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Stability of bio-blended residual marine fuel oil

Fuels - Alternative & New Fuels

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ABSTRACT

The FuelEU Maritime regulation has set targets that are leading fuel suppliers to consider incorporating various bio-based blending components to reduce the carbon intensity of marine fuels. However, these new blending components introduce challenges in the performance of maritime fuels, many of which are not yet well understood.

This study aims to investigate the compatibility of a selection of commercially available bio-blendstocks with very low sulfur fuel oil (VLSFO). The bio-blendstocks to be evaluated include different grades of cashew nutshell liquid (CNSL), as well as biodiesel-based products. The study will evaluate the impact of blending the bio-blendstocks with VLSFO at 30% and 50% by volume. The resulting fuel mixtures will be assessed for their stability, the potential formation of sediments or acids during storage and use, as well as their corrosive properties The bio-blendstocks and VLSFO will also be tested individually to provide a baseline for comparison.

The assessment will utilize both established test methods that are part of the ISO 8217 requirements for marine fuels, such as total sediments (ISO 10307-2) and acid number (ASTM D664), as well as novel oxidation stress testing specifically developed for residual fuel oils containing bio-based components.

The findings of this study aim to support fuel suppliers, buyers, and engine manufacturers in better understanding the new fuel options entering the marine fuel market, and the potential performance implications associated with the use of these bio-blended fuels.

1 INTRODUCTION

The global transition to renewable energy and environmentally friendly fuels has become a priority for reducing greenhouse gas emissions and mitigating climate change. The maritime transport industry, as a significant contributor to global emissions, faces growing pressure to adopt sustainable fuel options. This urgency has been amplified by the introduction of the FuelEU Maritime regulations, which mandate progressive reductions in the greenhouse gas intensity of energy used by large ships calling at European ports, regardless of flag. As from 2025 a 2% reduction compared to the reference value is mandated which will gradually increase to an 80% reduction by 2050. [1]

To meet these ambitious goals, the development of new fuels and fuel blends derived from food industry waste streams and other biobased materials or renewable sources is essential. This will aid the maritime sector to significantly reduce the carbon footprint, greenhouse gas emissions, and sulfur oxides (SOx) associated with traditional fossil fuels.

Marine fuels must adhere to ISO 8217 standards to be considered suitable for use. [2] These standards specify requirements for various grades of gasoil and residual fuel oil. In recent years, significant progress has been made in updating these standards to include several biobased products, broadening the scope for sustainable fuel options. The Bureau Veritas Fuels laboratories have significant experience with the analysis of a varied range of biofuels and feedstocks as well as marine fuels as per ISO8217 requirements. From our experience we can see the need for additional analysis to test for the increased potential of stability issues when blending biobased components into traditional fossil residual fuels. Clause 5.2 of ISO8217 mentions the fuel should be free of substances that could cause harm to the vessel, onboard machinery or personnel but does not specify a methodology to assess this requirement.

This study investigates the compatibility of several commercially available biobased products as blending components in Very Low Sulfur Fuel Oil (VLSFO) and Heavy Fuel Oil (HFO), which are widely used in the maritime industry.

The products of biological origin examined include Cashew Nut Shell Liquid (CNSL) and some of its derivatives, FAME Distillation Residue (FDR), MR1-100 (a blend derived from used cooking oil), and Rapeseed Methyl Ester (RME). The primarytfocus is on the stability and corrosion characteristics of these blends, evaluated using a combination of standard industry test methods and custom-designed experiments. Through this research, we aim to provide insights into the feasibility of integrating biobased products into marine fuels while maintaining compliance with existing standards and addressing key challenges such as fuel stability and material compatibility. This work contributes to the broader effort to decarbonize maritime transport and achieve long-term sustainability.

2 EXPERIMENTAL SETUP

For the pupose of checking compatibility, stability and corrosion characteristics of the bio-residual fuel oils several blend are made using commercially available residual fuel oils and blend components of biological origin which can be found below. These products are spot products with a specific composition that is an example of the product class they represent without being considered representative of that class as a whole.

