CIMAC CONGRESS 25
ZURICH, MAY 19 – 23, 2025

2025 | 499

Blending behavior of pure, esterified and hydrotreated pyrolysis oils

Fuels - Alternative & New Fuels

Fanny Langschwager, Universität Rostock, LKV

Ulrike Schümann, University of Rostock, LKV
Bert Buchholz, University of Rostock, LKV

DOI: https://doi.org/10.5281/zenodo.15191226

ABSTRACT

Alternatives to fossil fuels are necessary for the long-term success of the energy transition and the climate protection. The setup of a new or parallel distribution infrastructure is always a huge challenge if new fuel qualities are to be introduced in an existing market. This process can be extremely simplified and sped up if the new fuel qualities are compatible to the traditional fuels to such an extent that blending the new and traditional fuels is possible. Fuel blending, in this case the mixing of a fossil base fuel with biofuels, requires the mutual solubility of both components, at least within a reasonable concentration range. Furthermore, the physical and chemical properties of the blend should be identical or only slightly different to those of the traditional (fossil) fuel. That would allow the utilisation of the already existing distribution infrastructure and the application of the blend fuel in the existing engine technology. In this study different types of pyrolysis oils and processed pyrolysis oils are blended in conventional and future marine fuels. The blending of these fuels must be carried out under the condition that application-safe, homogeneous, stable and non-corrosive fuels must be produced in accordance to DIN ISO 8217. For the blending and mixing stability tests different procedures as well as methods are investigated and tested. It is known that pure pyrolysis oils are difficult to mix with conventional marine fuels. This is mainly due to the polar groups present within the pyrolysis oil molecules. These are to be intercepted by esterification, thus improving not only the standard properties but also the blending behaviour. Furthermore, hydrogenated pyrolysis oils with different oxygen contents are investigated and the mixing behaviour of such oils is examined more closely. It is expected that the lower the oxygen content of the oils, the better the miscibility in conventional fuels will be.

1 INTRODUCTION

Alternatives to fossil fuels are essential for the long-term success of the energy transition and climate protection. In the maritime sector, the choice of fuels will be a critical factor for reducing CO_2 emissions by 2050, as the impact of purely battery-electric systems is limited by their heavy weight, significant space requirements, and the need for land-based charging infrastructure. Therefore, the aim is to develop sustainable maritime fuels for ship propulsion systems which will significantly reduce greenhouse gas emissions, ideally not releasing additional CO_2. For this reason, intensive research is conducted into new, clean fuels and technologies and to ensure compliance with stricter emission limits in shipping in the future. The lifespan of ships is typically over twenty years, and they need to be able to refuel anywhere in the world. Therefore, it is essential to introduce climate-neutral fuels rapidly. These new fuels should be compatible with existing ships and can be blended with fossil fuels available worldwide. While initially more expensive, these new fuels or fuel components must also promote efficiency and emissions performance improvements. In the coming years, extensive research will be required to evaluate future fuels, often only available at the laboratory scale. This research will assess their suitability and impact on drive technologies, the environment, safety, value creation, and infrastructure. The goal is to derive well-founded strategic decisions based on these evaluations. This is the only way to achieve global climate targets and avoid environmental conflicts, especially in port and coastal areas.

To meet climate policy targets, large quantities of CO_2-neutral fuels will be necessary in the future. Currently, synthetic fuels cannot be produced on a large industrial scale, thereforebiogenic fuel sources must also be used to reduce the release of fossil CO_2 today. An alternative solution includes biogenic fuels such as pure vegetable oils, biodiesel (FAME), hydrogenated vegetable oils (HVO), biomethane and pyrolysis oils [1, 2]. Biofuels are already available in significant quantities and, making them a bridging technology to sustainably and substantially reduce greenhouse gas emissions in the short and medium term [3].

