the antioxidant into blank-sample biodiesel to achieve a final antioxidant concentration of 10 m/m%, i.e. the stock solution. The laboratory samples were then prepared using the stock solution and left to react in room temperature (20 °C) for at least one day prior to taking measurements. During this time, the samples were shaken by hand several times. The mixing was performed at random time. The reaction times for the measurement sets varied because it was assumed that a few days difference would not have an effect on the obtained results.

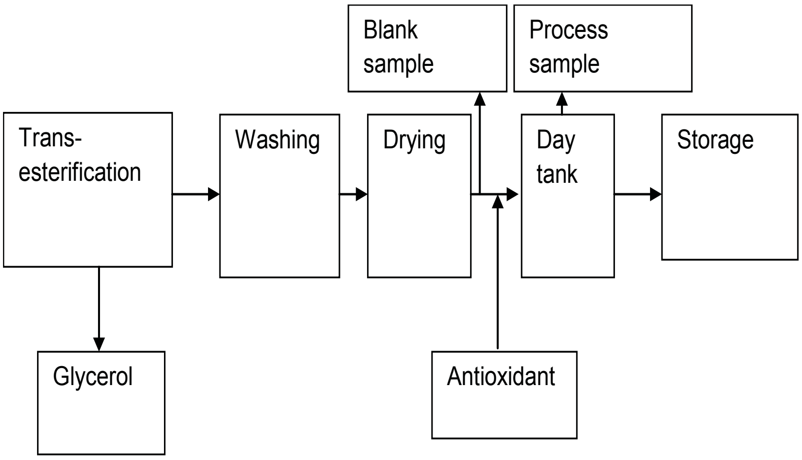

Fig. 2. Process diagram of antioxidant addition in the production process (Oxiris Chemicals, 2009).

The oxidation stability of biodiesels was studied using a Biodiesel Rancimat 873 instrument (Metrohm, Herisau, Switzerland), which meets the required EN 14112 standard (European Committee for Standardization, 2003). The air flow rate was set at 10 l h^{-1}, using 3.00 grams of a sample (±0.01 g) placed in the equipment's heating block at a temperature of 110°C. The vapors coming from the sample were directed into a measuring flask containing 50 ml of distilled water. The conductivity of the water was recorded by a computer. The induction times of the biodiesel samples were determined. Several sets of measurements were made for AFME with various concentrations of the antioxidant (Fig. 3). The measurements were repeated for all of the samples and the presented results show the mean values of these two parallel measurements.

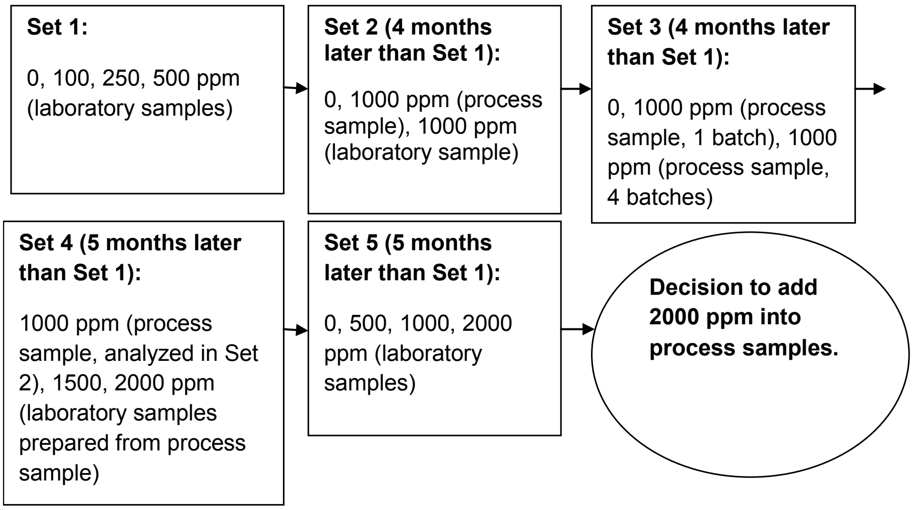

Fig. 3. Diagram of the measurement sets, the schedule and the samples.

In addition to oxidation stability, certain other properties of the biodiesel-antioxidant mixtures were measured for some of the samples. These properties are presented in Table 1. The purpose was to detect whether the addition of the antioxidant would alter certain properties of the AFME biodiesel. Measurements were carried out for a blank sample and a sample containing 500 ppm of the BioSineox antioxidant. The biodiesel for both the blank and the 500 ppm sample was obtained from the same production batch.

The water content was determined with a Karl Fischer Coulometer Mettler Toledo C30 according to the EN ISO 12937 standard. The iodine value and the acid value were measured according to the EN 14111 and EN 14104 standards, respectively. Both measurements represent titration methods that were performed employing a Mettler Toledo DL 70 ES titrator. The surface tension was measured with a Tensiometer TD 2 Lauda according to the manufacturer's instructions. The trace elements were measured using an ICP-OES PerkinElmer Optima 7000DV according to the EN 14538 standard and the manufacturer's instructions.

Table 1. Properties of animal-based fat methyl ester, blank sample (without antioxidants), and laboratory sample containing 500 ppm of BioSineox.

Property (unit)	**Limit, EN 14214**	**AFME, blank**	**AFME, 500 ppm, BioSineox**
Water content (ppm)	≤500	510	430
OSI (h)	≥6	2.5	6.5
Iodine value (g I_2 100 g^{-1})	≤120	77	76
Acid value (mg KOH g^{-1})	≤0.50	0.15	0.17
Surface tension (mN m^{-1})	-	30.0	30.9
Mg+Ca (mg kg^{-1})	≤5.0	<1.0	<1.0
Na+K (mg kg^{-1})	≤5.0	<1.0	<1.0
P (mg kg^{-1})	≤10.0	0	0

As Table 1 shows, oxidation stability reflects the most significant difference in performance between the blank and the 500 ppm sample. The BioSineox antioxidant improved the oxidation stability of the tested biodiesel by 160 %, while other properties showed only minor changes. The water content of the 500 ppm antioxidant sample appeared to reduce by 15 % in comparison with the blank sample. This may have resulted from a change in the chemical structure, as a number of chemical compounds interfere with water determination.

The first Rancimat measurements were carried out for an AFME series of four laboratory samples containing 0 (blank), 100, 250 and 500 ppm of the BioSineox antioxidant. The results are presented in Fig. 4. The error bars in Figure 4, (as well as in Fig. 5 and Fig. 6) are drawn based on the relative standard deviation, 4.5 %, measured for this method earlier. The six-hour limit was reached when 500 ppm of the antioxidant was added. It should be noted that the blank sample with 2.5 h yielded relatively high oxidation stability. Normally, the oxidation stability of AFME samples containing no antioxidants measures approximately 0.6 h.

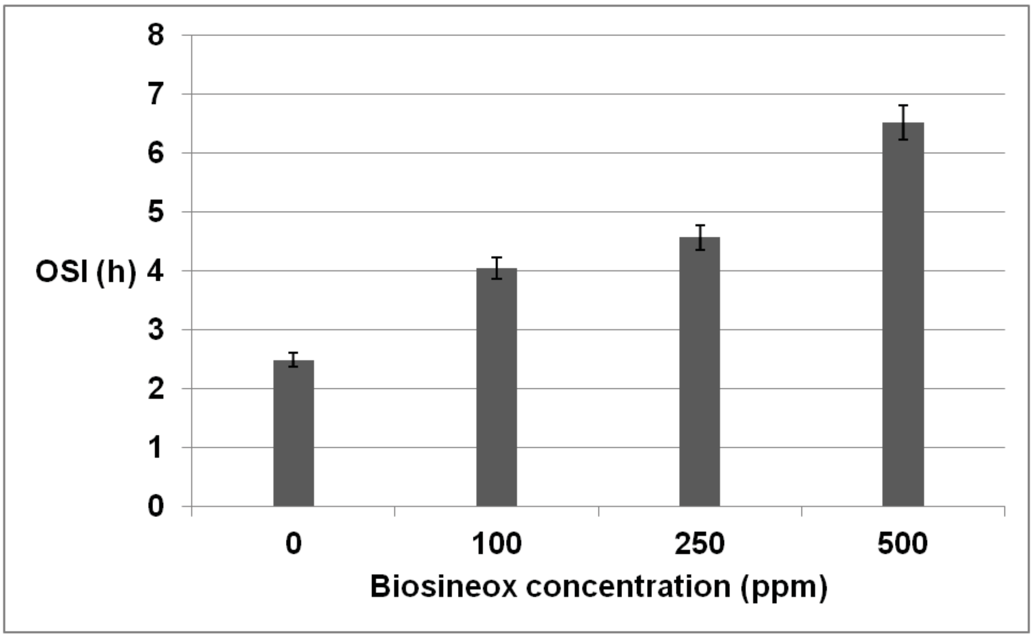

Fig.4. Measured oxidation stability indexes (h) for methyl ester samples containing different concentrations between 0 and 500 ppm of the BioSineox antioxidant.

In the second set of measurements, a blank sample was compared to a process sample and a laboratory sample, both containing 1000 ppm of BioSineox. The Rancimat result for the blank sample was 0.6 h. The Rancimat result for the 1000 ppm process sample was 3.2 h, while the 1000 ppm laboratory sample yielded 27 h oxidation stability.

In the third set of oxidation stability measurements, a blank sample was compared to two process samples containing 1000 ppm of the antioxidant. The process samples consisted of biodiesel from a single production batch and a mixture of four batches, respectively. The blank sample yielded an oxidation stability index of 0.6 h, whereas the one-batch sample reached 2.4 h and the four-batch sample 2.2 h oxidation stability.

The 1000 ppm process sample analyzed in the laboratory in the second set of measurements had previously yielded a result of 3.2 h. When the sample was reanalyzed, oxidation stability had declined to 2.7 h. Four weeks had elapsed since the initial measurement. Two more laboratory samples were produced from this 1000 ppm process sample by adding the BioSineox antioxidant to final concentrations of 1500 ppm and 2000 ppm, respectively. The results for both of the new samples exceeded the six-hour limit. The result for the sample containing 1500 ppm reached 7.1 h and for the sample containing 2000 ppm 12 h (Fig. 5).

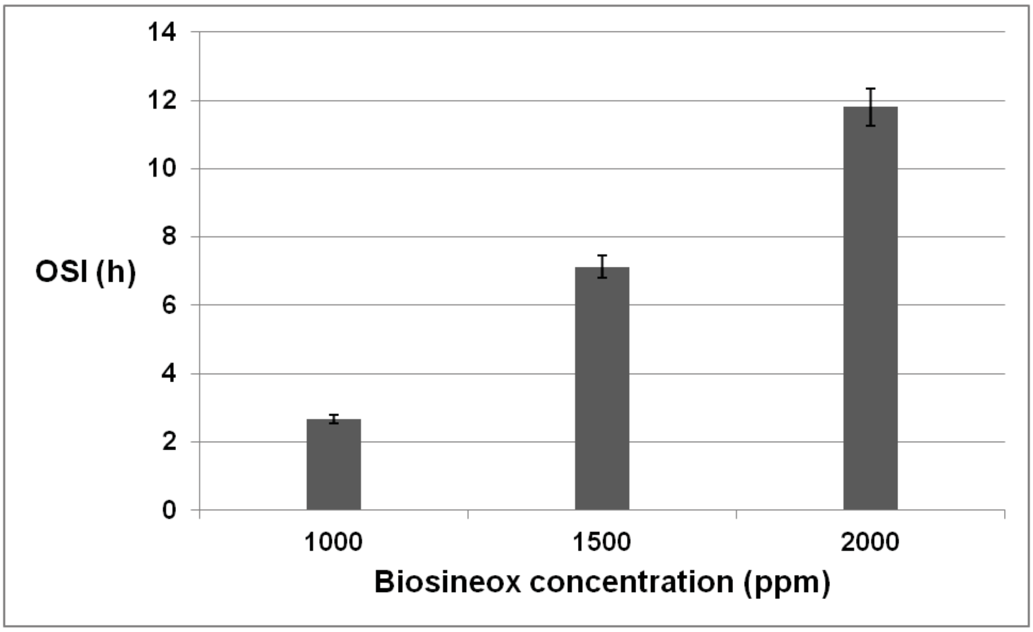

Fig. 5. Measured oxidation stability indexes (h) for methyl ester samples containing concentrations of 1000, 1500 and 2000 ppm of the BioSineox antioxidant.

In the final series of analysis, biodiesel samples were prepared in the laboratory containing the antioxidant at concentrations of 0, 500, 1000, 1500and 2000 ppm. The results are presented in Fig. 6.

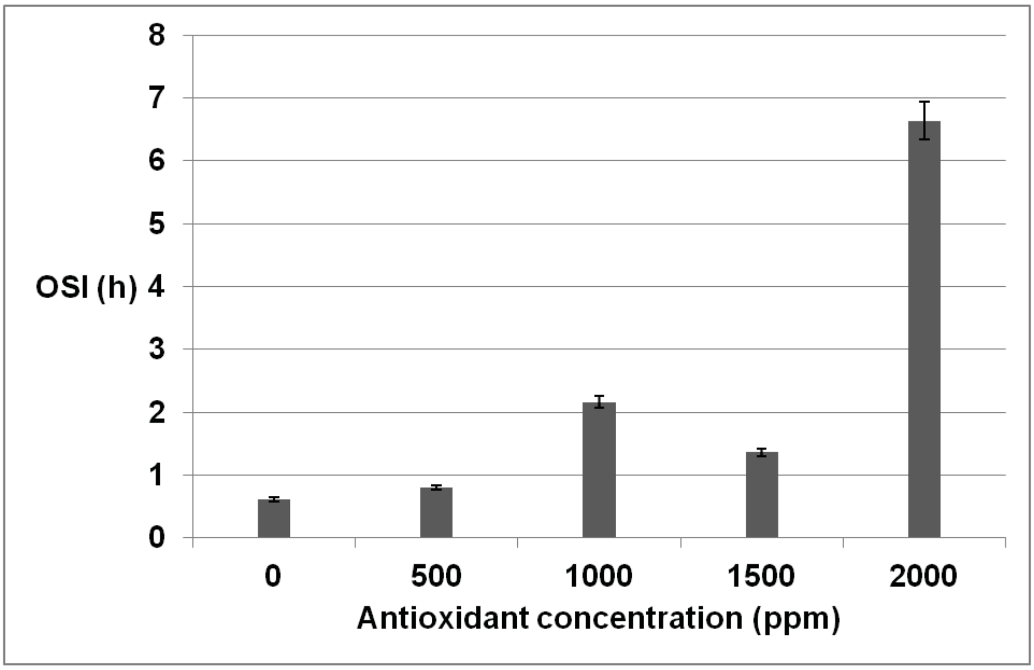

Fig. 6. Measured oxidation stability indexes (h) for methyl ester laboratory samples containing different concentrations between 0 and 2000 ppm of the BioSineox antioxidant.

The blank sample rendered an oxidation stability of 0.6 h, corresponding to the results from the two earlier blank samples. Also, the OSI for the 1000 ppm process sample was comparable to earlier results. However, the results for the 500 ppm, 1500 ppm and 2000 ppm laboratory samples proved lower than the previous results for these concentrations. While the 2000 ppm sample reached 57 % (Fig. 5), the 500 ppm and 1500 ppm samples equaled the previous OSI results (Fig. 4 and Fig. 5) only by 12 % and 19 %, respectively. One possible explanation for this contrastive outcome is that the samples in Fig. 6 were allowed a shorter reaction time than the samples of Fig. 5. The earlier samples (Fig. 5) were prepared in the laboratory by adding the antioxidant to a process sample that already contained 1000 ppm of the antioxidant. The first antioxidant addition had already been carried out in the process line four weeks prior to the measurements.