Residual fuels used :

- VLSFO
- HFO

Biobased products used

- Bio pyrolysis oil (CNSL based)
- Distilled bio pyrolysis oil (CNSL based)
- Refined CNSL
- FAME Distillation Residue (FDR)
- MR1-100
- Rapeseed methyl ester (RME)

The analytical protocol is performed on each of the following compositions:

- Each residual fuel as such (B0)
- 30 %m/m of biobased product in each residual fuel (B30)
- 50%m/m of biobased product in each residual fuel (B50)
- 100 %m/m of each biobased product (B100)

On these samples analyses are performed before and after a conditioning step to simulate prolonged time at elevated temperatures, under the influence of oxygen while bringing the samples into contact with carbon steel and copper specimens.

Conditioning is done at a temperature of 130°C under an airflow of 10L/h for a duration of 8 hours. These extreme conditions are meant to push the products under analysis to their limits to investigate any possible concerning behaviour that could be cause for further research under conditions that more closely mimic real-world operating and storage conditions.

The analyses that are performed before and after the conditioning step are :

- Density at 15°C
- Viscosity at 50°C
- Total sediments existent (TSE)
- Total acid number (TAN)
- Stability/spot test
- Microscopic evaluation

After each conditioning volatile acids are quantified by titration and the carbon steel and copper specimens used will be evaluated visually and weighed to determine the degree of corrosion.

2.1 Density

The Density measurement is performed according to EN ISO 12185. Samples are measured by means of automated equipment with the use of an oscillating U-tube at 50°C and converted to 15°C as per Table 53 B. Results are expressed in kg/L.

2.2 Kinematic Viscosity

Kinematic viscosity is an important parameter for engine operation. The kinematic viscosity has a considerable influence on pumpability and is used to set the temperature of the purifier on board a vessel. Kinematic Viscosity is measured at 50°C according to EN ISO 3104 procedure B. Automated viscometers are used for this determination and results are shown in mm²/s.

2.3 Total Sediments Existent

Total Sediments Existent gives an overview of the amount of solids present in the sample with the use of hot filtration. The filter residue is rinsed with a limited quantity of wash solvent consisting of heptane and toluene before being washed with a portion of heptane.

When this parameter is too high, filter blocking can occur within the fuel system which will limit the proper functioning of the engine. The measurement is performed according to ISO 10307-1 and results are given in %m/m. Within the ISO8217 standard method ISO 10307-2 is used (known as TSP) which uses the same filtration apparatus but involves a 24h thermal conditioning. [2]

2.4 Total Acid Number

The analysis is performed according to method ASTM D664. Total acid number checks for the acidity of the samples, however extremely weak acids will not be measured. Biobased products tend to break down in organic acids especially when consisting of triglycerides. This will influence the result of this analysis greatly and can be a good indication of oxidation and thermal stability.

A high TAN could lead to engine and fuel system issues due to corrosion of metal parts and damage to seals and gaskets as well as formation of sludges and deposits that can clog filters and otherwise impact engine performance.

It should be noted that when strong inflection points are measured a Strong Acid Number (SAN) determination should be performed, which is a separate titration. This would usually indicate the presence of strong acids which could be coming from chemicals or other sources. Spot checks for SAN on some of the investigated samples with the highest TAN were performed. As these tests all showed no presence of strong acids the SAN has no further relevance for this work.

2.5 Spot Test

When performing the spot test according to ASTM D4740 the compatibility or cleanliness of the sample can be verified. The sample is heated to 100°C for 30 minutes after which a glass rod is dipped into the sample. A drop of the heated fuel oil is then spotted onto a filter paper. The paper is kept in a horizontal position for 1h at 100°C after which the spot is evaluated for solids or inconsistencies by comparison to reference spots provided in the method. Each spot is assigned a rating from 1 to 5.
When inconsistencies are observed this points to instabilities in the blend which will reflect in a higher spot rating.

2.6 Microscopic evaluation

When inconsistencies are found with stability a microscopic evaluation is performed to have a closer look at the solids that are found. This is done with the use of a stereo microscope in combination with a fluorescent light source. The shape of the solids and the amount of clustering seen in the microscopic evaluation can indicate the severity of potential problems in for example filtering applications on board. The shape of the solids gives us more information about the nature of these particles. I.e. irregular shapes indicate solid particles and could be asphaltene like in nature and clustering is more likely to occur while spherical particles indicate different surface tension properties and less solid and clustering properties.