2 METHODOLOGY

The mixing stability of pyrolysis oils can be challenging due to their high polarity compared to the low polarity of conventional marine fuels such as MDO and HFO. To prevent mixing issues and improve fuel properties, various methods exist to further process pyrolysis oils into usable fuels. Pure pyrolysis oil from biogenic residues cannot be used in a diesel engine due to its high water content and acid number. To lower the acid number, it is possible to esterify the acid groups in the pyrolysis oils with alcohols. The water content could also be decreased by using higher alcohols (> butanol). Another possibility is to hydrotreat the pyrolysis oils. With this technique, the oxygen content (alcohol, acid, ketone, aldehyde groups) is decreased. The better the hydrotreatment, the lower the oxygen content from the resulting product. The most important fuel properties are then determined from these products to prove their basic suitability as fuel candidates. Furthermore, the potential blending ratios are identified, followed by conducting blending tests.

2.1 Fuel analysis

The following fuel parameters were determined from the fuel samples to assess their suitability as a fuel or as possible blend components (Tab.1).

Table 1: Overview of tested fuel parameters

Parameter	Test specification
Density	DIN EN ISO 12185
Viscosity	DIN EN 16896
CAN/TAN	ASTM D664
Water content	DIN 51777
Flash point	DIN EN ISO 2719
Cloud Point	ASTM D7689
Pour Point	ASTM D7346
Element scan	ICP-OES

Since esterified and partly hydrotreated pyrolysis oils differ significantly in their polarity from fossil fuels, it was necessary in some cases to adapt the analytical methods. In particular, the use of suitable solvents, as well as filter and hose material, were necessary for the analytical measurements. The Carboxylic acid number (CAN) is an analytical parameter to assess the acid content in pyrolysis oils. While Total acid number (TAN) quantifies all acids, including non-corrosive phenolic acids. CAN focuses on moderate to strong organic acids that can exhibit corrosive properties. The determination of CAN and TAN acids is performed simultaneously using potentiometric titration according to ASTM D664 standard. The key difference lies in the choice of endpoint: TAN is determined at pH 11, whereas CAN is measured at the inflection point between pH 8 and pH 9.

2.2 Blending

Blending must be carried out under the condition that application-safe, homogeneous, stable and non-corrosive fuels must be produced according to ISO 8217:2024. Therefore, special attention was paid to critical variables such as acid number, flash point, density, viscosity as well as storage, thermal and mixing stability. The fuel samples were blended as drop-in components with fossil marine

fuels as well as alternative fuels, according to ISO 8217:2024. The requirement standard for marine fuels comprises seven distillate and bio-distillate grades, four grades for residual marine fuels with sulphur content below 0.50%, five grades for bio-residual marine fuels and five categories for residual marine fuels with sulphur content above 0.50 %. In addition, up to 100% FAME or 100% paraffinic diesel fuel is now allowed if they meet the relevant standards. DF grades can contain up to 100% FAME and DM grades can contain up to 100% paraffinic diesel fuel. The addition of FAME to residual fuels is also permitted in the bio-residual fuel grades.

3 ESTERIFIED PYROLYSIS OILS

The esterified Pyrolysis oils (EPO) were produced within the PyroMar project by the partner Fraunhofer UMSICHT. The aim of the project was to produce fuel components consisting entirely of biogenic residues as blending components to marine fuels to produce marine fuel blends. The initial feedstocks are straw, leaves, landscape conservation hay, forest residues, shrub cuttings and beech wood. These materials were converted into pyrolysis oil (bio-oil) by means of ablative fast pyrolysis. To reduce the acid number and to improve miscibility with fossil fuels, the pyrolysis oil was esterified with longer chain alcohols catalytically produced from biogenic residues (straw). The acid-catalyzed conversion of pyrolysis oils with alcohols aims to convert its corrosive (organic acids) and reactive (aldehydes and ketones) components to esters, acetals and ketals, which have then lost their unfavourable properties and can thus remain in the product. When higher alcohols are used in this process, water can be separated simultaneously. This is because, starting from a carbon chain length of four atoms (butanol), water and the alcohol become immiscible. As a result, they can be easily separated. The reaction occurs under continuous reflux, allowing the condensate to form distinct liquid phases. Solid acids such as sulfonated ion exchange resins are particularly suitable as catalysts, as these can be removed by sieving at the end of the reaction, unlike liquid acids, and reused.