As for the final series, the samples (Fig. 6) were prepared four days later than the 10 m/m% stock solution, and the samples were analyzed one day after preparation. It is probable that the mixtures of biodiesel and the antioxidant were allowed for an insufficient amount of time to blend and react properly.

The first laboratory samples yielded higher OSI results with lower antioxidant concentrations. A 500 ppm addition of BioSineox sufficed to exceed the six-hour level. The blank sample also yielded a relatively high result, 2.5 h, while the later blank samples yielded only 0.6-hour results. This, along with variation of the raw material, may help explain the smaller amount of the antioxidant reaching the desired level of biodiesel oxidation stability. The promising result that lower concentrations of the antioxidant had achieved high enough oxidation stability for some of the laboratory samples cannot overcome the fact that concentrations of 2000 ppm were required in process samples.

Some studies on vegetable oil based biodiesels have indicated that lower concentrations of antioxidants suffice to reach the desired six-hour level. According to Chakraborty and Baruah (Chakraborty & Baruah, 2012) a concentration of 500 ppm of the TBHQ (tert-butylhydroxyquinone) antioxidant achieved the limit of six hours for a vegetable oil based biodiesel from *Terminalia belerica*, while a biodiesel sample containing no antioxidant reached oxidation stability of 3.8 h. According to the same study, the PY (pyrogallol) and PG (propyl gallate) antioxidants efficiently rendered the six-hour result with a concentration of only 100 ppm. Ruy (Ruy, 2010) has examined the effect of an antioxidant on soybean oil based biodiesel. With the concentration of 100 ppm, the addition of TBHQ resulted in oxidation stability of more than six hours and the concentration of 2000 ppm yielded oxidation stability exceeding 40 hours. However, Ruy discovered that the BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) antioxidants helped oxidation stability meet the specification at the 1000 ppm level (Ruy, 2010). Altogether, these results underline what was previously mentioned, i.e. an antioxidant's efficiency may vary depending on the raw material. Thus, all of the antioxidants and raw materials require individual examining.

The requirement for high antioxidant concentrations has also been observed in studies that have examined certain antioxidants used in the production of AFME. For instance, the Ionol BF 1000 antioxidant has previously been used in the production of biodiesel. The results for BioSineox and AFME mixtures reported here and those for Ionol BF 1000 treated methyl esters presented by Vauhkonen et al. (2011) show that the antioxidant concentrations must be at least 2000 ppm for these antioxidants to reach the OSI limit of six hours (Vauhkonen et al, 2011). The low reproducibility of the results in this study necessitates further research in order to ensure a sufficient OSI in general and for AFME in particular.

Conclusions

In the current study, the BioSineox antioxidant was added to animal-based fat methyl ester in order to determine the smallest possible concentration that would improve oxidation stability to the level of six hours.

Based on the results obtained here, the following can be concluded: To ensure biodiesel reaching the six-hour OSI limit in Rancimat tests, a minimum concentration level of 2000 ppm of the BioSineox antioxidant is required in the process sample.

The increase of the six-hour requirement to a minimum of eight hours in the standard 14214 necessitates further research in order to find the optimum concentration of the antioxidant. Most probably, the concentration needs to be higher than 2000 ppm.

Acknowledgement

The authors acknowledge the assistance of Harry Björkqvist and other representatives of Feora Ltd for this study. The authors would also like to thank Annika Svahn for her assistance with laboratory work, Carolin Nuortila for her comments on the manuscript and Susanna Rönn for revising the English of the manuscript.

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Publication II

STORAGE STABILITY STUDIES WITH COMMERCIALLY AVAILABLE SOY BEAN METHYL ESTER

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ABSTRACT: Commercially available soy bean methyl ester was stored for 12 months. The material of the storing vessel and temperature varied. The materials used were steel and polyethylene and the temperatures 4°C and 20°C. Certain properties related to storing stability were monitored before and after storage. The properties were the ester content, viscosity, acid number and oxidation stability. The amounts of metals (Al, Cu, Fe, Mn, Si, V, Zn) were also measured for fresh biodiesel and after one year of storage. This was done to find out if corrosion occurs in long term storage and if the biodiesel dissolves metals from the steel vessel. No corrosion was detected and the other properties fulfilled the requirements of Standard EN 14214 even after 12 months storage except the oxidation stability index. The main result was that commercial soy bean methyl ester can be stored in proper conditions for one year.

Keywords: biodiesel, biofuel, quality, storage, transesterification, vegetable oil.

1 INTRODUCTION

The two most significant issues for biofuel development worldwide are energy security and climate change. In Europe and the United States, every third vehicle sold has a diesel engine. A marginal replacement of fossil diesel fuel by biodiesel (for example, blending them together) can slow down climate change and extend the adequacy of supplies of crude oil even though the capacity of biofuel production will hardly be large enough to replace petroleum derived fuels completely. Capacity is not the only problem biofuel usage has since it can also cause technical difficulties in engine compatibility. Together with engine compatibility, the fuel must also fulfill the quality assurance and standardization requirements to secure acceptance by consumers. US and EU standards are the most used standards and other biofuel producing nations are often following them. [1]

Storage stability is one of the main quality parameters. The deterioration of the properties of biofuel during storage is more serious than with fossil fuels. Improving oxidation and storage stability is an important issue for commercializing the biodiesel. [2]

The oxidative stability of biodiesel is threatened primarily during extended storage. Generally, factors such as the presence of air, elevated temperatures or presence of metals facilitate oxidation. [3]

Changes in certain properties such as flash point, ester content, heating value, cetane number, acid number, kinematic viscosity, density, and the amount of insoluble contaminants (polymeric species) may occur. Engine fuel filters and injectors may become blocked if polymerization or the formation of acids occur, while acids also form a corrosive environment for the fuel injection equipment. Injector blockage has been reported to occur via the increase in viscosity. Moreover, undesirable oxidation products can also affect the performance of the fuel pumps and injectors due to increased wear. [4]

The acid number (acid value) describes the development of acidic materials during oxidation. The polymerization caused by oxidation will increase the viscosity of the sample and kinematic viscosity is the most common physical property to measure. [5]

Metals, especially copper and iron, in addition to air, heat and light are parameters that are investigated as being pro-oxidizing. [6] Besides oxidation, metals also have effects on other fuel quality parameters as well as the whole engine system. Copper and vanadium cause environmental pollution. Aluminium, copper, manganese and zinc are reported to have problems of corrosion in the engine. These elements can end up in the fuel as contaminants from the refining process. The origin can also be natural, especially in the case of fossil fuels. [7] That can cause trouble when biodiesel is blended with fossil fuel. Even if the blend percentage of biodiesel is moderately low, the metals in fossil fuel can reduce the quality of the fuel for the reasons described earlier. Metals can also originate from the engine. [8] In that case their effect on fuel quality and oxidative stability is not significant, but they can affect engine wear and possibly engine emissions.

Jain and Sharma (2013, 2014) studied the storage stability of Jatropha curcas biodiesel contaminated with metals. The storage period was 6 months and the concentrations of metals were a maximum of 2 ppm. The authors found that beyond a concentration of 2 ppm, the oxidation stability index became almost constant as the concentration of metal increased. They assumed that the influence of metals is catalytic, as even small concentrations of metals had almost the same effect on the oxidation stability as large concentrations. [9,10]

Fuels are often stored in IBC containers made of high density polyethylene or in steel barrels. Methyl esters have a tendency to develop acidic material during storage. The acidity can cause corrosion on metal surfaces. The temperature affects the changes that occur in the fuel.

The biodiesel studied was commercially available. Soy bean methyl ester, SME, was chosen for examination in this study because soy bean is a global cultivation plant and will be major oil crop for biodiesel production at least until the year 2020. [11]

In this study, the aim was to find out if the storage vessel material, steel or polyethylene, or storage temperatures of 4 °C and 20 °C affect the fuel quality when the storage time is 12 months. Another aspect was to follow how certain properties which are known to be related to the deterioration will change over time. The properties were ester content, viscosity, oxidation stability and acid number. Also, metal contents (Al, Cu, Fe, Mn, Si, V, Zn) were measured in fresh samples as well as those stored for 12 months. The purpose was to find out if corrosion occurs and if the SME dissolves metals from the steel can.

2 EXPERIMENTAL

The soy bean methyl ester samples were stored in two high density polyethylene bottles produced for chemicals and in two tin-plated steel cans produced for paints. All the holders had a volume of 1 litre. One plastic bottle and one can were stored at 20°C in a dark cupboard. Another plastic bottle and another can were stored in a refrigerator which was set at a temperature of 4°C. The samples were stored for 12 months. The followed properties (ester content, viscosity, oxidation stability and acid number) were measured by the SME supplier at the end of the year 2012. The metal contents (Al, Cu, Fe, Mn, Si, V, Zn) were measured at the University of Vaasa in the beginning of 2013. All these properties were re-measured after 12 months storage time at the University of Vaasa. The methods described in the materials and methods section are those which were used by the University of Vaasa.

3 MATERIALS AND METHODS

A batch of 1000 l of soy bean methyl ester was purchased to the University of Vaasa at the end of 2012. The supplier was Archer Daniels Midland Company, ADM, USA.

3.1 Elemental analyses

The concentrations of metal elements were measured by a Perkin Elmer ICP OES spectrometer 7000DV. In this method a weight sample is diluted with kerosene in a weight ratio of 1:1. The solution is injected into the spectrometer plasma. Calibration was made by the known concentrations of multi standards. The elements measured by this method were Al, Cu, Fe, Mn, Si, V and Zn. The defined standards (emission intensities in known concentrations) and the presence and concentration of the element are evaluated by comparing the intensity of the light against these standards. The analyses were performed according to Standards SFS-EN 14538 and SFS-EN 14107, as well as according to the manufacturer's advice. [12,13]

3.2 Acid number

The acid number was analyzed by a titrator Metrohm Titrando 888. The method is a potentiometric titration method. The sample is diluted with iso-propanol and titrated by potassium hydroxide. The measurement is produced according to Standard EN 14104. [14]

3.3 Oxidation stability index

The oxidation stability index was measured by a Biodiesel Rancimat 873 instrument. The method describes the fastened oxidation stability of biodiesel. The sample is heated and air flow is conducted through it. Vaporizing compounds of the sample drift with air into water and the conductivity of the water is measured. The end point is achieved when the conductivity increase is at its highest. The method is described in Standard EN 14112. [15]

3.4 Viscosity

The viscosities were measured by a Stabinger SVM 3000 rotational viscometer. The measurement is based on a torque and speed measurement. The device calculates the dynamic viscosity from the rotor speed. The device also has a density measuring cell that employs an oscillating U-tube principle. The kinematic viscosity is calculated automatically based on these measurements. [16]

3.5 Ester content

The ester content was measured by a Perkin Elmer gas chromatograph Clarus 580. Methyl heptadecanoate is used as an internal standard for this method. It is suitable for biodiesels containing methyl esters between C14 and C24 and when ester content is higher than 90 % (m/m). The method is described in Standard EN 14103. [17]

4 RESULTS AND DISCUSSION

The measured results are listed in Table I.

Table I: Results measured for SME samples stored for 12 months.

Property	SME fresh	SME, 20 °C plastic	SME, 4 °C plastic	SME, 20 °C steel	SME, 4 °C steel
Ester content (% m/m)	99.50	98.6	98.5	98.9	98.9
Viscosity at 40°C (mm²/s)	4.08	4.13	4.11	4.12	4.10
Oxidation stability, 110°C (hours)	9.2	6.9	7.8	7.3	8.1
Acid number (mgKOH/g)	0.12	0.18	0.16	0.17	0.15
Al (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
Cu (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
Fe (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
Mg (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
Si (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
V (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5
Zn (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5

Relative standard deviations measured in analysis methods: ester content 0.57 %, viscosity 0.073 %, oxidation stability 4.5%, and acid number 7.9 %. The limit of detection for ICP OES used for analyzing metal contents is not measured.

4.1 Oxidation stability, unsaturation and acidity

For SME stored at 20°C in a plastic bottle the decrease in the oxidation stability index was 25 % and for SME stored at 4°C in a plastic bottle it was 16 %. A decrease of 21 % was measured for SME stored at 20°C in a steel can and 13% for SME stored at 4°C in a steel can. The highest OSI value measured after 12 months storage was 8.1 hours for SME stored in a steel can at 4 °C temperature. This was the only sample which reached the 8 hour limit set in Standard EN 14214 after 12 months storage.

As a comparison, Serrano et al. (2013) reported an 83 % decrease in induction period (from 2.9 to 0.48 h) for neat SME in 6 months. The lower resistance to long term oxidation was most probably due to a higher polyunsaturated FAME fraction (61.3%). [18] In this study, the induction period decreases were minor even though the storage time was longer than in the study by Serrano et al. In the current study, the unsaturation was assessed based on the linolenic acid methyl ester and iodine value. The linolenic acid content was at an appropriate level (7.70 %, m/m) for SME. The Standard EN 14214 allows it to be maximum 12 % m/m. The iodine value for SME was higher than the 120 g iodine/100 g limit set in EN 14214, as it was 131 g iodine/100 g.

An increase in the acid number measured after 12 months was indicated in all the samples. The increase varied from 50 % to 25 % in the order SME 20°C, plastic bottle> SME 20°C, steel can> SME 4°C, plastic bottle> SME 4°C, steel can. The differences between the samples were, however, minor and the highest acid number was only 0.18 mg KOH/g.

Yang et al. (2014) studied the storage stability of soy bean methyl ester over one year. The acid number of the sample increased from 0.33 to 0.66 mg KOH/g sample during at storage time of 12 months. [19] The increase in acid number, 97 %, was then higher than obtained in this study.

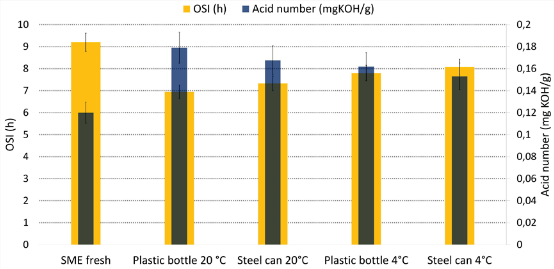

Figure 1: The oxidation stability index and acid number results of fresh sample and samples stored for 12 months.

In Fig. 1 it can be seen that after the storage time, the sample which had the highest oxidation stability index had the lowest acid number, and the sample which had the lowest oxidation stability index had the highest acid number. Even though the differences were minor, this was to be expected. It is commonly known that an increase in oxidation causes an increase in the acid number. [20]

4.2 Viscosity and ester content

In the present study, the deterioration in the viscosity and ester content was minor during the 12 months of storage and all the samples fulfilled the requirements set in Standard EN 14214 for those properties even after the storage. The deterioration change in percentage varied between 0.5 and 1 % in both properties. The storage ageing was thus not significant regarding viscosity and ester content.

Berrios et al. (2012) studied the storage stability of sunflower methyl ester and used cooking oil methyl ester and its blends with fossil diesel fuel. The storage time was 6 months and the storage conditions varied. All the samples showed an increase in the viscosity after storage and the neat biodiesel samples did not reach the requirements of Standard EN 14214 after the storage time. [21] Probably the feedstock used in their study was more prone to form acids and oxidized polymeric compounds than the SME examined here. They also reported a higher increase in the acid number than was found in this study.

4.3 Metals

The metal analysis results remained unchanged (close to zero level) during the storage time. In this study, the metals did not dissolve from the steel cans into the fuel.

Fernandes et al. (2013) studied the compatibility of galvanized and carbon steel with soy bean methyl ester. They found a minor (2 µg g-1) zinc release when biodiesel was exposed to galvanized steel over a storage period of 56 days. The amount was so small that it did not speed up the deterioration of the biodiesel. Iron was not detected in biodiesel exposed to carbon steel. The authors also reported that the addition of antioxidant reduced zinc corrosion. [22]

In this study, antioxidants were not studied, but as the SME was commercially available it can be assumed that it included antioxidants. It should also be noted that the detection limits of the metal analysis were only 1 mg g-1. However, the storage time was considerably longer than in the Fernandes et al. study. It can be stated that the results in both studies demonstrated the fact that corrosion is not a significant problem when biodiesel is stored in a steel vessel for a reasonable time.