2.7 Sample conditioning

Sample conditioning was conducted using Rancimat equipment, which is typically employed

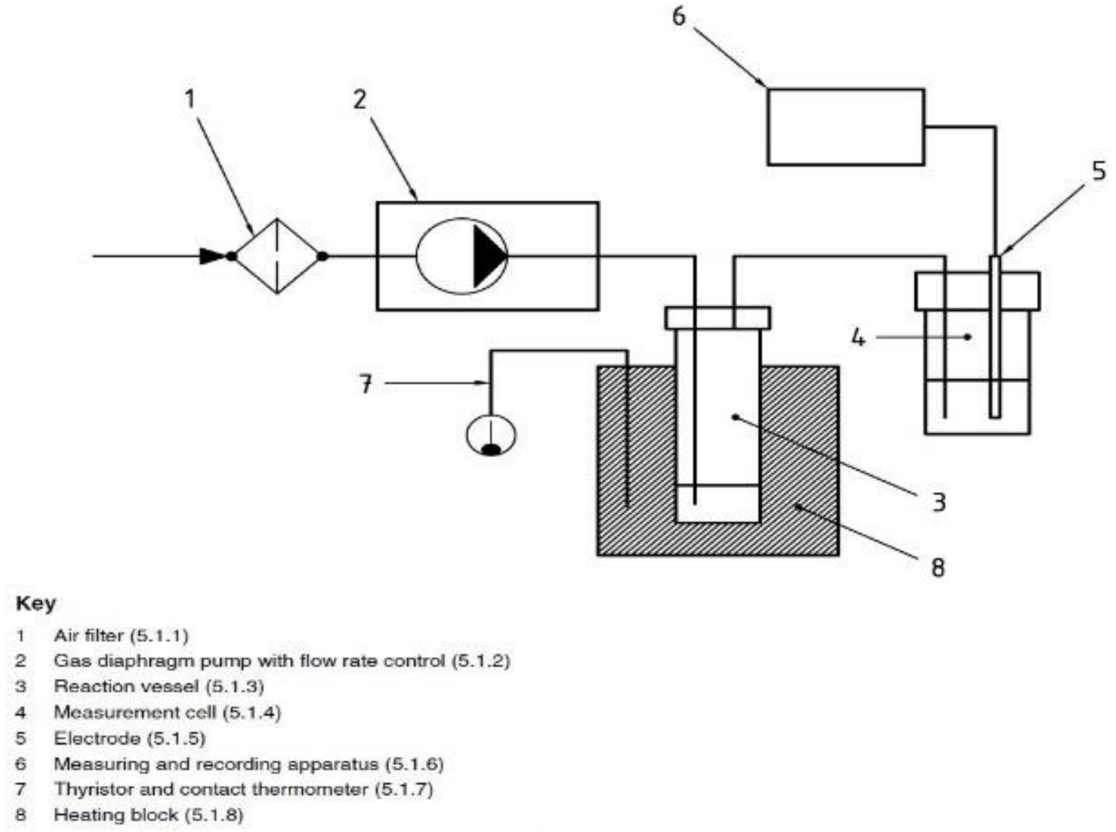

Figure 1 Diagrammatic representation of the Rancimat apparatus

for the oxidation stability testing of FAME or FAME-containing fuels, as outlined in methods EN 14112 and EN 15751. Adjustments were made to the standard operating conditions for the purpose of this study.

The samples were subjected to prolonged heating at 130°C under an airflow of 10 L/h for a duration of 8 hours. Each sample portion consisted of 15 grams of the product, a carbon steel (C1020) specimen weighing approximately 12 grams, and a copper specimen weighing approximately 3 grams. Demineralized water (50 grams) was placed in the receiver cup to collect volatile compounds, including oxidation products.

Carbon steel was included as it represents the primary material used in ship fuel tanks and pipelines, making it crucial for assessing material compatibility and the potential for corrosion or deposit formation.

Copper was added as a catalyst to investigate its influence on the oxidation reactions of the biobased blends, given its known catalytic properties in promoting oxidative processes and to evaluate potential copper corrosion.

After conditioning, the samples were analysed for changes in density, viscosity, Total Acid Number (TAN), Total Sediments Existent (TSE), and compatibility through spot tests. Microscopic evaluations were performed to characterize the deposits formed during conditioning. The steel and copper specimens were visually inspected and weighed before and after conditioning to assess mass changes and surface effects such as corrosion or deposit adhesion. Both specimens were thoroughly rinsed with heptane and dried prior to final weight recording.