3.1 Fuel analysis

In order to assess the suitability of the esterified pyrolysis oil samples as a fuel or a possible blend component key parameters were determined. The following table shows the determined fuel parameters of two selected esterified pyrolysis oils. It should be noted here that the two esterified pyrolysis oils have very high CAN and TAN values and therefore only a blend rate of 3.5 and 7.5 % would only be possible in this case.

Table 2: Fuel parameters from two esterified pyrolysis oils (EPO 1: straw-based pyrolysis oil esterified with butanol with a ratio of 3:1, EPO 2: rape straw-based pyrolysis oil esterified with hexanol with a ratio of 1:1) *ISO 8217:2024 – Bio-residual marine fuels

Parameter	Limit Value*	EPO 1	EPO 2
Density at 15 °C [kg/m^3]	1,010.0	1,082.2	929.8
Viscosity at 50 °C [mm^2/s]	500	32.68	8.752
CAN [mg KOH/g]	-	59.2	17.7
TAN [mg KOH/g]	2.5	72.1	32.9
Water content [%]	0.5	0.6	0.4
Flash point [°C]	60	55.6	65.8
Sulfur content [%]	0.5	< 0.1	< 0.1

*ISO 8217 – Bio-residual marine fuels

From all results obtained, the following general conclusion can be drawn with regard to the product quality achieved:

- all hereby tested EPO´s are “ultra-low sulfur” fuel components. (sulfur contents < 0.05 %)
- The CAN (Carboxylic acid number) values of the EPO range between 10 - 80 mgKOH/g and limit the blend rate to marine fossil fuels to < 25 % and less depending on the acid content (CAN) of the fuel.
- Using high-density heavy fuel oils, the high densities of the EPO could in some cases be a limiting factor at blends fractions above 10 %.
- If hexanol replaces butanol as the alcohol for esterification, the flash point limit according to ISO 8217 can be maintained (butanol flash point: 35 °C, hexanol flash point: 60 °C).
- The water contents of EPO are between 0.1 - 2.7 % and limit the blend ratio with marine fossil fuels possibly to < 18 %

The fuel characteristics of esterified pyrolysis oils indicate their potential as drop-in components for marine fuels. However, due to their high acid numbers, only blends containing up to 25% esterified pyrolysis oils and 75% marine fuel are currently feasible.

3.2 Blending

Initial investigations on fuel blends revealed that the esterified pyrolysis oils had very poor miscibility with marine distillate fuels. Figure 1 illustrates various blend rates of an esterified pyrolysis oil that was esterified with butanol and mixed with a marine distillate. As already described, the high acid number of esterified pyrolysis oils limit the blend

ratio to below 25%. However, it was not possible to achieve sufficient mixing of the esterified pyrolysis oil in MDO at low blend rates. Furthermore, the figure shows that stable blends of ≥ 80% esterified pyrolysis oils and ≤ 20% marine distillate can be prepared and are stable. A similar result was obtained by blending tests using an HFO. Mixing instabilities became evident immediately after the preparation of the blends. Determination of the TSP value was not possible in this case, as the solvents required for TSP measurement were incompatible with the esterified pyrolysis oils or the esterified pyrolysis oil blends. Therefore, various additives were tested to improve the compound stability.

Dispersant additives were tested to improve the stability of the blends. The additives were tested in different concentrations and fuel mixtures. In most cases, the additive did not improve the blend stability or did not improve it sufficiently. However, one additive produced stable blends of up to 7% for a special VLSFO at ambient temperature (22°C) and at 50°C.