4.4 General discussion

In the current study, the oxidation stability was found to drop slightly while the other quality parameters which are related to oxidation of the fuel also deteriorated. The same result was found in the BIOSTAB project in 2003. [23] In this study researched at the University of Vaasa, the fuels were stored for a period of one year in storage conditions that were slightly different. The properties of the samples were at a good quality level although only one sample reached the oxidation stability index of 8 hours after one year of storage. In the BIOSTAB project, the results were similar. The project concluded that biodiesel can be stocked under normal storage conditions without a dramatic change of quality for one year. The oxidation stability, along with the peroxide value, were the properties that were prone to change the most. The peroxide value was not, however, monitored in this study.

Further studies should more thoroughly concentrate on investigating the blending of biodiesel with fossil diesel and the fuel properties in higher blends (over 20 %) of biodiesel. Also, metallic compounds should be taken under review. The main issues are how harmful the corrosion effect is on automotive components and will it accelerate wear in engine parts. Additionally the effect on emissions and fine particles should be monitored.

5 CONCLUSION

The aim of this study was to explore the effect of storage conditions on SME fuel quality. Fresh SME fulfilled the requirements of Standard EN 14214 except in the case of iodine value. The properties followed for 12 months were ester content, viscosity, oxidation stability, acid number and metal contents (Al, Cu, Fe, Mn, Si, V, Zn). No significant changes were found in samples that were stored in two different temperatures, 4°C and 20°C, and in two different storage vessel materials, plastic and steel. All other properties for all the samples fulfilled the requirements of the Standard EN 14214 for the whole storage time except for the oxidation stability index which was on the desired level (above 8 hours) only for the sample stored at 4°C in a steel can. The biggest deterioration in percentage, 50 %, was in the acid number for SME stored in a plastic bottle at 20°C. However, the result (0.18 mgKOH/g) clearly met the requirements of Standard EN 14214. The materials of the storage vessels did not affect the quality of the fuel. Metals did not dissolve from the steel cans into the fuel. According to the results of this study, good quality methyl ester can be stored for one year in proper conditions without a notable deterioration. Steel and polyethylene are appropriate materials for biodiesel storage.

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7 ACKNOWLEDGMENTS

The biodiesel utilized in this study was purchased within the TREAM project which was funded by the Finnish Funding Agency for Technology and Innovation (TEKES).

The authors also wish to thank Mrs. Anne Mäkiranta and Mrs. Sonja Heikkilä for the constructive discussions during this study, and Mr. John Shepherd for proofreading the English of this article.

Agronomy Research **14**(x), xx–xx, 2016

Publication III

The effect of sulphur content on B20 fuel stability

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Abstract. The aim of this study was to investigate if a high amount of sulphur is favourable for the fuel blends' storage stability. The parameters that correlate with the storage stability of the fuel blends were compared with two B20 fuel samples consisting of 20 vol% biodiesel and 80 vol% fossil diesel. The studied parameters were the oxidation stability (OSI), acid number and kinematic viscosity. The measurements were carried out straight after mixing the blends, and again after 4 and 9 weeks. One of the B20 samples was prepared from rapeseed methyl ester (RME) and fossil diesel fuel containing 6.6 mg kg^{-1} sulphur and the other from the same RME but the fossil diesel fuel contained 186 mg kg^{-1} of sulphur. According to the results of this study, the fuel containing less sulphur had slightly better quality during the entire study. Though, the OSI of the fuel containing more sulphur decreased less in percentages than it did for the fuel containing less sulphur. As a conclusion, the study gives a reason to assume that the sulphur may be favourable to fuel blends' storage stability but it should be studied for a longer time to confirm this statement.

Key words: FAME, fuel blends, B20, diesel fuel, storage stability, sulphur.

INTRODUCTION

During the recent decades, the sulphur content of liquid engine fuels has drastically decreased to reduce harmful effects of exhaust sulphur compounds both on the engine components and pollutant emissions. At the same time, the need to increase the use of renewable fuels has grown to also reduce greenhouse gas (GHG) emissions.

Fuel sulphur increases soot and particulate matter emissions in the exhaust of all kind of internal combustion engines, causes corrosion and also has a deleterious effect on advanced after treatment systems used for CO, HC, NOx and particulate reduction. (Kalghatgi, 2014) The fuel sulphur also causes corrosion inside the engine cylinder. In combustion, it will oxidize to sulphur dioxide. SO_2 will be further oxidized to SO_3 and then again react with water. Formed sulphuric acid, H_2SO_4, will condensate on the metal surfaces and cause corrosion. (Heywood, 1988) This aspect makes the desulphurization important but refining processes which remove the sulphur from the fuel simultaneously reduce fuels lubricity. After processing, the lubricity may be returned by adding certain additives. However, fatty acid methyl esters, i.e. biodiesels, are found to enhance the lubricity when they are mixed together with diesel fuel oil. (Kalghatgi, 2014; Guibet, 1999)

In Europe, the automotive diesel fuel standard, EN 590:2013 allows the fuel to contain a maximum of 10 mg kg^{-1} sulphur (EN 590:2013, 2013) but elsewhere in the world the limitations are not as strict. Diesel fuels containing 100-500 mg kg^{-1} sulphur are commonly in use in many regions outside Europe. E.g. Brazil has two diesel types which are divided by the sulphur content to S10 and S500, whose limits are 10 mg kg^{-1} for bigger cities and 500 mg kg^{-1} for rural areas. (ANP #50, 2013) Non-road diesel in Brazil has a limit of 300 mg kg^{-1}. (ANP#71, 2011) Though, the levels all over the world have been reduced considerably after the 1990's. (Guibet, 1999; Kalghatgi, 2014)

Sulphur emissions, both gaseous and particles, are harmful for human health. An acute exposure can cause trouble in breathing and a long-time exposure for those emissions can cause heart disease, pulmonary illness or even untimely death. In the environment sulphur oxides are reactive and form H_2SO_4 which comes down with the rain and the acid rain again depletes the nature in many ways. Moreover, buildings disintegrate because of the acid rain. (Pan, 2011)

When increasing the share of renewable fuels, fuel blends form a realistic and feasible way and therefore, different blends of bio- and fossil fuels are becoming more frequent. In Europe, the maximum fatty acid methyl esters (FAME) content in diesel fuel is 7 vol% according to the EN 590:2013 but higher percentages are also available and targeted around the world. Storage stability is one of the main quality parameters related to biodiesels. The deterioration of the properties of FAMEs during storage is more serious than for fossil fuels. Improving oxidation and storage stability is an important issue for commercializing the biodiesel. (Bouaid et al., 2009) Some studies have indicated that higher sulphur contents may affect beneficially the oxidation stability of the fuel blends. (McCormick & Westbrook, 2007)

The aim of this study was to investigate if a high amount of sulphur is favourable for the fuel blends' storage stability. The parameters that correlate with the storage stability of the fuel blends were compared in two B20 fuel samples consisting of 20 vol% biodiesel and 80 vol% fossil diesel. One of the samples was mixed with rapeseed methyl ester (RME) and distillate fuel oil (DFO) containing 6.6 mg kg^{-1} sulphur (later in text: B20 (6.6 mg kg^{-1} S)) and the other was mixed using the same RME but DFO which contained 186 mg kg^{-1} sulphur (later in text: B20 (186 mg kg^{-1} S)). The fuel containing 6.6 mg kg^{-1} sulphur did not contain any bio component before mixing it with RME. The information about added biodiesel for DFO which contained 186 mg kg^{-1} sulphur was not available but the supplier assumed that it did not contain any biodiesel before mixing it with RME.

The analyses carried out for these two samples were oxidation stability (OSI), acid number (AN) and kinematic viscosity (KV). The samples were analysed straight after mixing, after 4 weeks and after 9 weeks of storage. The storage conditions were not specified extremely accurately but the samples were similarly placed in a dark cupboard at room temperature (around 20°C). These mentioned properties (OSI, AN, KV) of RME were measured before mixing it with DFOs. The measured properties of RME fulfilled the requirements set for FAME fuel in Standard EN 14214:2012.

MATERIALS AND METHODS

RME used as the bio component in fuel blends was a product of ecoMotion GmbH, Germany. RME is ISCC EU certified and meets Standard EN14214:2012. Fuel had been produced three years before this study and delivered to the University of Vaasa in 2012. Still the fairly old RME fulfilled the requirements for Standard EN 14214:2012 in terms of the properties measured in this study. The information about added antioxidant was not available.

DFO containing 6.6 mg kg^{-1} sulphur was a product of Neste and it was produced in Finland. It did not contain any bio component before mixing it with RME. DFO containing 186 mg kg^{-1} sulphur was Rubilene 813 fuel and it was produced in Brazil. The information about added biodiesel was not available but the supplier assumed that it did not contain any biodiesel before mixing it with RME.

Acid number

The acid number was analysed by a titrator Metrohm Titrando 888. The method is a potentiometric titration method. The sample is diluted with iso-propanol and titrated by potassium hydroxide. The measurement was produced according to Standard EN 14104:2003. (SFS-EN 14104, 2003)

Oxidation stability

The oxidation stability was measured by a Biodiesel Rancimat 873 instrument. The method describes the accelerated oxidation stability of biodiesel. The sample is heated and air flow is conducted through it. Vaporizing compounds of the sample drift with air into water and the conductivity of the water is measured. The end point is achieved when the conductivity increase is at its highest. The method is described in Standard EN 15751:2014. (SFS-EN 15751, 2014)

Viscosity

The viscosities were measured by a Stabinger SVM 3000 rotational viscometer. The measurement is based on torque and speed measurements. The device calculates the dynamic viscosity from the rotor speed. The device also has a density measuring cell that employs an oscillating U-tube principle. The kinematic viscosity is calculated automatically based on these measurements. (Anton Paar, 2012)

RESULTS AND DISCUSSION

The results of kinematic viscosity, acid number and oxidation stability measurements are presented in Table 1. All the obtained results are arithmetic means of two replicate measurements.

Table 1. The analyses results for B20 fuels.

Property	B20 (6.6 mg kg^{-1} S)	B20 (186 mg kg^{-1} S)	RME
Kinematic viscosity, 40 °C (mm^2 s^{-1})			
Fresh	3.7	3.4	4.5
4 weeks	3.7	3.4	
9 weeks	3.7	3.4	
Acid number (mgKOH g^{-1})			
Fresh	0.07	0.08	0.19
4 weeks	0.06	0.09	
9 weeks	0.07	0.09	
Oxidation stability (h)			
Fresh	36	29	9.5
4 weeks	34	29	
9 weeks	33	28	

The relative standard deviations are: kinematic viscosity 1%, acid value 7.9% and oxidation stability 4.5%. These had been determined for the analysis methods earlier.

The kinematic viscosity of both samples remained constant during the 9 weeks of time (Fig.1). During the whole study, the viscosity of the sample B20 (6.6 mg kg^{-1} S), 3.7 mm^2 s^{-1}, was higher than it was for B20 (186 mg kg^{-1} S), 3.4 mm^2 s^{-1}.

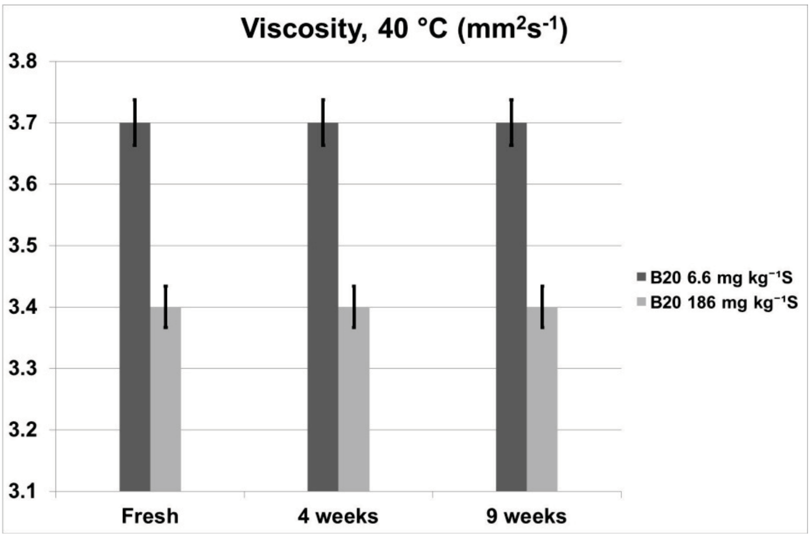

Figure 1. The results of viscosity measurements.

The acid number of the sample B20 (186 mg kg^{-1} S) was higher for fresh sample and it increased more than it did for the sample B20 (6.6 mg kg^{-1} S) (Fig.2). The result of the sample B20 (186 mg kg^{-1} S) increased from 0.08 to 0.09 mgKOH g^{-1}. For the B20 (6.6 mg kg^{-1} S) the result seemed at first to decrease from 0.07 to 0.06 mgKOH g^{-1} but it increased back to the level of 0.07 mgKOH g^{-1} after 9 weeks of storage. This phenomenon happened probably due to the measurement precision.

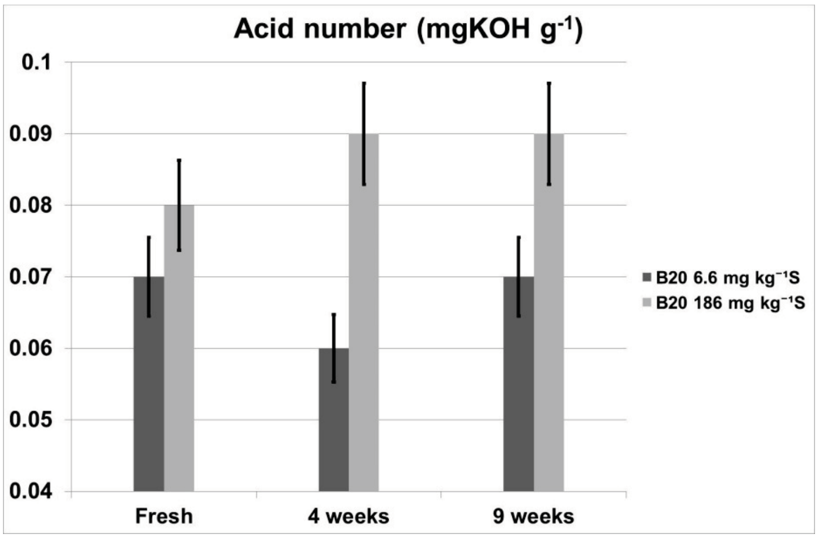

Figure 2. The results of acid number measurements.

Fig.3 shows that the oxidative stability of the sample B20 (6.6 mg kg^{-1} S) (36, 34, 33 hours) was higher during the whole study than it was for the sample B20 (186 mg kg^{-1} S) (29, 29, 28 hours). The decrease in OSI was 8% for the sample B20 (6.6 mg kg^{-1} S) when it was only 3% for the sample B20 (186 mg kg^{-1} S).