The demineralised water used in the conditioning step is analysed for volatile acids, which can be formed as part of the oxidation and decomposition reactions of the biobased products. The analysis follows a titration method using phenolphthalein as an indicator and 0.1N KOH solution

This conditioning process provides insights into both the chemical stability of the blends and their interactions with common materials in marine fuel systems, ensuring a comprehensive evaluation of their practical applicability.

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3 RESULTS

3.1 VLSFO (B0)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9418 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	165.8 mm²/s	N/A (*)
TAN	ASTM D664	0,20 mg KOH /g	0,15 mg KOH/g
TSE	ISO 10307-1	0,04 %m/m	1,01 %m/m
Spot test	ASTM D4740	2	5
∆m Steel	In-house		1,1 mg (+0,01 %m/m)
∆m Copper	In-house		<0.01 mg (<0,01 %m/m)
Volatile acids	In-house		0,04 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of the density and viscosity by the same methods used before conditioning not possible.

Table 1 VLSFO B0 results

The unblended VLSFO is tested under the same conditions as the bio-residual blends to provide a baseline for later comparison. The conditioning resulted in the formation of a sludge-like material as evidenced by the significant increase in TSE.

Figure 2 Metal specimens VLSFO, before conditioning shown on the left, after conditioning on the right.

Discoloration can be noticed on both the steel and copper specimen but not to the degree it can be considered corrosive. No significant change of mass was recorded.

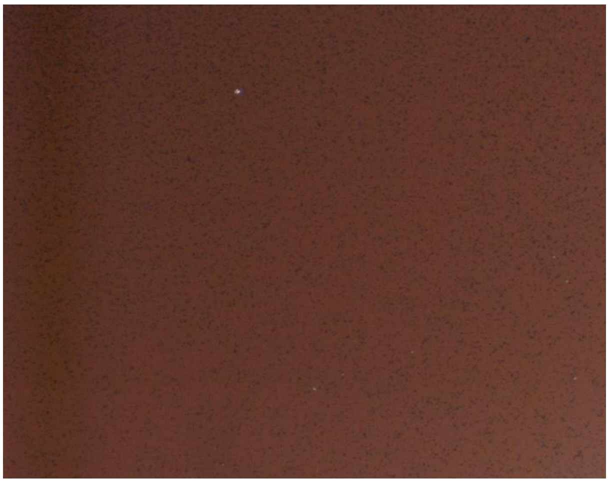

Figure 3 - Microscopic evaluation VLSFO after conditioning

A microscopic evaluation of the sample after conditioning shows the presence of deposits which were not present before conditioning.

3.2 HFO B0

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9901 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	387,5 mm²/s	N/A (*)
TAN	ASTM D664	0,20 mg KOH /g	0,15 mg KOH/g
TSE	ISO 10307-1	0,02 %m/m	0,04 %m/m
Spot test	ASTM D4740	1	1
∆m Steel	In-house		0,7 mg (+0,01 %m/m)
∆m Copper	In-house		<0,1 mg (<0,01 %m/m)
Volatile Acids	In-house		0,03 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of the density and viscosity by the same methods used before conditioning not possible.

Table 2 HFO B0 results

The unblended HFO is tested under the same conditions as the bio-residual blends to provide a baseline for later comparison. The conditioning formed deposits that rendered the sample unable to be accurately measured for viscosity and density but a much smaller increase in TSE was noticed than with the neat VLSFO.

Figure 5 Metal specimens HFO, before conditioning shown on the left, after conditioning on the right.

Slight discoloration can be noticed on both the steel and copper specimen No significant change of mass was recorded. The sample is not to be considered corrosive.

3.3 Bio Pyrolysis Oil (BPO)

3.3.1 Bio Pyrolysis Oil (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	1,0261 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	N/A (**)	N/A (*)
TAN	ASTM D664	N/A (**)	15,7 mg KOH/g
TSE	ISO 10307-1	0,01 %m/m	<0,01 %m/m
Spot test	ASTM D4740	1	5 (***)
∆m Steel	In-house		16,8 mg (+0,14 %m/m)
∆m Copper	In-house		0,1 mg (<0,01 %m/m)
Volatile Acids	In-House		2,09 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of the density and viscosity not possible.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

(***) Strong discoloration after ageing, see **Error! Reference source not found.**

Table 3 BPO B100 results

Even though the sample could not be measured before aging we can notice a very high TAN after conditioning.