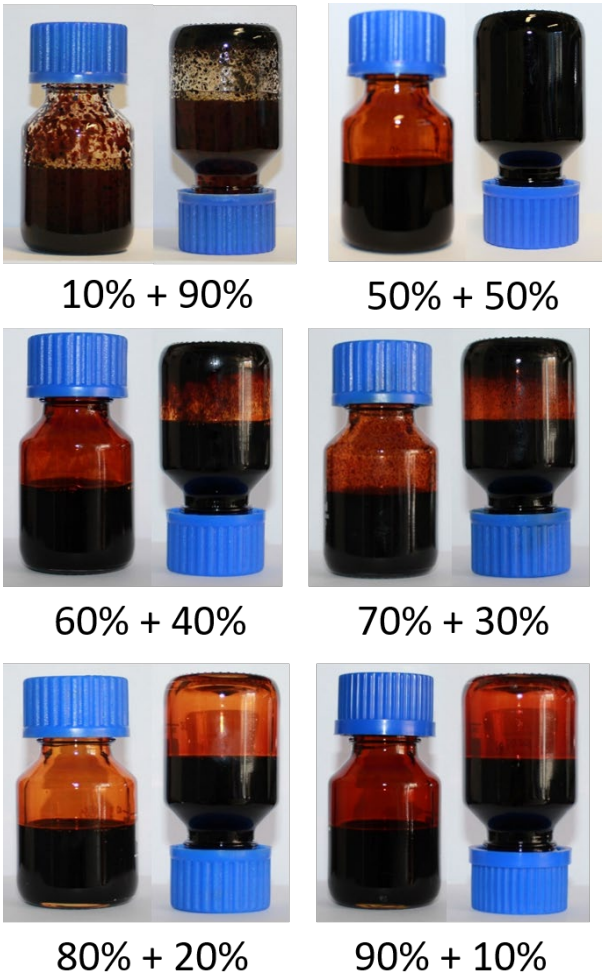

Figure 1: Blending tests of esterified pyrolysis oils with marine distillate fuel in different blending ratios (blending ratio EPO:MDO)

In addition, it has been shown that miscibility and mixture stability also depend on the composition of the heavy fuel oil. Initially, a correlation was suspected between the aromatic content of the heavy fuel oil and the mixing stability of the blends with esterified pyrolysis oils. However, no clear correlation between heavy fuel oil´s aromatic content and the blends´ mixing stability could be determined. Furthermore, mixing experiments with different esterified pyrolysis oils and a heavy fuel oil were carried out. Here, as well moderate to poor miscibility was observed as well, which could also not be improved by adding the additive. This was exacerbated by chemical instabilities in some cases. A possible explanation is the stability of the blends depends both on the heavy fuel oil and on the composition of esterified pyrolysis oils (feedstock, stoichiometric ratio of pyrolysis oil and alcohol component) which is difficult to predict in practice. However, the pyrolysis oil intermediates are fully miscible with two different base components from the e-fuels/biofuels sector. However, these components were also not suitable as solubilisers in the form of a third blending component in blends of pyrolysis oil intermediates and marine fuels.

4 PARTLY HYDROTREATED PYROLYSIS OILS

The partly hydrotreated pyrolysis oils (PHPO) were produced within the REFOLUTION project by BTG and SINTEF. Due to the limited sample volume from small-scale test tubes, not all key parameters of the samples could be determined. Furthermore, these samples were not fractionated and should be considered as intermediates. However, blending tests were performed to examine the stability of the blends.

4.1 Fuels analysis

Due to the limited sample amount of the partly hydrotreated pyrolysis oil samples, only selected fuel analytics could be conducted. Table 3 summarises the most important fuel parameters measured of two exemplary samples.

Table 3: Fuel parameters from two partly hydrotreated pyrolysis oils

Parameter	Limit value*	PHPO 1	PHPO 2
Density at 15 °C [kg/m^3]	1,010.0	974	938
TAN [mg KOH/g]	2.5	51.3	7.4
Oxygen content [%]	-	13.2	5.8

*ISO 8217 – Bio-residual marine fuels

All samples of partly hydrotreated pyrolysis oil have high densities. However, when classified as bio-residual marine fuels, they would conform to the

required specifications. Through the process of hydrotreating, the oxygen content in the original pyrolysis oil reduced from 37% to 13.2% in HPO 1 and to 5.5% in HPO 2. This decrease is also reflected in the total acid number values. As the oxygen content in the samples decreases, the total acid number values also decrease. However, it should be noted, that the acid values do not comply with the standard. Nevertheless, PHPO samples can still be used as a blend component, thus complying with the standard.