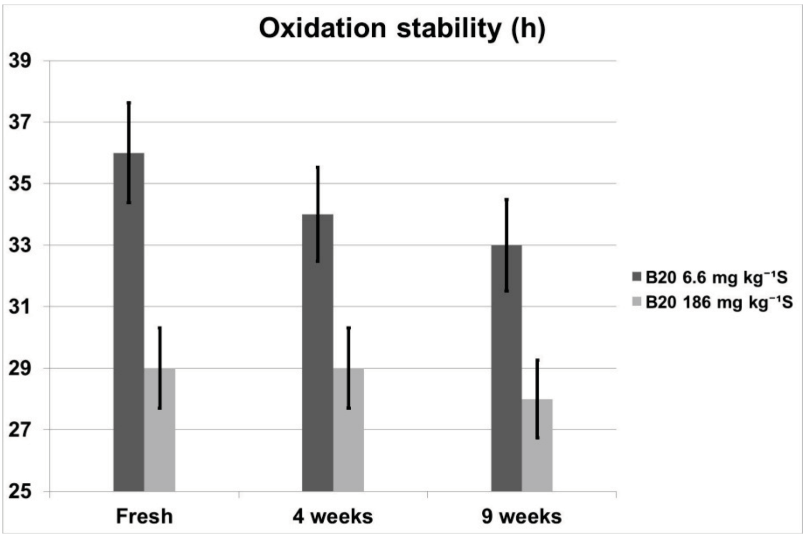

Figure 3. The results of oxidation stability measurements.

Karavalakis et al. (2010) have studied the oxidation stability of biodiesel blends and they have found it a very complicated process. They say that the most important factors affecting the blends' stability are the biodiesel composition and used antioxidants. Also, according to McCormick & Westbrook (2007), the stability of the biodiesel is the most important factor which affects the blends storage stability.

In this study, the biodiesel in both samples was the same and the reason for the difference in OSI of the fresh blend samples was more likely caused by the diesel fuel which also is conceivable according to Karavalakis et al. and McCormick & Westbrook. However, as mentioned, the process is so complex that analyses made in this study are not comprehensive enough to reveal the reason for the quality difference between the diesel fuels. Most probably, the difference is due to oxidative and thermal stability of the diesel fuel. (McCormick & Westbrook, 2007) The OSI results of the both DFOs used in this study would have been useful as refence measurements and the OSI analyses of DFOs have necessarily to be included in the future investigations.

McCormick & Westbrook mentioned that sulphur compounds can work as antioxidants and the same conclusion is also supported by the study of Karavalakis et al. (McCormick & Westbrook, 2007; Karavalakis et al., 2010) As mentioned above, here the decrease in OSI was 8% for the sample B20 (6.6 mg kg^{-1} S) when it was only 3% for the sample B20 (186 mg kg^{-1} S). This may indicate the antioxidative effect sulphur has. To prove this thesis, also indicated by the current study, a longer follow-up study should, however, be implemented.

Karavalakis et al. (2011) showed in another study, that even 4-6 weeks storage time may cause OSI to decrease under the 20 hours limit due to natural ageing. The 20 hours limit is set in Standard EN 590:2013 for automotive diesel fuels. In this study, both the samples remained clearly above the 20 hours limit for 9 weeks. The other measured properties were also at a proper level though the adopted RME was produced 3 years before this study.

CONCLUSIONS

As one conclusion, the study gave a reason to assume that the sulphur may be favourable to fuel blends' storage stability. The decrease in OSI was 8% for the sample B20 containing less sulphur when it was only 3% for the sample B20 containing more sulphur. This may indicate the antioxidative effect sulphur has. The phenomenon should, however, be studied for a longer time to confirm this statement.

As another conclusion, it can be stated that even a long time stored RME had a sufficiently good quality to use as a biocomponent in blending. In this study, the OSI of both the B20 samples remained clearly above the 20 hours limit for 9 weeks even though they were prepared using RME which was produced 3 years ago.

ACKNOWLEDGEMENTS. The authors would like to acknowledge Mr. Jukka Nuottimäki from Neste and Mr. Tapani Katila from AGCO Power. The diesel fuels utilized in this study were supplied by those gentlemen. The biodiesel utilized in this study was purchased within the TREAM project which was funded by the Finnish Funding Agency for Technology and Innovation (TEKES).

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Agronomy Research **XX**(x), xx–xx, 2017

Publication IV

Effects of sulphur on the storage stability of the bio and fossil fuel blends

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Abstract. In this study, the aim was to find out if mixing two common fuels together could be beneficial for both the environment and storage stability of fuel. It is obvious, that adding biodiesel to fossil fuel will decrease its sulphur content and reduce its carbon monoxide and hydrocarbon, sulphur dioxide and soot emissions. But will the high sulphur content enhance the storage stability of the biodiesel? Four B20 samples were produced, consisting of 20 vol% biodiesel and 80 vol% fossil diesel. The samples were prepared from rapeseed methyl ester (RME), low sulphuric fossil diesel fuel and high sulphuric diesel solvent. The blends had different sulphur contents of 6, 76, 149 and 226 mg kg^{-1}. For these B20 fuel samples, the parameters were compared that correlate with the storage stability of the fuel blends. The studied parameters were the oxidation stability (OSI, according to EN 15751:2015), acid number (AN, according to EN 14104:2003) and kinematic viscosity (KV, by Stabinger SVM 3000 rotational viscometer). The measurements were carried out straight after mixing the blends, and again after 4, 8 and 12 weeks. According to the results, the fuel containing less sulphur slightly lost its oxidation stability within three months. Instead, the oxidation stability of high sulphuric samples improved within the same time frame. As a conclusion, the study gave a reason to assume that – in spite of its known drawbacks – the sulphur may be favourable to fuel blends' storage stability but the phenomenon and chemistry should be studied in more detail.

Key words: Biofuel, blending, FAME, diesel fuel, B20, stability, sulphur.

INTRODUCTION

During the recent decades, the sulphur content of liquid engine fuels has drastically decreased to reduce harmful effects of exhaust sulphur compounds. The reasons for the fuel sulphur limitations are both technical and environmental; sulphur pollutes the air and poisons the catalysts in emission control systems. Fuel sulphur also increases soot and particulate matter emissions in the exhaust of all kind of internal combustion engines, causes corrosion and also has a deleterious effect on advanced after treatment systems used for CO, HC, NOx and particulate reduction (Kalghatgi, 2014; Zhao et al., 2016). Moreover, the fuel sulphur causes corrosion inside the engine cylinder. In combustion processes, sulphur oxidizes to sulphur dioxide SO_2. It will be further oxidized to SO_3 and then again react with water. Formed sulphuric acid, H_2SO_4, will condensate on the metal surfaces and cause corrosion (Heywood, 1988). This aspect makes the de-sulphurization important but refining processes which remove the sulphur from the fuel simultaneously reduce fuels lubricity.

Sulphur emissions, both gaseous and particles, are also harmful for human health. An acute exposure can cause trouble in breathing and a long-time exposure for those emissions can cause heart disease, pulmonary illness or even untimely death. In the environment, sulphur oxides are reactive and form H_2SO_4 which comes down with the rain and the acid rain again depletes the nature in many ways. Moreover, buildings disintegrate because of the acid rain (Pan, 2011).

In parallel with the fuel de-sulphurization development, the need to increase the use of renewable fuels continues to grow to also reduce greenhouse gas (GHG) emissions. In countryside, there may also be possibilities to utilize own yield of rapeseed or other oils as biodiesel fuel through transesterification and this could be financially beneficial for the farmers. In rural areas, there is an increasing need for cheap, both fossil and renewable, fuels in agricultural engine applications. Due to the environmental aspects, the fuel sulphur content is widely regulated but the content still remains quite high in the developing countries in Asia and Southern America. The cheapest fuels are not the cleanest, i.e., the sulphur contents in non-road fuel may in those regions be as high as 500 mg kg^{-1} while in Europe, the automotive diesel fuel standard, EN 590:2013 allows the fuel to contain a maximum of 10 mg kg^{-1} (SFS-EN 590:2013, 2013).

Due to the environmental reasons on one hand and to the agricultural needs, on the other hand, different blends of bio- and fossil fuels are becoming more popular. High sulphuric fossil fuels and the effect, they have on blends' properties, need to be studied further to find an economic, environmental and technical balance between de-sulphurization, fuel blending, and the usage of renewable components. It is also noteworthy that after de-sulphurization processing, the fuel lubricity must usually be returned by adding lubricity additives into the fuel. However, biodiesels or fatty acid methyl esters (FAMEs) have also been found to enhance the lubricity when they are mixed with diesel fuel oil (Guibet, 1999; Kalghatgi, 2014). Blending of FAME with low sulphur fossil diesel thus also improves the fuel lubricity.

The storage stability is one of the main quality parameters related to FAMEs. The deterioration of the properties of FAMEs during storage is more serious than for fossil fuels. Storage conditions, like ambient temperature, have of course an effect on storage time. Improving oxidation and storage stability is an important issue for commercializing the biodiesel (Bouaid et al., 2009). Some studies indicate that higher sulphur contents may beneficially affect the oxidation stability of the fuel blends (McCormick & Westbrook, 2007; Sirviö et al., 2016). Sulphur is an essential compound for living organisms. For a long time, organic sulphuric compounds, like glutathione, have been well known of their action to protect cells from free radicals and reactive oxygen compounds (Meister & Anderson, 1983). It has also been shown that glutathione can reduce the lipid peroxidation caused by reactive oxygen radicals (Roxas et al., 1997). In other words, an example of the anti-oxidative effect of sulphur compounds can be found from biochemistry. Biodiesel oxidation is a complex process of radical chain reactions. Hydroperoxides are formed first during degradation and they react further to form secondary oxidation products (Fattah et al., 2014). In living organisms and fuel blends, the reaction environments and reaction chains differ and it cannot be stated that the phenomenon is the same. Still, there is an interesting similarity and it needs to be studied further.

To investigate how the sulphur of fossil diesel may affect the OSI and other properties of biodiesel-fossil fuel blends, fuel blends were prepared having different sulphur contents. In Europe, the maximum FAME content in diesel fuel is 7 vol% according to the EN 590:2013 (SFS-EN 590:2013, 2013) but higher percentages are also available and targeted around the world. For example in the United States, the 20% blend fraction is becoming more common. B20 and B30 fuels do even have their own Standard, EN 16709, which specifies the quality of those fuels with a high biodiesel content (SFS-EN 16709:2015, 2015). That is why B20 fuels were chosen to be investigated in this study. Fuel blending may, however, cause operating risks. The fuels need to be stable and compatible with engine and other blended fuels. Several studies have been made to figure out how biodiesels and their blends affect the lifetime of the engines. A review of short run tests reports that biofuels can replace conventional diesel fuel but a long run analysis is needed for assessment of the engine life. Problems that may occur are carbon deposition, lubricating oil dilution, piston ring sticking and injector nozzle choking (Patel et al., 2016).

In this study, the aim was to find out how sulphur affects the storage stability of the prepared fuel blends. It was interesting to see if mixing two common non-road fuels could be beneficial for both the environment and storage stability of fuel in developing countries. It is clear, that adding non-sulphuric biodiesel to fossil fuel will decrease their blends' sulphur content and reduce emissions and other adverse effects. But will the high sulphur content enhance the storage stability of the biodiesel?

MATERIALS AND METHODS

In the current study, the parameters were investigated that correlate with the storage stability of the fuel blends. Four B20 fuel samples were compared consisting of 20 vol% biodiesel and 80 vol% fossil diesel. All of the samples were prepared by mixing rapeseed methyl ester (RME), diesel fuel oil (DFO) containing 6.6 mg kg^{-1} sulphur, and high sulphuric diesel solvent. Different amounts of sulphuric diesel solvent were added into the B20 samples. The achieved sulphur concentrations were 6 mg kg^{-1} (B20 1), 76 mg kg^{-1} (B20 2), 149 mg kg^{-1} (B20 3), and 226 mg kg^{-1} (B20 4). The aim was to figure out how the storage stability of the fuel blends change as a function of time when the samples were stored in stable conditions (in dark, at 20°C) for 12 weeks.

The fuel samples were made by mixing three different compounds; RME, DFO and ICP diesel solvent, which contained 1000 mg kg^{-1}, sulphur. The total volumes of the samples were 500 ml and the dilution was carried out as presented in Table 1.

Table 1. Dilution ratios of the B20 samples.

Sample	RME (ml)	DFO (ml)	Diesel solvent (ml)
B20 1	100	400	0
B20 2	100	360	40
B20 3	100	320	80
B20 4	100	280	120

The analyses carried out for these four samples were the oxidation stability (OSI), acid number (AN) and kinematic viscosity (KV). The samples were analysed straight after mixing and after 4, 8 and 12 weeks of storage. The storage conditions were a dark cupboard at room temperature (around 20°C). The OSI, AN, and KV of both RME and DFO were determined before mixing them together and adding high sulphuric diesel solvent. For the prepared sulphur containing B20 samples, the sulphur contents were measured straight after mixing. After the whole storage time, the elemental analysis (CHNO) was carried out for the samples.

RME used as the bio component in the fuel blends was a product of ecoMotion GmbH, Germany. RME is ISCC EU certified and meets Standard EN14214:2012 (SFS-EN 14214:2012, 2012). Fuel had been produced three years before this study and delivered to the University of Vaasa in 2012. Still, RME fulfilled the requirements of Standard EN 14214:2012 in terms of the properties measured in this study. The ester content of RME was not measured. Any information about the most likely added antioxidant of RME was not available.

DFO was a product of Neste and it had been produced in Finland. It did not contain any bio component before mixing it with RME. DFO contained 6.6 mg kg^{-1} sulphur.

CONOSTAN Premisolv™ ICP Solvent containing 1000 mg kg^{-1} sulphur was a product of Conostan®, Canada. Conostan® is a division of SCP SCIENCE. According to the safety data sheet of this solvent, it contained sulphur as n-dibutyl sulphide in diesel fuel.

Acid number

The acid number of the blends was analysed by a titrator Metrohm Titrando 888. The method is a potentiometric titration method. The sample is diluted with iso-propanol and titrated by potassium hydroxide. The measurement was produced according to Standard EN 14104:2003 (SFS-EN 14104, 2003).

Oxidation stability

The oxidation stability was measured by a Biodiesel Rancimat 873 instrument. The method describes the accelerated oxidation stability of biodiesel. The sample is heated and air flow is conducted through it. The vaporizing compounds of the sample drift with air into water and the conductivity of the water is measured. The end point is achieved when the conductivity increase is at its highest. The method is described in Standard EN 15751:2014 and according this Standard the maximum induction period is 48 hours (SFS-EN 15751, 2014).

Viscosity

The viscosities were measured by a Stabinger SVM 3000 rotational viscometer. The measurement is based on torque and speed measurements. The device calculates the dynamic viscosity from the rotor speed. The device also has a density measuring cell that employs an oscillating U-tube principle. The kinematic viscosity is calculated automatically based on these measurements (Anton Paar, 2012).

Elemental analysis

The elemental analysis was measured by a Thermo Scientific Flash 2000 instrument. It determines the mass fractions of carbon, hydrogen, nitrogen and oxygen. Sulphur may also be analyzed in case its amount is high enough. The analysis was produced according to Standard ASTM D5291 (ASTM D5291-16, 2016).

Sulphur content

The sulphur contents were measured by a Thermo Scientific, iCAP 6500 duo instrument. In this method, the samples are decomposed by an ultrasonic oven and transformed from organic to water-soluble form. The solution is injected to spectrometers plasma. Calibration was made by the known concentrations of the standards. The defined standards (emission intensities in known concentrations) and the presence and concentration of the element are evaluated by comparing the intensity of the light to these standards. The method was an in-house method produced based on Standard ISO 10478 (ISO 10478, 1994).

RESULTS AND DISCUSSION

The analyses results related to storage stability are presented in Table 2 and elemental analyses results in Table 3. All the obtained results are arithmetic means of at least two replicate measurements. The OSI, AN and KV results are also depicted in Figures 1, 2 and 3, respectively, and the elemental analyses in Figure 4.

Table 2. The storage stability analyses results for DFO, RME and B20 fuels.

Property	DFO	RME	B20 1	B20 2	B20 3	B20 4
Oxidation stability (h)						
Fresh	72*	11	45	47	47	51
4 weeks			44	47	51	54
8 weeks			42	48	52	55
12 weeks		10	42	47	53	56
Acid number (mgKOH g^{-1})						
Fresh		0.19	0.07	0.06	0.06	0.07
4 weeks			0.06	0.06	0.06	0.06
8 weeks			0.07	0.06	0.08	0.07
12 weeks			0.07	0.07	0.07	0.07
Kinematic viscosity, 40°C (mm^2 s^{-1})						
Fresh	3.5	4.5	3.6	3.4	3.2	3.1
4 weeks			3.6	3.4	3.2	3.1
8 weeks			3.6	3.4	3.2	3.1
12 weeks			3.7	3.4	3.2	3.1

The relative standard deviations are: KV 1%, AN 7.9%, and OSI 4.5%. These had been determined for the analysis methods earlier. For the OSI results above 48 hours, the reproducibility is approximately 9.5 hours. The OSI results above 48 hours should be announced >48 hours according to Standard EN 15751.
*The measurement was stopped after 72 hours.

Table 3. Elemental analyses result for B20 fuels.

Property	B20 1	B20 2	B20 3	B20 4
C (m-%)	83.7	83.5	84	83
H (m-%)	13.2	13.2	13.8	13.7
N (m-%)	0.2	0.2	0.2	0.2
O (m-%)	2.2	2.2	2.2	2.2
S (mg kg^{-1})	6	76	149	226

The relative standard deviations for these methods were not determined.

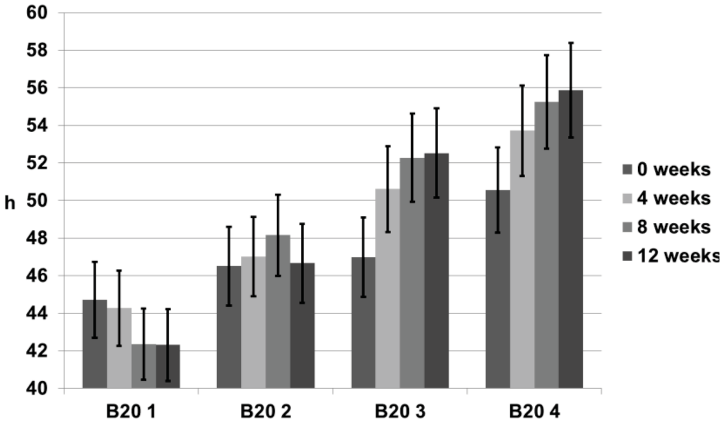

Figure 1. Oxidation stability results for B20 fuels. The sulphur concentrations were 6 mg kg^{-1} (B20 1), 76 mg kg^{-1} (B20 2), 149 mg kg^{-1} (B20 3), and 226 mg kg^{-1} (B20 4).

Fig.1 shows how the oxidation stability of the samples changed during 12 weeks:

- B20 1, decreased 5% (from 46 to 42 h)
- B20 2, remained almost constant (varied between 47 and 48 h)
- B20 3, increased 12% (from 47 to 53 h)
- B20 4, increased 10% (from 51 to 56 hours).

For the OSI results of above 48 hours, the reproducibility is approximately 9.5 hours. According to Standard EN 15751:2014, the OSI results of above 48 hours should therefore be announced as >48 hours. In this study, the trend in the results was, however, so clear that the actually measured values were chosen to announce.

It should also be noted that, as fresh, the OSI was the longer, the higher was the sulphur content.

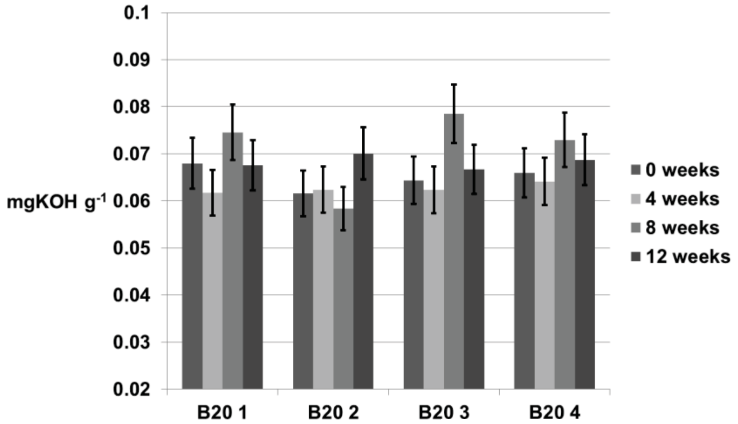

Figure 2. Acid number results for B20 fuels. The sulphur concentrations were 6 mg kg^{-1} (B20 1), 76 mg kg^{-1} (B20 2), 149 mg kg^{-1} (B20 3), and 226 mg kg^{-1} (B20 4).

Fig. 2 shows that the acid numbers of all the samples remained within 0.06-0.08 mgKOH g^{-1} during the whole study. There were no significant differences between the samples and the results did not change during the storage. Thus, the sulphur content did not either seem to affect the AN.

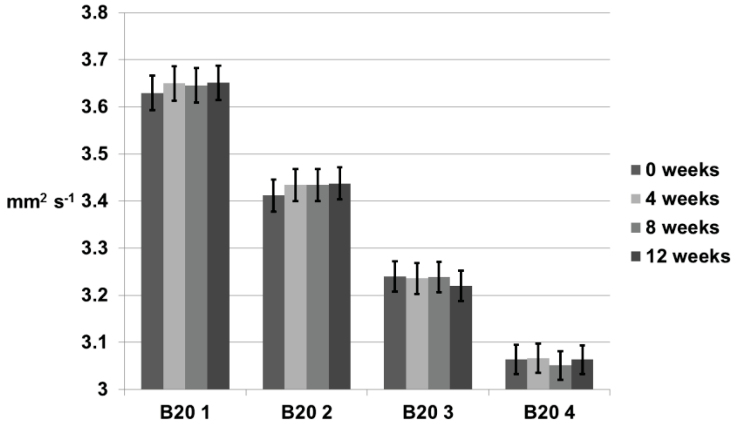

Figure 3. Kinematic viscosity results for B20 fuels. The sulphur concentrations were 6 mg kg^{-1} (B20 1), 76 mg kg^{-1} (B20 2), 149 mg kg^{-1} (B20 3), and 226 mg kg^{-1} (B20 4).

Fig. 3 shows that the kinematic viscosities remained quite constant during the storage time of 12 weeks for all the samples. The differences between the samples were due to different mixing ratios. For the samples B20 2, 3 and 4, the diesel solvent containing sulphur lowered the KV in relation to its mixing ratio.

Pölczmann et al. (2016) studied the storage stability of diesel fuels containing biodiesel and made a mathematical correlation between a) the viscosity increase and oxidation stability decrease and b) between the acid number increase and oxidation stability decrease. As a result of their study, the authors conclude that the found correlation could reduce the number of needed analyses in biodiesel quality follow-up. According to them, the kinematic viscosity and acid number could be estimated based on the oxidation stability result (Pölczmann et al., 2016).

However, this was not clearly seen in the present study because no correlation was observed between the oxidation stability and acid number nor kinematic viscosity. In the current study, the amount of samples was, though, small and the timescale was shorter (12 weeks against 150 weeks in Pölczmann et al.).

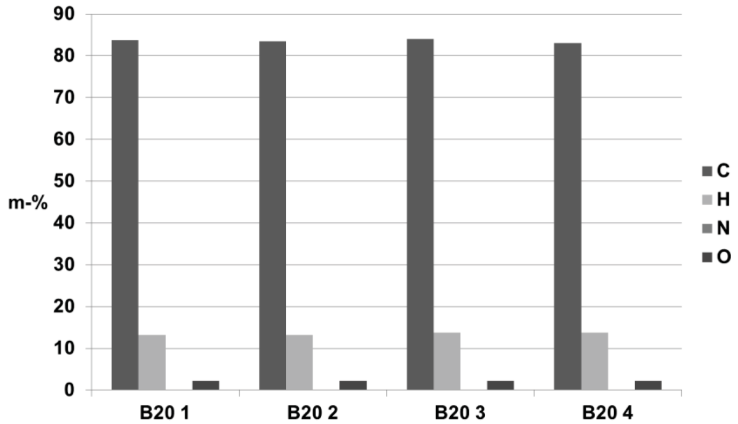

Figure 4. Elemental analyses result for B20 fuels. The sulphur concentrations were 6 mg kg^{-1} (B20 1), 76 mg kg^{-1} (B20 2), 149 mg kg^{-1} (B20 3), and 226 mg kg^{-1} (B20 4).

Fuels mainly consist of carbon and hydrogen and some small quantities of sulphur, nitrogen, and oxygen (Riazi, 2005). Even at its highest in the present study, the amount of added sulphur was not high enough to cause differences in elemental contents of the fuels, Table 2, Fig. 4. It can, thus, be assumed that adding diesel solvent did not affect the elemental composition of the samples. It needs, however, to be kept in mind, that the elemental contents are approximate. The measured sulphur values of 6, 76, 149 and 226 mg kg^{-1} were very close to the calculated values of 5, 78, 151 and 226 mg kg^{-1}.

The form of the sulphur compound is determining. In fossil fuel, sulphur can be found in cyclic compounds such as thiophenes and benzothiophenes as well as in noncyclic compounds such as mercaptanes and sulphides (Ma, 2010). In this study, the added sulphur was n-dibutyl sulphide which is a simple hydrocarbon chain that contains sulphur in the middle, and it is a noncyclic compound, Fig. 5.

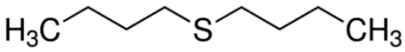

Figure 5. Structure of n-dibutyl sulphide. (Sigma Aldrich, 2016)

In the presence of water, sulphur may form sulphuric acid and the acids will promote oil thickening and oxidation, e.g., in lubricating oils (Folkson, 2014). This phenomenon may also occur within fuels. Biodiesel is hydrophilic and it is possible that its moisture content will increase during three years of storage. The water content of RME was not measured. Most likely, based on the other analysis results, it can be assumed that no water was present in the studied samples and the increasing amount of sulphur did not affect adversely the oxidation stability, quite the contrary.

McCormick & Westbrook (2007) mentioned that sulphur compounds can work as antioxidants and the same conclusion is also supported by the studies of Karavalakis et al. (2010) and Sirviö et al. (2016). Sirviö et al. (2016) was a prestudy in relation to this research theme. In that study, the B20 sample containing more sulphur loosed its oxidation stability less than the B20 sample containing less sulphur. Karavalakis et al. have found that the oxidation stability behaviour of biodiesel blends is a very complicated process. They say that the most important factors affecting the blends' oxidation are the biodiesel composition and used antioxidants. Additionally, according to McCormick & Westbrook (2007), the stability of the biodiesel is the most important factor from the point of view of the blends storage stability.

In this study, the biodiesel and fossil diesel were the same in all samples but the mixing ratios of the diesel solvent containing sulphur varied from 0 (B20 1) to 22% (B20 4). Most likely, the reason for the difference in the oxidation stability of the fresh blend samples was, thus, the different sulphur content. For the diesel solvent, the oxidation stability was not measured but the oxidation stability of the DFO was high (measurement was stopped at 72 hours). The DFO quality was, thus, not a threat to the stability of the blends.

As mentioned above, the decrease in OSI was 5% for the sample B20 1 while the oxidative stability increased by 12 and 10% for the samples B20 3 and 4, respectively. This may indicate the antioxidative effect of sulphur. To prove this thesis, again indicated by the current study, the chemistry of the fuel blends and organic sulphur should be studied more detailed.

Karavalakis et al. (2011) showed in another study, that even a 4-6 weeks storage time may cause OSI to decrease below the 20 hours' limit due to natural ageing. The 20 hours' limit is set in Standard EN 590:2013 for automotive diesel fuels. In this study, the OSI of all the samples remained clearly above the 20 hours' limit for 12 weeks. The other measured properties were also at a proper level though the adopted RME was produced 3 years before this study.

CONCLUSIONS

The aim of this study was to find out if increasing sulphur content is beneficial for storage stability of the fuel blend. Four B20 fuel samples were produced consisting of 20 vol% biodiesel and 80 vol% fossil diesel. All the samples were prepared from rapeseed methyl ester (RME), diesel fuel oil (DFO) containing 6.6 mg kg^{-1} sulphur, and a high sulphuric diesel solvent (n-dibutyl sulphide in diesel fuel). The measured sulphur contents of the samples were 6, 76, 149 and 226 mg kg^{-1}. The effects of the sulphur content on the oxidation stability, acid number (AN) and kinematic viscosity (KV) of the blends were investigated. Based on the study, the following conclusions could be drawn:

- There is a reason to assume that the sulphur may be favourable to fuel blends' storage stability. The decrease in oxidation stability was 5% for the sample B20 containing the lowest amount of sulphur while the other samples behaved differently. During the storage, the oxidation stability of the sample containing 76 mg kg^{-1} sulphur remained quite constant and for the samples containing 149 and 226 mg kg^{-1} sulphur, the OSI increased by 12 and 10%, respectively. This may indicate the antioxidative effect sulphur has. The phenomenon and chemistry should, however, be studied more thoroughly and for a longer period to confirm this statement.

- The other properties related to storage stability, i.e., AN and KV seemed not to vary much within the storage time of 12 weeks. Any clear correlations between the oxidation stability and the acid number and kinematic viscosity were not observed in the examined samples.

ACKNOWLEDGEMENTS. The authors would like to acknowledge Mr. Jukka Nuottimäki, Ms. Jenni Nortio and Mr. Markku Kuronen from Neste for their expertise and comments for the study. The diesel fuel utilized in this study was also supplied by them. The biodiesel of this study was purchased within the TREAM project which was funded by the Finnish Funding Agency for Technology and Innovation (TEKES). The authors would also like to thank Mrs. Pia Välimäki for her indispensable help with the analyses.

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Publication V

CIMAC 2016 | 025

B20 FUEL EFFECTS ON ENGINE LUBRICATING OIL PROPERTIES

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ABSTRACT

Lubricating oil has several functions in an engine. It decreases friction, cools down the engine, acts as an insulation material and bonds contaminants. During recent years, the use of various renewable fuels in different engines has steadily increased, in particular in the form of different blends of fossil and renewable fuels. It has been assumed that these new fuels may affect lubricating oils in a different way compared with conventional fossil fuels. Indeed, biodiesels have often been observed to lower lubricant oil quality and to shorten the oil draining interval. As an example, the kinematic viscosity of the lubricating oil has been reported to decrease linearly with the percentage of fuel in the oil. Oil dilution by the fuel, the fatty acid methyl ester percentage, total acid number and the change of wear metals are factors that are followed to find out if and to what extent the new fuels or their blends have affected the oil.

At the moment, the Standard EN 590 allows a 7% increase of biodiesel in fossil fuel in automotive use. Nevertheless, even higher percentages are in use, for instance in agricultural machines. In automotive use, the allowed biodiesel content also seems to be increasing.

In this study, a fuel mixture containing 20 Vol-% biodiesel and 80 Vol-% fossil diesel (later in the text B20) was used in an endurance engine test and the lubricating oil sample was analyzed fresh and after 207, 357 and 553 hours of engine operation. The main objective was to find out how long-term use of high-quality B20 fuel affects the engine lubricating oil. During the 500 hours' study, small changes in wear metals, total acid number and viscosity were detected, but as a whole, B20 had only a minor effect on the lubricating oil. The results thus showed that high-quality lubricating oil can be used for more than 500 hours of engine operation without any notable problems when commercial B20 fuel is used as the engine fuel.

INTRODUCTION

There is significant pressure to increase renewable fuel usage in all kinds of internal combustion engines. However the fuel compatibility in different perspectives needs to be taken into account with regard to renewable fuels, especially FAME type biodiesels. Biodiesels are the most studied group of biofuels and regardless of the challenges they present in terms of engine usage, they are still of great interest. They are low-priced and their availability is fairly widespread all over the world. The effects on engines and after-treatment systems of neat B100 biodiesel and its blends have been widely investigated, and the effect depends on the biodiesel percentage or blend level used. Even low biodiesel blends may cause cumulative effects in the engine and slightly higher levels, B20 or B30, can be even more prone to cause insoluble formation and filter plugging than neat biodiesel. Neat biodiesel itself or as used for blend preparation should meet the specifications set in Standard EN 14214. The variability of non-standard fuel is a problem and constrictions in the blend or biodiesel use are often related to fuel quality. [1]

The use of renewable fuels causes challenges for lubricant technology. It has been assumed that new fuels, especially FAME type biodiesels, may affect lubricating oils in a different way compared with conventional fossil fuels.