4.2 Blending

The standard values TSE, TSP, and TSA are commonly used to assess fuel stability. However, due to the limited quantaties of partially hydrogenated pyrolysis oils, these standard values could not be determined. As a result, the stability of the mixture was assessed through visual inspection. Therefore, blending of HPO with MDO and FAME were conducted on a small scale. After mixing, the samples were left to rest for 24 h to observe any potential segregation of the fuels.

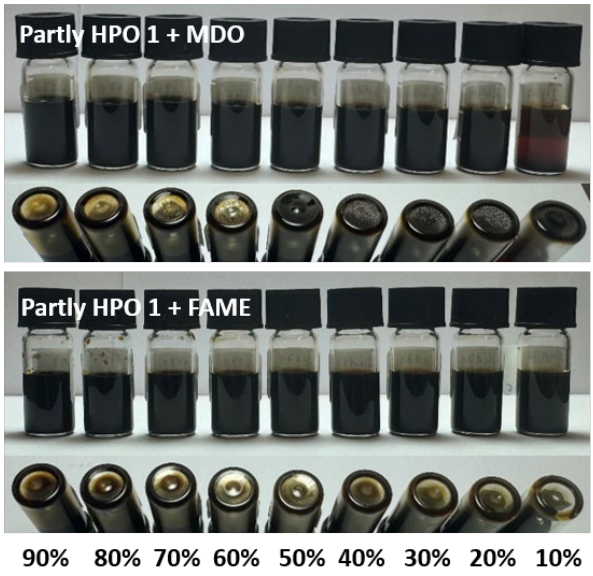

Figure 2: Blending tests of one partly hydrotreated pyrolysis oils with MDO and FAME in different blending ratios (blending ratio PHPO1:MDO/FAME) after 24h

Figure 2 shows that the chosen example, PHPO 1, has poor miscibility with MDO. Phase separation can be observed at a blend ratio of 10% PHPO in MDO. Additionally, when the blend ratio reached up to 70%, deposits formed at the bottom of the sample bottles, indicating that complete miscibility between the two blend components did not occur. This behaviour is similar to that of esterified pyrolysis oils. At high contents (> 80%) of esterified or partly hydrotreated pyrolysis oils, miscibility with MDO is given, but not at lower blend rates. Investigations are still ongoing whether further reduction of the oxygen content in the processed pyrolysis oils enhances miscibility in MDO.

Additionally, as shown in the figure (bottom panel), the tested sample is fully miscible with FAME across all blend ratios. This behaviour was also observed for other tested samples. The difference in miscibility of partly hydrotreated pyrolysis oils (polar) in MDO (nonpolar) and FAME (polar) likely arises from polarity effects. By including 100% FAME in ISO 8217, FAME can be a good alternative to overcome the miscibility issues of blending pyrolysis oils and conventional marine fuels.

5 FULLY HYDROTREATED PYROLYSIS OILS

The fully hydrotreated pyrolysis oils (HPO) were also produced within the REFOLUTION project from the partner BTG. In addition to the production and characterisation of sustainable marine fuels, the project also focuses on the production of sustainable aviation fuels. For this purpose, various fractions were obtained and characterised from the hydrogenated product.

5.1 Fuel analysis

The hydrogenated products were fractionated at different temperatures. The heavier fractions of the HPO product were then analysed in terms of their suitability as a marine fuel based on certain fuel parameters. The results for two selected HPO fractions are shown in the following table 4.

Table 4: Fuel parameters from two hydrotreated pyrolysis oils

Parameter	Limit value**	HPO 1	HPO 2
Density at 15 °C [kg/m^3]	900.0	891.4	908.9
Viscosity at 40 °C [mm^2/s]	11.00	3.99	4.72
TAN [mg KOH/g]	0.5	0.05	0.08
Water content [ppm]	0.3	24	28
Flash point [°C]	60	61	75
Cloud Point [°C]	-	-34.5	-31.1
Pour Point [°C]	-6	-36	-33
Sulfur content [%]	0.5	<0.1	<0.1