Biodiesel is less stable and less volatile than traditional diesel. Especially in diesel fuel blend, the lower volatility will cause the biodiesel to accumulate in higher concentrations in the oil than will mineral diesel, and it is claimed to be the main reason for problems in vehicle operation when using biodiesel. The fuel dilution may increase the acidity and make the oil thicker, produce a higher total acid number and kinematic viscosity, and e.g. lead to oil degradation and further to the corrosion of engine parts, piston deposits, sludge or wear. This all shortens the oil changing intervals. [2], [3]

Lubricating oil has several functions in an engine. Modern lubricant oils protect the engine and ensure prolonged engine lifetime. Engine durability is partly protected by inhibiting wear. This happens via hydrodynamic film lubrication between surfaces by the lubricant oil itself, or boundary lubrication by anti-wear additives in the oil which protect surfaces. Lubricant oil also prevents deposit formation by combustion products. The risk areas for this are the piston ring area and its grooves. Deposits may also block oil filters. Piston skirt and ring groove deposits are often reported to occur in neat biodiesel engines. [4] Lubricant oil ages over time and it may become acidic. Acidity can also increase through contamination caused by unburnt fuel or combustion gases. Both of these may cause corrosion in engine parts, and the lubricant oil should work to prevent it. Corrosion prevention and lubricant oil stability may be enhanced by additives.

In addition to wear prevention, other basic functions of lubricant oil are to improve fuel economy and assist in sustaining a low level of emissions. The engine and fuel economies are increased directly by reducing the viscosity of the fluid and the friction of the surfaces and by handling oxidation and contaminants. A lower amount of contaminants decreases soot formation in diesel combustion. The effect of lubricant oil on good emission performance is through its ability to decrease wear and formation of deposits. [2] The lubricant oil also cools down the engine, especially the piston, and acts as an insulation material in hot regions of the engine. It also maintains gas and oil leakages at the lowest possible level. [5]

At the moment, the Standard EN 590 allows a 7% increase of biodiesel in fossil fuel in automotive use. Nevertheless, even higher percentages are in use, for instance in agricultural machines. In automotive use, it seems that the allowed biodiesel content will also increase in the future.

Against this background, the main objective of the current study was to find out how long-term use of high-quality B20 fuel affects the engine lubricating oil. In this study, B20 fuel was used in an endurance engine experiment and the lubricating oil sample was analyzed fresh and after 207, 357 and 553 hours of engine operation.

EXPERIMENTAL

MATERIALS - The lubricant used during the engine operating was commercially available Valtra Engine CR-4, 10W-40 (ACEA E9, API CJ-4). The commercially available biodiesel fuel fulfilled the requirements of Standard EN 14214 except for the iodine value, which was slightly above the limit of 130 mg I/100 g. The raw material of biodiesel was soy bean oil and the supplier of the fuel was Archer Daniels Midland Company, ADM, USA. Fossil diesel was purchased from Teboil in Vaasa, Finland. The experimental engine was a high-speed, turbocharged, intercooled AGCO POWER non-road engine.

METHODS - The engine experiment was a long-term one; the total duration was 553 hours. The aging run was carried out by using B20 as fuel. The engine was equipped with a common-rail injection system and it fulfilled the EU Stage 3B/US Tier 4 interim emissions legislation. The test engine specification is presented in Table 1. The average power during the 553 hours test cycle was 41.0 kW.

Table 1. Test engine specification.

Engine	49AWI
Cylinder number	4
Bore (mm)	108
Stroke (mm)	134
Swept volume (dm3)	4.9
Rated speed (rpm)	2100
Rated power (kW)	103
Maximum torque with rated speed (Nm)	462[a]
Maximum torque with 1500 rpm (Nm)	583[a]

[a] Conformable to measured torques obtained with B20 fuel.

B20 fuel was produced by weighing and mixing at the University of Vaasa (UV), Finland. The fuel analyses were also produced at UV. The biodiesel Vol-% of the blend was determined in the laboratory by an in-house method which was based on the density measurement. The oxidation stability of B20 fuel was measured every second week during the experiment. The method was a Rancimat method, following Standard EN 15751. The acid number of the fuel was analyzed according to Standard EN14104. The element analyses were produced according to Standards SFS-EN 14538 and SFS-EN 14107, as well as the manufacturer's advice.

The condition of the lubricating oil was monitored at the operating hours of 0, 207, 357 and 553. The samples were analyzed in the laboratory of Fluidlab Oy, Turku, Finland. The methods used in the oil analyses are given in Table 1 in the section "Results". Based on the results of the analyses, the lubricating oil was not replaced during the 553 hour run. The temperature of the lubricating system was not monitored for scientific accuracy during the experiment. The total volume of the lubricating oil in the system was 8 liters. New oil was added to the system after 189, 256, 357 and 464 hours: 1 liter at a time. The total volume of the samples taken was 1 liter. The oil consumption was 0.12 g/kWh during the experiment.

This is a normal value for heavy-duty diesel engines, though slightly smaller values may also be achieved.

RESULTS

The results of the fuel analyses are presented in Table 2 and the oil analyses in Table 3. The properties that are known to indicate deterioration of the oil or had a notable change during the endurance experiment are described in the text and presented in the figures in more detail after the tables.

Table 2. Biodiesel content, acid number, element analyses and oxidation stability index results for B20 fuel specification. Blend 1.

B20 (SME)	
Property and unit	Result
Biodiesel content (V-%)	19.6[a]
Biodiesel content (V-%)	19.1
Acid number (mg KOH/g)	0.06
Na, K (ppm)	2
Mg, Ca (ppm)	2
P (ppm)	1
Zn (ppm)	<1
Cu (ppm)	<1
Pb (ppm)	<1
OSI (h)	29

[a] The value of biodiesel content (V-%) is an average of ten B20 blends.

The analyses results of the B20 fuel presented in Table 2 were quite typical of mixed fuel containing 20 Vol-% of biodiesel. Several batches of B20 fuels were prepared. The properties did not vary.

Table 3. Results of oil analyses.

			Operating hours			
Property	**Method**	**Unit**	0	207	357	553
Viscosity, kinematic (40 °C)	**ASTM D 445, DIN 51562**	**mm^2/s**	93	82	83	85
Viscosity, kinematic (100 °C)	**ASTM D 445, DIN 51562**	**mm^2/s**	14	12	12	12
Viscosity index	**ASTM D 2270, ISO 2909**		151	145	144	143
TBN	**ASTM D 664**	**mgKOH/g**	10.1	9.49	9.49	8.49
TAN	**ASTM D 664**	**mgKOH/g**	2.14	2.74	2.88	4.50
Oxidation	**JOAP**	**A/cm**	1	3	4	2
Nitration	**JOAP**	**A/cm**	0	0	0	0
Additives ICP	**ASTM D 5185, in – house**	**ppm**				
Calcium			2108	2308	2542	2760
Magnesium			4	4	7	12
Boron			16	10	8	7
Zinc			1090	1064	1169	1240
Phosphorus			934	865	937	966
Barium			0	1	1	1
Sulfur			3259	3712	3835	3844
Corroding metals ICP	**ASTM D 5185, in – house**	**ppm**				
Iron			1	11	17	22
Chromium			0	0	1	1
Tin			0	0	0	1
Aluminium			0	1	2	2
Nickel			0	0	0	0
Copper			0	13	49	420
Lead			0	5	5	6
Molybdenum			0	0	0	0
Contaminants ICP	**ASTM D 5185, in – house**	**ppm**				
Silicon			12	34	36	35
Potassium			3	6	8	9
Natrium			0	4	10	19
Water content	**ASTM D 6304 C**	**ppm**	140	30	70	30
Fuel dilution	**DIN 51451, JOAP**	**%**	1.18	0.38	<0.30	<0.30
Biodiesel content	**DIN 51451**	**%**	<0.30	<0.30	<0.30	<0.30
Soot content	**DIN 51452, JOAP**	**%**	<0.1	<0.1	<0.1	<0.1

The viscosity of the lubricating oil declined slightly during the 553 engine run hours. (Fig. 1.) However, the decline was reasonable, being 8.6 % (from 93 to 85 mm2) at the measuring temperature of 40 °C and 14.3 % (from 14 to 12) at 100 °C. The decline can be seen in Fig.1.

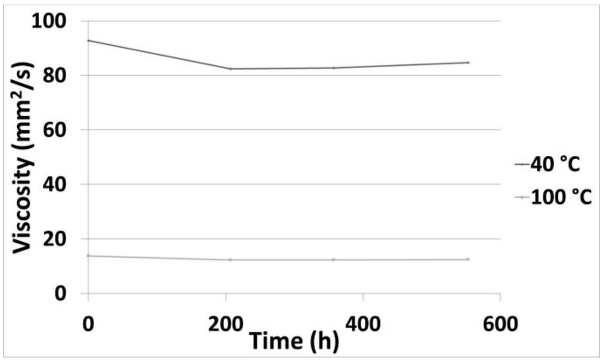

Fig.1. Viscosities of the oil at 40 °C and 100 °C after 0, 207, 357 and 553 hours.

The changes in total base number and total acid number of the oil are presented in Fig. 2. The total base number decreased from 10.1 to 8.49 mgKOH/g (15.9%) but the value after 553 hours remained quite high: values from 6 to 9 mgKOH/g are an acceptable level even for fresh engine oil. [6] The total acid number increased from 2.14 to 4.50 mgKOH/g, which in percentages meant a 52 % climb. Some references recommend changing the oil if the total acid number is over 2.50 mgKOH/g.[7] In this study, this limit would have been reached after 200 hours. However, the starting value of the total acid number was relatively high and at the end of the experiment run the remaining TBN-TAN was still about 4 mgKOH/g. It is generally accepted that the oil is operable when TBN-TAN has a positive value.

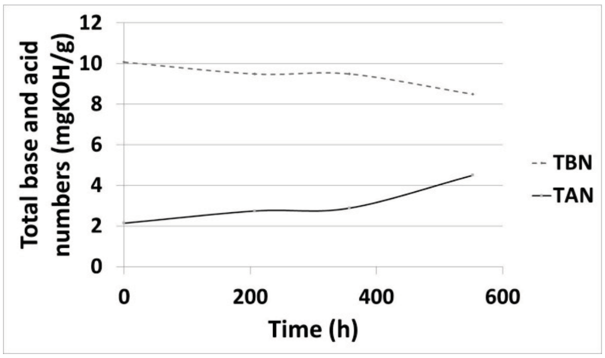

Fig.2. Total base number (TBN) and total acid number (TAN) of the oil after 0, 207, 357 and 553 hours.

The fuel dilution, FAME content and soot levels (Fig. 3) remained at a relatively low level during the engine running hours.

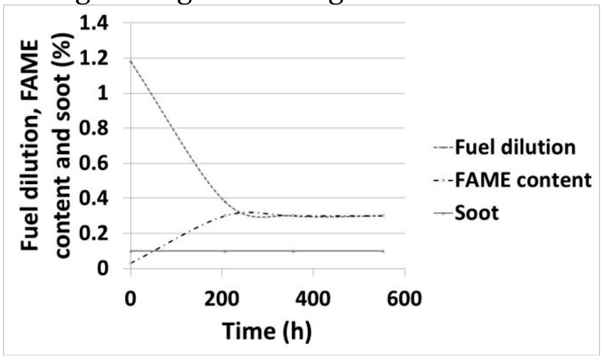

Fig.3. Fuel dilution, FAME content and soot content of the oil after 0, 207, 357 and 553 hours.

Of all the corroding wear metals, only copper and iron contents increased during the engine running hours, copper significantly. As it can be seen in Fig.4., the copper content of the oil was high, 420 ppm at the end of the experiment.

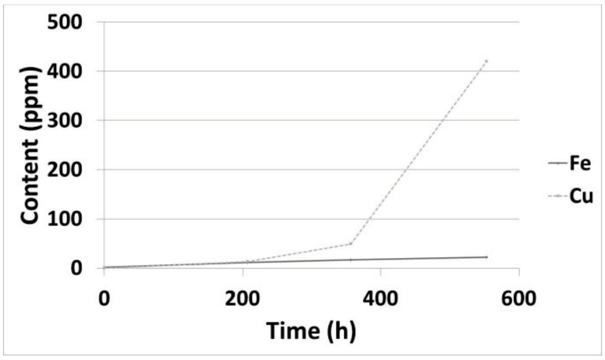

Fig.4. Iron and copper contents of the oil after 0, 207, 357 and 553 hours.

The results of the magnesium, sodium, silica and potassium contents are presented in Fig.5. All these contents increased slightly during the experiment. Magnesium is an additive, but the others are contaminants. The fuel contained small quantities of Mg, Na and K and it can be assumed that some of the increase in these elements in the oil came from the fuel.

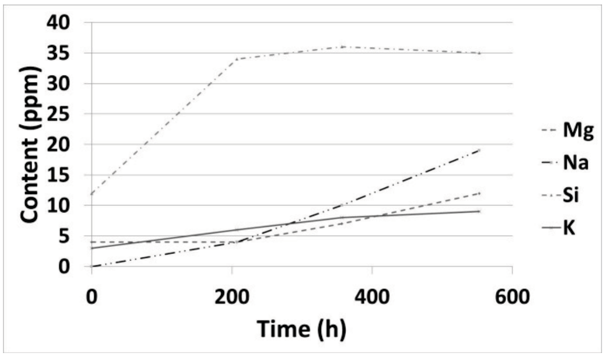

Fig.5. Magnesium, sodium, silica and potassium contents of the oil after 0, 207, 357 and 553 hours.

Sulfur, calcium, zinc and phosphorus are all lubricant oil additive metals. Their contents in the oil are presented in Fig.6. The contents of sulfur and calcium had notably increased after 553 hours. The contents of zinc and phosphorus stayed nearly constant during the experiment.

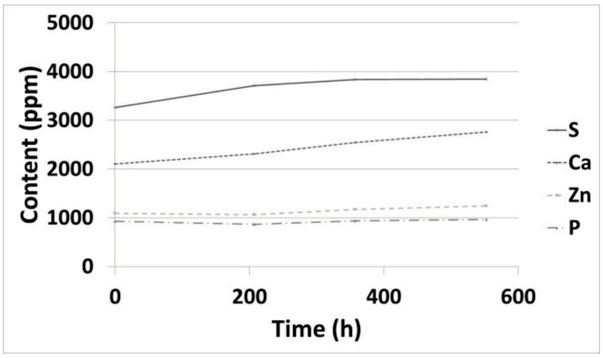

Fig.6. Sulfur, calcium, zinc and phosphorus contents of the oil after 0, 207, 357 and 553 hours.

DISCUSSION

Thornton et al. also studied the impact of 20 % soy bean methyl ester fuel blend on oil dilution. [3] They found higher results for biodiesel oil dilution than those obtained in the current study. Thornton et al. reported as high as 10.1 % biodiesel oil dilution and 4.1 % diesel oil dilution when the oil age was 158 hours. In the B20 study reported in this paper, the values of fuel dilution and FAME content did not increase during the 500 hours engine run as was presented in Fig. 3.

The acidity level is an important parameter to follow in long term engine run tests. The deposit formation is related to oxidized fraction of the oil and acidic products of combustion cause corrosion and wear in the cylinder and ring regions. [5] In the current study, the total base number (TBN) decreased from 10.1 to 8.5 mgKOH/g after 553 hours. The total acid number increased from 2.1 to 4.5 mgKOH/g in the same time range. The remaining TBN-TAN then gives 4.0, which is still quite a high value. Thornton et al. reported that the TBN decreased down to 4.5 mgKOH/g, but in their study the TAN remained almost constant at 2 mgKOH/g during the aging. The TBN-TAN at the end of their study then gives 2.5 mgKOH/g.

In this study, the amount of copper increased significantly between 357 h and 553 h, being 420 ppm at the end of this research. Other contaminants were not at such a high level. However, the high copper content probably did not indicate damage in bearings or other engine parts. In the case of damage, other wear metal contents, such as lead, would also have to increase. Thornton et al. did not report the amount of copper, but in their study the amount of iron was 12 ppm. In the study reported in this paper, the iron content was 22 ppm after 500 hours. Because no FAME was detected in the lubricant oil, the high contaminant content of copper did not correlate with biodiesel dilution in this study.

In both the studies discussed here, the conclusion is essentially the same: no obvious aging caused by biodiesel was detected. The changes in the lubricant oil during the aging time or engine running time were assessed to be normal lubricating oil aging and the engine oil change time was not yet exceeded.

Yüksek et al. studied the effect of 100 % biodiesel on lubricating oil. They reported ac. 60 % decrease in viscosity and a 29 % decrease in TBN when the oil properties after 150 hours of engine run were compared to petroleum diesel. The oil dilution was also relatively high:

3.5 % for biodiesel, while oil dilution did not appear at all in petroleum diesel fuel. [8] The study of Yüksek et al. thus suggests that B100 fuel may be more challenging for the lubricating system than B20 fuel. In the current study, however, the results of the analyses of oil properties were close to what can be assumed if the fuel is petroleum diesel.

For B10 fuel compared to petroleum diesel, some studies have concluded that, e.g. the oil dilution in the case of petroleum diesel can be even higher than with B10. The viscosity reduction in this B10 study was only minor.[9] However, for B30 fuel, some studies report a relatively high oil dilution result: 11 %, even though the other properties of the oil were close to those compared to petroleum diesel. [10]

It can be assumed that a good quality fuel containing biodiesel from 10 to 20 % does not have a degrading effect on the lubricating oil, but the higher the biodiesel percentage is, the higher is the risk of oil contamination, and hence an increase in the risk of the deterioration of other properties. The higher the biodiesel content in the fuel is, the more frequently oil analysis is recommended to be taken. [11]

It still needs to be remembered that some studies have reported a deterioration of lubricant oil quality in biodiesel engines after 600 hours of engine run. E.g. soot accumulation has been reported to increase strongly after 600 hours. Still, this same phenomenon has been found in petroleum diesel engines after 800 hours of engine run. [4] The endurance test of the present study was too short to prove this assertion.

CONCLUSIONS

Based on the results of the current 553 h study, the following conclusions can be drawn:

- B20 had only a minor effect on the lubricating oil.
- High-quality lubricating oil can be used for more than 500 hours of engine operation without any notable problems when commercial B20 fuel is used as the engine fuel. Compared to mineral oil based lubricating oil, synthetic, high-quality lubricating oil contains more efficient additives and is produced from base oil which is of a better quality. As a concrete consequence, the engine oil change time lengthens.

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Publication VI

Feasibility of new liquid fuel blends for medium-speed engines

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Abstract. Several sustainable liquid fuel alternatives are needed for different compression ignition (CI) engine applications to reduce GHG emissions and ensure proper primary energy sources for the engines. The reduction of fossil reserves together with the concern related to emissions does have promoted the research of alternative fuels in internal combustion engines (ICEs). In the present study, five different fuel blends were therefore thoroughly investigated. As the basic renewable fuel, rape seed methyl ester (RME) was used. It was blended with low-sulfur light fuel oil (LFO), kerosene, marine gas oil (MGO), and naphtha. Of these fuels, MGO was a circulation economy fuel, manufactured from used lubricants. Naphtha was renewable since it was a by-product of a renewable diesel production process using tall oil as feedstock. The blend of RME and naphtha was, hence, fully renewable and it has not been studied before. Besides with RME, naphtha was also blended with LFO. The main aim of the current study was to determine all the most important properties of the five fuel blends to create fundamental knowledge about their suitability for, in particular, medium-speed CI engines. The share of renewables within these five blends varied from 20 vol-% to 100 vol-%. The investigated and compared properties were the cetane number, distillation, density, viscosity, cold properties and lubricity. According to the results, all the studied blends may be operable in medium-speed engines when the proposed target of 35% of renewable share of the total energy consumption set by the European Parliament. Blending of new renewable fuels with more conventional ones relieves the technical transitional period so long as the availability of renewable fuels is limited. In this study, especially 100% renewable naphtha-RME blend is an interesting supplement in biofuel genre.

Keywords. Fuel blends, alternative fuels, renewable energy, medium-speed engines.

1. Introduction

The use of diesel or CI engines in heavy-duty transportation, off-road machines, power generation and shipment has spread all over the world. The engine technology is at a high level. The CI engines are very reliable stand-alone prime movers and they show the highest fuel conversion efficiency of all thermal prime movers within an output range of approx. 100 kW to 100 MW. Most of the engines still burn conventional liquid petroleum based fuels. In the mentioned applications, liquid fossil fuels will, most probably, also dominate for the next few decades.

Nevertheless, the share of gaseous and renewable liquid fuels increases rapidly since the greenhouse gas (GHG) emissions shall be strongly reduced in the near future. Renewable, alternative fuels could relieve the biased usage of fossil fuels. The energy efficiency and sustainability must be continuously improved since it further promotes the reduction of GHG emissions. [1] The European Parliament has proposed three key targets to increase cleaner energy and enhance the energy efficiency by the year 2030. The first one is to improve energy efficiency by 35%. The second target is to have at least 35% share for renewables in energy consumption and the third one is to reach at least a 12% share of energy from renewable sources in transport. [2]

The pollutant exhaust emissions of CI engines are already strictly limited. The most stringent standards concern the on-road engines but even the off-road and power plant engine legislation is very tight. Recently, the emissions limits of marine engines have also become stricter, first the limits of oxides of nitrogen, but now even the sulphur and particulate matter limits. For the EU inland waterways, the pollutant emissions must already be strongly reduced, also including the particulate number emissions. The development of the emissions legislation, thus, tightly guides the engine development and simultaneously directs the transfer from fossil fuels to more sustainable alternative fuels.

On the other hand, the fuels must be cost-effective. Many countries and regions prefer local fuels to increase the self-sufficiency of the energy generation. The production of renewable electricity, e.g. wind or solar power, increases globally, but for a large part it is highly intermittent. The role of conventional energy production is to keep the electricity grids in balance. Engine-driven power plants suit extremely well to this task since the plants can be started, loaded and stopped very quickly. Gas engines are one favorable option but the availability of gaseous fuels is still limited.

Several sustainable liquid fuel alternatives are therefore needed for different CI engine applications to reduce GHG emissions and ensure proper primary energy sources for the engines. The reduction of fossil reserves together with the concern related to emissions does have promoted the research of alternative fuels in ICEs. In theory, those fuels are able to diminish the emissions and several advantageous results have already been obtained in practice. To ensure the positive progress in the energy security and sustainability, alternative fuels need to be increasingly available.

For CI engine applications, one reasonable solution is to use various blends of renewable and fossil liquid fuels until the availability of renewable fuels reaches the sufficient extent. Together with special renewable fuels, fuel options originating from circular economy can also be blended with conventional fuels. For instance in Finland, the government has targeted to promote circular economy, which in fuel production means that waste greases and cooking oils plus lubricating oils can be used as fuel raw material.

To be able to promote the transit from conventional fossil fuels to renewable alternatives, a large amount of additional research is required about various alternative fuels and in particular about their blends with conventional fuels. Before engine experiments, a lot of novel information has to be gathered about the blend properties through several fuel analyses.

In the present study, five different fuel blends were therefore thoroughly investigated. As the basic renewable fuel, RME was used. It was blended with low-sulfur LFO, kerosene, MGO, and naphtha. Of these fuels, MGO was a circulation economy fuel, manufactured from used lubricants. Naphtha was renewable since it was a residue of a renewable diesel production process using namely tall oil as feedstock. The blend of RME and naphtha was, hence, fully renewable. Besides with RME, naphtha was, however, also blended with LFO.

The main aim of the current study was to determine all the most important properties of these blends to create fundamental knowledge about their suitability for, in particular, medium-speed CI engines. The measured and analyzed properties were the cetane number, distillation curve, density, kinematic viscosity, cold properties and lubricity. Even though the primary focus was on the blend suitability for marine and power plant engines, the results can for a large part also be exploited when selecting sustainable options for off-road engine applications.

2. Materials and methods

2.1 Fuels

Rapeseed methyl ester (RME) was a product of ASG Analytik-Service Gesellschaft mbH, Germany. It contained 1000 mg/kg of butylated hydroxytoluene (BHT) as antioxidant and it was delivered to the University of Vaasa (UV) in January, 2017. RME fulfilled the requirements of Standard EN 14214:2012 [3].

Naphtha was a product of UPM, Finland. It is a residue of the manufacturing process for renewable diesel based on wood and forest residues via tall oil. Naphtha was delivered to the UV in February 2017.

Light fuel oil (LFO) was a product of Oy Teboil Ab, Finland. It was sulphur free, winter grade diesel and it was delivered to the UV in September 2016. LFO fulfilled the requirements of Standard EN 590:2013. [4]

Kerosene was a product of Neste, Finland. It was delivered to the UV in September 2016.

Marine gas oil (MGO) was a product of STR Tecoil, Finland. It was marine fuel produced from recycled lubricating oils and it was delivered to the UV in September 2016.

Table 1 shows the studied fuel blends and their blending ratios. Table 2 shows the analyses results of the neat fuels received from the suppliers.

Table 1. Fuel blends and their blending ratios.

Fuels	Blending ratio (vol-%)
LFO+RME	80:20
Kerosene+RME	80:20
MGO+RME	80:20
RME+Naphtha	80:20
LFO+Naphtha	80:20

Table 2. The analyses results of the neat fuels.

Parameter	Method	RME	LFO	Naphtha	Kerosene	MGO
Density (15°C), kg/m^3	EN ISO 12185	883.2	826.7	722.1	787.3	842.5
Kinematic viscosity (40°C), mm^2/s	EN ISO 3104	4.49	1.84	0.50	0.94	7.69
Flash point, °C	EN ISO 2719	179	63	20	38	110
CFPP, °C	EN 116	-14	-45			-13
Sulphur content, mg/kg	EN ISO 20884/ EN ISO 20846	<5	8.3		1000	<100
Cetane number	EN 15195	53	52	34	41	68
Sulphated ash (775°C), % (m/m)	ISO 3987	<0.001		0.005	0.001	<0.001
Water content, mg/kg	EN ISO 12937	<30	68		35	22
Total contamination, mg/kg	EN 12662:1998	20	1.5			
Copper strip corrosion	EN ISO 2160	1	1a			1a
Oxidation stability, h	EN 14112	12				
Oxidation stability, g/m^3	EN ISO 6245		1			5
Cloud point, °C	EN 23015	-3	-29	<-20	<-20	-10
Acid value, mg KOH/g	EN 14104	0.49			0.002	
Iodine value, g I/100g	EN 16300	110.8				
Ester content, %(m/m)	EN 14103:2015	98.5				
Linolenic acid content, %(m/m)	EN 14103:2015	8.7				
Phosphorus content, mg/kg	EN 14107	<4				
Alkali content (Na+K) mg/kg	EN 14538	<1				
Metal content II (Ca+Mg)	EN 14538	<1				

2.2 Methods

Several properties were determined for the selected fuel blends to assess how suitable the blends are for CI engines. Below, the analysis methods of the properties are described.

Cetane number. The cetane number (CN) describes the ignition quality of the fuel. Both physical and chemical properties are taken into account in the determination of the CN. It can be used to consider if alternative fuel is applicable to CI engines. One way to measure it is the ignition quality tester, IQT. In this instrument, the fuel is injected into a heated chamber which has been filled with compressed air. The ignition delay is measured and the CN is calculated based on it. [5, 6] In this study, cetane numbers were analysed by the IQT according to Standard EN15195 [7].

Oxidation stability. The oxidation stability (OSI) is one of the most important properties for biofuels. FAME oxidizes easily compared with petroleum diesel fuel. The test methods for petroleum diesel fuel, FAMEs and their blends differ. [6, 8] The oxidation resistance is determined by a procedure where the change of the inherent stability is measured under accelerated oxidizing conditions. The methods for analysing the oxidation stability of the fuels provide a basis for the estimation of their storage stability.

In this study, the oxidation stability was measured by a Biodiesel Rancimat 873 instrument. The method is described in Standard EN 15751:2014. According to this standard, the maximum induction period is 48 hours. [9] The OSI was not measured for the LFO+naphtha blend.

Cold properties. The cold flow performance of a diesel fuel depends on its composition. It is described by different critical temperatures based on the formation of wax crystals as the fuel is cooled during the test. Paraffins with chain lengths typically ranging from 10 to 30 carbon atoms have a limited solubility in the fuel. When the fuel is cooled, the paraffins heavier than C15 will come out of solution as wax. This can block fuel lines and filters and cause malfunction at low temperatures. [5] Paraffins are advantageous for the cetane number and other combustion properties and all of them cannot be removed from the fuel [6]. The cold flow properties are evaluated by three different methods: cloud point, pour point, and cold filter plugging point (CFPP).

Cloud point. The cloud point is a temperature at which the wax first becomes visible when the fuel is cooled in a test procedure. It is a subjective measure because it is evaluated by the human eye. [8]

Pour point. The pour point is a temperature at which the wax crystals grow and the fuel forms gel which stops flowing [8].

CFPP. The CFPP is the lowest temperature at which 20 ml of fuel will pass through a fine wire mesh screen of 45 micrometres nominal aperture in less than 60 seconds. The fuel is cooled and checked at every 1°C intervals. This is the most accepted method of these three. [8]

In this study, the cloud points were measured according to Standard ASTMD7689, pour points ASTMD7346 and CFPPs EN116 [10, 11, 12].

Distillation. The distillation curve describes the temperature range where the mixture of hydrocarbon vaporizes when the mixture is heated slowly at the atmospheric pressure [6]. The light fraction of fuel is distilled first and is, thus, more volatile than the heavy fraction. The volatility affects the development of the combustion. The heavy fraction portion is the last part to distillate. It may not be too broad because the fuel atomization into fine droplets is important to the evolution of combustion and this is diminished if the heavy fraction is too large. The heavy fraction content also affects emissions. [5] In this study, the distillation was produced according to Standard EN ISO 3405 [13].

Density. The air-fuel mass ratio is the determining value in the combustion chamber. The variation of fuel density affects the mass of the fuel injected because the injection is usually controlled by setting the injection system to deliver a predetermined volume of fuel. That is the reason why the density is controlled within a narrow range. In modern engines, it affects power, fuel consumption and emissions. A lower content of heavy aromatics usually means a lower fuel density and this may contribute to reducing HC, CO and particulate emissions. A minimum value for the fuel density is given to ensure a sufficient maximal power from an engine that has a volume-based fuel flow control. A maximum value of density is given to help to avoid the smoke formation at full load. The smoke would result from the increase in the average equivalence ratio in the combustion chamber as smoke is formed by incomplete combustion. The density is dependent on the temperature. [5, 8]

Viscosity. The kinematic viscosity of the fuel depends on the fuel density and factors affecting the fuel viscosity are similar to those affecting the density. The changes in viscosity cause direct changes on engine operation. Too viscous fuel increases pumping losses in the injection system and the injection pressure at the pump end may increase when conventional in-line pumps are adopted. All this may cause disturbances in the combustion process. On the other hand, a too low viscosity may cause the injection pump to seize. Too low viscosity may also increase the leakage at the injection pump and injector tips. This affects the pressure and delivered volume at the injector and may cause fuel leakage into the cylinder late during expansion. It is important to remember that even when the fuel is modified to adjust the viscosity, it must still meet the viscosity specifications. [5, 8]

In the present study, the densities and viscosities were measured by a Stabinger SVM 3000 rotational viscometer according to Standard ASTM D7042 [14, 15].