**ISO 8217 – Distillate and bio-distillate marine fuels

Nearly all parameters presented meet the requirements of ISO 8217. The only exception is the density, which exceeds the limits for HPO 2. However, this sample could serve as a component in a blend to meet the required specifications. The density could also be adjusted by distilling the fraction at lower temperatures (see HPO 1). It should be noted that pyrolysis oils and fuels containing pyrolysis oil are not yet approved under

ISO 8217. However, the fuel properties of HPOs can be evaluated in relation to this standard. Based on current findings, the so far determined values for HPO 1 fall within the specified limits of the standard. Moreover, the very low water content, low acid number, and low sulphur content are particularly noteworthy. All the samples shown also meet the flash point limit and demonstrate excellent cold behavior (cloud and pour point). Therefore, in purely formal terms, it can be concluded that a suitable fuel fraction could be obtained from hydrogenated pyrolysis oil that aligns with the standard, pending verification of compliance with additional parameters.

For in-depth chemical characterisation, HPO samples were analysed using gas chromatography-mass spectrometry (GC-MS), which led mainly to the identification of cycloalkanes and aromatic compounds. Additionally, as a complementary technique, high-resolution Fourier Transform Ion Cyclotron mass spectrometry (FT-ICR MS) was used to analyse HPO samples. In combination with electrospray ionisation (ESI), polar compounds can be analysed in particular. FT-ICR MS enables, due to its extremely high mass accuracy and mass resolving power, the calculation of sum formulae (C, H, N, O, S) directly from the measured mass. For the investigated HPOs, a total of approx. 1000 molecular formulae were detected. Among them, mainly CH species (hydrocarbons), oxygen-containing (up to 7 oxygen atoms per sum formula) as well as nitrogen-containing compounds were identified.

5.2 Blending

The pre blending tests of HPO were carried out with marine diesel fuel, FAME (fatty acid methyl ester), HVO (Hydrotreated vegetable oil) and methanol in small scale (ratios: 25:75, 50:50, 75:25 m:m %).

Figure 3 shows an example of the results of the blending tests. The figure indicates that HPO is well-miscible with MDO, HVO, and FAME. The only exception was the miscibility of HPO with methanol in these tests. As expected, these two fuels are not fully miscible; however, low miscibility can still be observed.

After the preliminary tests indicate that HPO could be easily mixed with MDO, HVO and FAME, additional blends were prepared, and their fuel parameters were determined. The following table summarises the results of two selected blends.

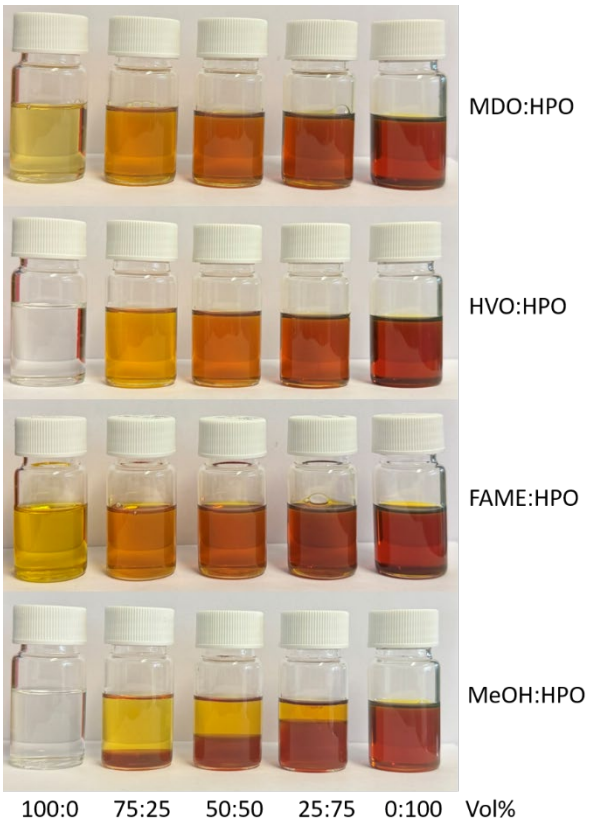

Figure 3: Blending tests of HPO with MDO, HVO, FAME and MeOH in different blending ratios

The fuel parameters of the investigated HPOs would likely align with the ISO 8217 specification, assuming this fuel were approved under the standard. Based on the laboratory results, it can be concluded that the HPO samples are potentially suitable candidates for use as marine fuel.