Flash Point. The flash point is a minimum temperature where a fuel forms a flammable mixture with air under a fixed condition. It is the lowest temperature at which the fuel can vaporize to form an ignitable mixture in air. It has no direct effect on the engine performance but it is used to quantify the flammability hazard of the fuel in storage and distribution. [5, 8] The flash points were measured according to Standard ASTM D93-A [16].

Lubricity. Diesel fuel needs to have sufficient lubricity to ensure the integrity of the fuel system. Naturally, there are low concentrations of polar compounds in the diesel fuel and they lubricate the engine high-pressure fuel pumps by forming a protective layer on the metal surfaces. The lubricity is measured by the size of the wear scar in a high-frequency reciprocating rig (HFRR) test. A hardened steel ball vibrates in loaded contact with a hardened steel plate immersed in the fuel tested. The wear scar has to be equal to or smaller than 460 micrometers. [5] In this study, the lubricity was measured according to Standard EN ISO 12156-1 [17].

3. Results and discussion

The results of the analyses are presented in Table 3 and Figure 1.

Table 3. Results of the properties of blends and neat rapeseed methyl ester.

		Flash point, °C	OSI, h	Density, kg/m^3	Kinematic viscosity, mm^2/s	CFPP, °C	Cloud point, °C	Pour point, °C	Cetane number	Lubricity, HFRR, µm/60 °C
Sample	Blending ratio	ASTM D93-A	EN 15751	ASTM D7042	ASTM D7042	EN116	ASTM D 7689	ASTM D 7346	EN 15195	ENISO 12156-1
RME+Naphtha	80:20	20	15	850	2.75	-19	-9	-18	52	174
LFO+Naphtha	80:20	20	-	805	1.37	-32	-29	-50	51	391
LFO+RME	80:20	67	42	837	2.24	-29	-21	-39	53	171
Kerosene+RME	80:20	43	69	807	1.26	-29	-30	-72	44	170
MGO+RME	80:20	125	42	853	6.83	-8	-5	-18	64	169
RME		170	13	883	4.51	-14	-5	-15	54	196

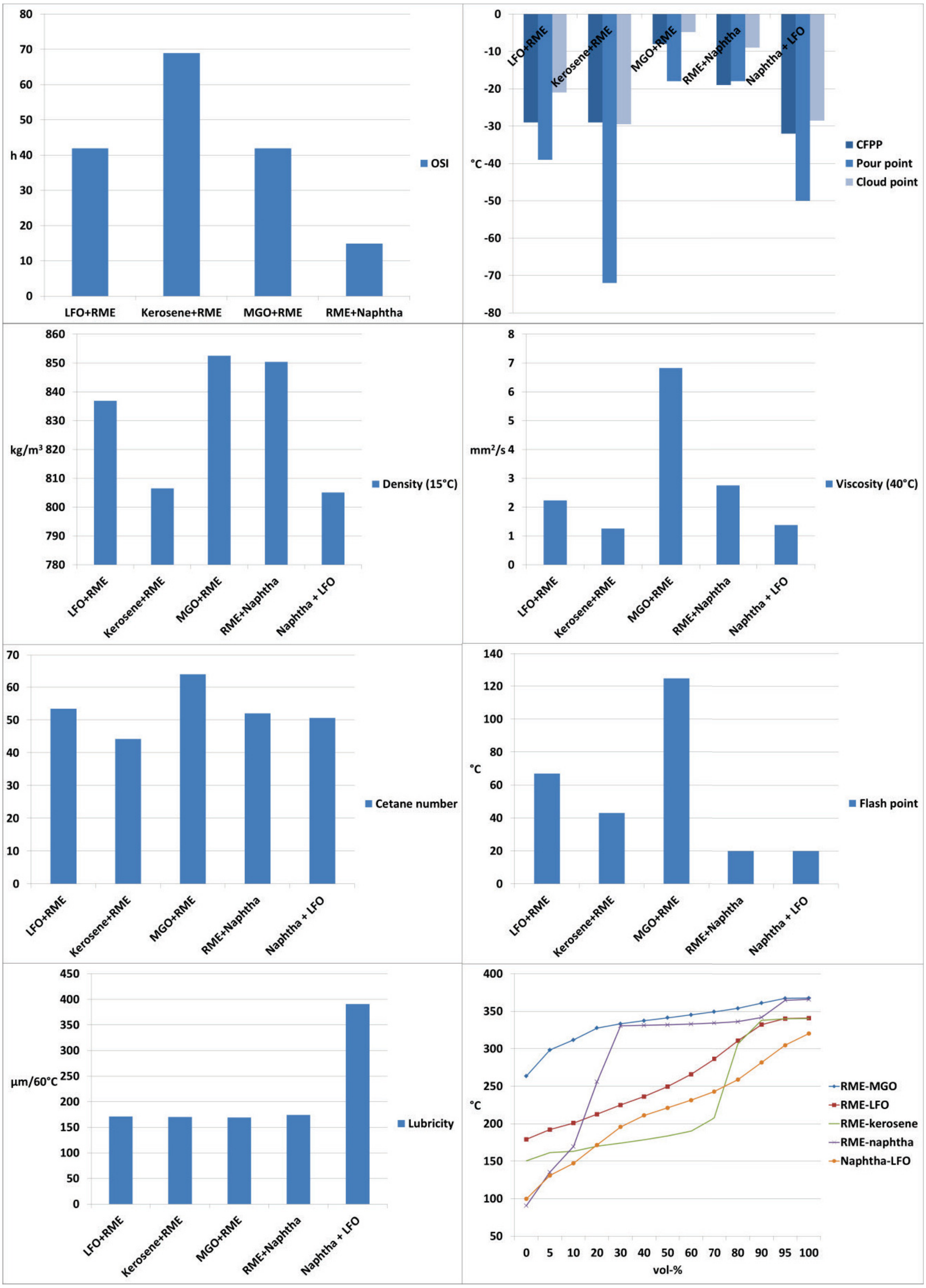

Figure 1. Analysis results of the blends.

3.1 Blend of naphtha and RME

The distillation for RME-naphtha blend started at below 100°C (Fig.1). For this blend, it can be clearly seen that the fractions of naphtha (20 V-%) distillate first below 350°C and the rest are heavier fractions of RME. The lubricity of neat naphtha is, most probably, excessively high (i.e., poor) for engines, and it may be assumed to cause problems in the entire engine fuel system. Still, this RME-naphtha blend showed good lubricity, being 174 µm at 60°C. When using naphtha as CI engine fuel, additives or blending would be the means to reduce lubricating problems.

While RME improved the lubricity of the blend, adding 20 V-% naphtha into RME enhanced the cold properties (e.g. CFPP of the blend was -19°C when it was -14°C for neat RME) and the OSI (from 13 h to 15 h) of the blend compared to neat RME. The cetane number stayed quite high at 52 and the density and viscosity (850 kg/m^3 and 2.8 mm^2/s) were at an acceptable level even though the viscosity was still relatively low. The volatility of naphtha lowered, however, the flash point under the detection limit of the method, approximately down to 20°C. The safety properties of naphtha are, thus, relatively low and its storage and distribution may demand for particular actions. If these actions are taken into account, the blend of naphtha and RME is suitable for medium-speed engines.

3.2 Blend of naphtha and LFO

The distillation for LFO-naphtha blend started at below 100°C (Fig.1). The curve shape of naphtha-LFO is more even than it is for naphtha-RME, most probably due to the lighter fractions of LFO compared to fractions of RME. Despite the poor lubricity of neat naphtha, the lubricity for this blend was at an acceptable level being 391 µm/60°C. The cold properties of the LFO-naphtha sample were good; CFPP was -32°C which was the lowest of all the samples measured. The OSI was not measured for this sample. The cetane number stayed quite high at 51 and the density and viscosity (805 kg/m^3 and 1.4 mm^2/s) were relatively low. These may cause power losses, if the engine has a volume-based fuel flow control, and leakages in the injection system. As for the other naphtha blend, another frailty of this fuel was its low flash point (20°C) and its storage and distribution may demand for particular actions. Despite of its frailties, the blend of naphtha and LFO seems to be feasible in medium-speed engines.

3.3 Blend of MGO and RME

The blend of MGO and RME started to distillate at a quite high temperature of 264°C (Fig.1). The distillation end was at 368°C. This blend showed good lubricity, being 169 µm at 60°C. The cold properties of the MGO-RME sample were rather weak; CFPP was -8°C which was the highest of all the samples measured. The OSI was, instead, at a decent level being 42 hours. The blend also showed a high cetane number, 64. The density was 853 kg/m^3 and viscosity 6.8 mm^2/s. The density was at a decent level, as the marine standard sets a maximum limit of 890 kg/m^3 for the lightest MGO quality but according to the standard, the viscosity should not exceed 6.0 mm^2/s. MGO-RME blend seems to be safe to handle, as its flash point was as high as 125°C. According to these results, the blend of MGO and RME is usable in medium-speed engines.

3.4 Blend of kerosene and RME

The blend of kerosene and RME started to distillate at rather low temperature, 150°C, and the end point was at 201°C (Fig.1). The lubricity of this blend was 170 µm/60°C. The blend's cold properties were, however, relatively favorable even for northern areas since its CFPP was -29°C. The blend also showed relatively good oxidation stability, as the OSI result was 69 hours or clearly above the highest given detection value (48 hours) set in Standard EN 15751. Kerosene contained 0.1 m-% (1000 ppm) of sulphur which may enhance its oxidation stability. This phenomenon is described in the results sections of Paper III and IV. The cetane number was the lowest of all the blends, being 44. The density was 807 kg/m^3 and viscosity 1.3 mm^2/s. The flash point was rather low, 43°C.

3.5 Blend of RME and LFO

The distillation of LFO-RME sample started at 179°C (Fig.1), it rose evenly and the distillation ended at 341°C. The lubricity of FAME blends is usually at a decent level, as it also was in this study, being 171 µm/60°C. The cold properties were at an acceptable level, e.g. the CFPP was -29°C. The oxidation stability index, which often restricts the commercialization of FAMEs and their blends, was at a good level being 42 hours. The cetane number (53) was appropriate. The density was 837 kg/m^3 and viscosity 2.2 mm^2/s. The rather high flash point (67°C) indicated that the fuel is safe to use. The blend of LFO and RME is suitable for medium-speed engines. The properties of the LFO-RME blend fulfilled all the requirements set in Standard EN 590, which is the diesel standard for automotive applications.

3.6 Summary of results and discussion

The blends studied here were pioneering. There are no other published studies in terms of neither renewable naphtha and RME blend nor naphtha and LFO blend. The blend of renewable naphtha and RME and the blend consisting of circulation economy product MGO and RME were relatively new and not studied before. Based on the results, both of them can be used as alternative fuels. In terms of the measured properties, these blends may be feasible in marine, power plant and off-road applications when the target of 35% of renewable share of total energy consumption must be reached. The naphtha and RME blend was an interesting supplement in biofuel genre as it was 100% renewable. RME had a positive effect on naphtha's viscosity, as the viscosity of neat naphtha was 0.5 mm^2/s and for this blend it was 2.8 mm^2/s. RME also improved the lubricity up to an acceptable level.

For both naphtha blends, Naphtha-RME and naphtha-LFO, which was also studied, the cold properties of neat biodiesel and LFO were enhanced when naphtha was added. The cetane number of neat naphtha was only 34, but for both these naphtha blends, the cetane number was above 50. These blends have really low flash points which require that safety aspects should be assured in their storage and usage.

The MGO-RME blend appeared to be a beneficial option as a marine fuel in large regions globally apart from arctic areas. In arctic regions the restricted cold properties may limit the feasibility. MGO is high-quality fuel for reducing sulphur emissions in ships. The studied circulation economy MGO contained less than 100 ppm of sulphur. For a sake of comparison, the heavy fuel oil in Finland is allowed to contain sulphur maximum 1,00 m-% which is equal to 10 000 ppm [18]. Adding non-sulphur RME to MGO decreases the blends' sulphur content even further. Moreover, the used lubricating oil is a reasonable raw material for marine fuel. The volumes of RME and MGO may still be limited, thus restricting the availability of this blend.

The RME-kerosene blend, which also was studied, showed extremely good oxidation stability and kerosene could perhaps be used to enhance the oxidation stability of FAMEs. This should, though, be studied more in detail. The neat kerosene contained 1000 ppm of sulphur. Based on the blending ratio, the sulphur content of the blend was approximately 800 ppm. According to the results obtained in earlier studies [19, 20], the high sulphur content may have improved the oxidation stability of kerosene-RME blend.

Regarding alternative fuels, the diversity forms one of the complications. When the properties of the renewable blending components are known, some conclusions of the blend properties can be drawn. When the fuels are new and not studied before, there is a need for a detailed study of certain properties to estimate their feasibility to CI engines. In this study, RME could not be considered as new fuel, neither the RME-LFO blend. Kerosene-RME blend had also been studied before [21] like neat waste-oil based marine diesel [22, 23] but the results of naphtha and MGO blends were pioneering. The results of the study create valuable fundamental new knowledge and knowhow even for engine research and development.

Blending of new renewable fuels with more conventional ones relieves the technical transitional period so long as the availability of renewable fuels is limited. The fuel blending and decisions on which fuels could be used is needed to be made case by case. The main parameters are in which application the fuel is used and what are the fuel options for blending. That is why all the information about different blends and their properties is important. The diversity of alternative fuels is large and makes the engine development demanding but there are also several straightforward options for medium-speed engine fuels.

4. Conclusions

The main aim of the current study was to determine all the most important properties of certain renewable-fossil fuel blends to create fundamental knowledge about their suitability for, in particular, medium-speed compression-ignition (CI) engines.

The share of renewables within these five blends varied from 20 vol-% to 100 vol-%. Rapeseed methyl ester (RME) was blended with renewable naphtha in a ratio of 80 vol-% of RME and 20 vol-% of naphtha. This fuel blend was 100% renewable and had not been studied before. Moreover, naphtha was blended with DFO in a ratio of 20 vol-% naphtha and 80 vol-% light fuel oil (LFO). RME was also blended together with LFO, kerosene and circulation economy based marine gas oil (MGO) in a ratio of 20-vol% of RME and 80 vol-% of fossil share. The investigated and compared properties were the cetane number, distillation, density, viscosity, cold properties and lubricity.

According to the received results, the following conclusions could be drawn:

All the studied blends may be operable in marine, power plant and off-road applications when the target of 35% of renewable share of total energy consumption must be reached.

100% renewable naphtha-RME blend is an interesting supplement in biofuel genre.

In terms of both naphtha blends the cold properties of neat biodiesel and LFO were enhanced when naphtha was added. These blends have really low flash points which require that safety aspects should be assured in their storage and usage.

The MGO-RME blend appears to be a beneficial option as a marine fuel in large regions globally apart from arctic areas where its unfavorable cold properties may limit the feasibility. The volumes of these both fuels may still be limited, thus restricting the availability of this blend. Nevertheless, MGO is high-quality fuel for reducing sulphur emissions in ships.

The RME-kerosene blend showed extremely good oxidation stability and kerosene could perhaps be used to enhance the oxidation stability of FAMEs. This should, though, be studied more in detail.

Blending of new renewable fuels with more conventional ones relieves the technical transitional period so long as the availability of renewable fuels is limited.

Acknowledgements

The authors wish to thank STR Tecoil for delivering MGO, Neste for delivering kerosene and UPM for delivering naphtha for research purposes. This study was implemented within Hercules-2 –project.

Funding: This work has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 634135.

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