Table 5: Fuel parameters from two HPO Blends (HPO Blend 1: 30% HPO + 70% MDO, HPO 2: 30% HPO + 70% MDO containing 7% FAME)

Parameter	HPO Blend 1	HPO Blend 2
Density at 15 °C [kg/m^3]	865.1	866.9
Viscosity at 50 °C [mm^2/s]	2.99	3.02
TAN [mg KOH/g]	0.09	0.09
Water content [ppm]	41	45
Flash point [°C]	75	75
Cloud Point [°C]	-13.1	-14.1
Pour Point [°C]	-12	-12
Sulfur content [%]	< 0.1	< 0.1

As part of the project, additional investigations are planned to confirm the suitability of the fuel for marine use. This includes the characterisation of selected HPO blends using the diesel thermal oxidation tester to verify claims regarding the potential for deposit formation associated with HPO. Furthermore, tests will be conducted with HPO fuel and blends in the high-pressure, high-

temperature injection chamber, investigating their spray and combustion behaviour. Finally, the HPO fuels and fuel blends will be examined in a medium-speed single-cylinder research engine, and their suitability as an alternative fuel will be tested. Han et al. run successful HPO and diesel fuels Blends (up to 50% HPO) in a single-cylinder heavy-duty research engine [4].

6 CONCLUSIONS

Processed pyrolysis oils serve as a sustainable alternative to traditional fuels. Various techniques exist to further process strongly polar pyrolysis oil into fuel suitable for marine applications. For example, it was demonstrated that esterifying the pyrolysis oil can reduce the acid number and water content in the products. However, the reduction in the acid number was not sufficient. However, the limited miscibility of esterified pyrolysis oils with conventional marine fuels (MDO, HFO) complicates this issue, indicating that the esterification process alone cannot resolve the mixing instabilities.

Furthermore, it could be shown that partly hydrotreated pyrolysis oils are another alternative for sustainable marine fuels. However, the total acid numbers not being sufficiently reduced and the mixing stability in MDO blends not be guaranteed. Nonetheless, the good miscibility in FAME should be emphasised. The main question is to what extent the oxygen content, or the polarity of the products, needs to be reduced to overcome these mixture instabilities. Fully hydrotreated pyrolysis oils, depending on their specific fraction, demonstrated excellent fuel properties that meet industry standards. The nearly complete removal of oxygen resulted in a non-polar product with outstanding blending capabilities in both conventional and alternative fuels (FAME).

7 ACKNOWLEDGMENTS

The authors would like to thank the German Federal Ministry for Economic Affairs and Climate Action (BMWK) for funding the PyroMar project under grant agreement No. FKZ 03EI5412A-C.

The authors would also like to thank the European Union programme for funding the project Refolution under the grant agreement number 101096780.

8 REFERENCES AND BIBLIOGRAPHY

[1] Tyrovola, T.; Dodos, G. S.; Kalligeros, S.; Zannikos, F. (2017): The Introduction of Biofuels in Marine Sector, Science Journal of Environmental Science and Engineering A 6: 415-421

[2] Wojcieszyk, M.; Kroyan, Y.; Larmi, M.; Kaario, O.; Zenger, K., 2019. Effect of alternative fuels on marine engine performance, SAE Technical Paper 2019-01-2230

[3] Kalghatgi, G.; Levinsky, H.; Colket, M., 2018. Future transportation fuels, Progress in Energy and Combustion Science, 69, 103-105

[4] Han, J.; Somers, L.M.T.; van de Belt, B.; 2024. Experimental investigation performance and amission of hydrotreated pyrolysis oil in a heavy-duty engine with EGR, Fuel Processing Technology, 255,

9 CONTACT

Dr. rer. nat. Fanny Langschwager

University of Rostock

Chair of combustion engines and piston machines

Albert-Einstein-Straße 2

18059 Rostock

Germany

fanny.langschwager@uni-rostock.de