Figure 4 Metal specimens BPO, before conditioning shown on the left, after conditioning on the right.

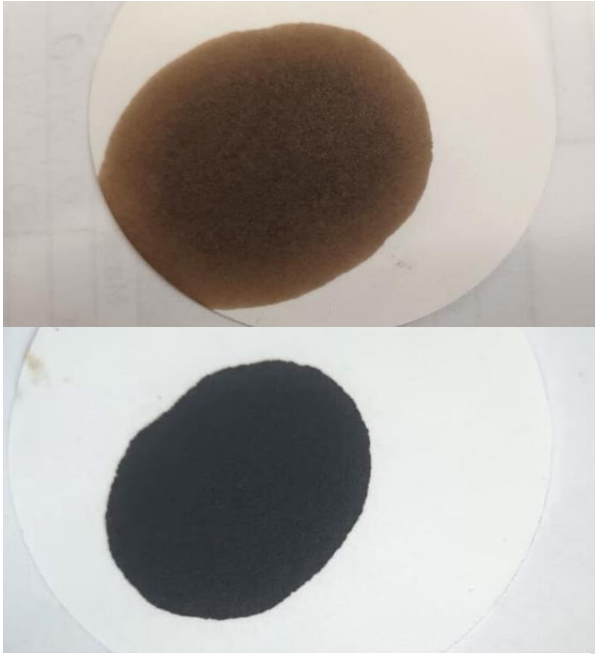

Figure 6 BPO B100 Spot test, before conditioning (top) and after conditioning (bottom)

After conditioning the steel specimen shows signs of corrosion. The specimen has increased in mass which can be attributed to the visible deposits as shown in Figure 5. These deposits were not soluble in organic solvents such as heptane or toluene. The copper specimen shows localised signs of corrosion but no increase in mass of any significance.

3.3.2 VLSFO / BPO blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9652 kg/l	N/A (*)	0,9816 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	121,1 mm²/s	N/A (*)	95,15 mm²/s	N/A (*)
TAN	ASTM D664	8,70 mg KOH/g	1,78 mg KOH/g	14,17 mg KOH/g	5,74 mg KOH/g
TSE	ISO 10307-1	N/A (**)	0,08 %m/m	0,05 %m/m	0,05 %m/m
Spot test	ASTM D4740	5	1	5	1
∆m Steel	In-house	59,5 mg (+0,48%m/m)		181,6 mg (+1,50%m/m)	
∆m Copper	In-house	68,5 mg (+2.16 %m/m)		79,9 mg (+2.39 %m/m)	
Volatile Acids	In-house	0,71 mg KOH/g		0,79 mg KOH/g	

(*) A sludge-like material formed deposits that made measurement of the density and viscosity by the same methods used before conditioning not possible.

(**) Blank filter could not be properly rinsed.

Table 4 VLSFO/BPO B30 & B50 results

Results for the VLSFO/BPO blends show that the conditioning led to a decrease of TAN and an increase in compatibility. The microscopic evaluation confirmed less insoluble material is found after conditioning.

While performing the analysis of the unconditioned B30 blend an insoluble sludge was formed during the heating process of the blend before filtration. The sludge that was formed showed strong adhesive properties to the glass beaker and could not be removed with the use of a solvent or a spatula.
This phenomenon was not observed after conditioning or with the other blend concentrations indicating that the influence of the composition of the VLSFO and BPO can cause stability issues at different blend concentrations.

Figure 7 Microscopic evaluation of the B30 VLSFO/BPO blend before conditioning (top) and after conditioning (bottom)

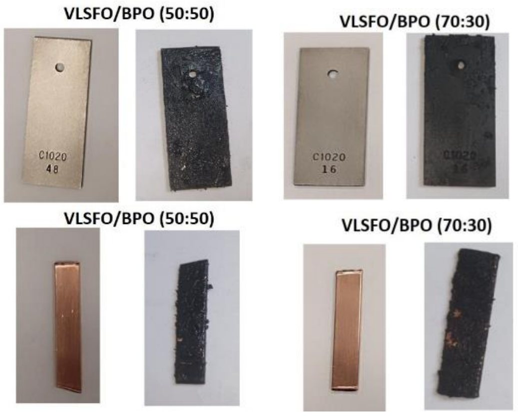

Figure 8 VLSFO / BPO metal specimens, each pair shows the specimen before conditioning on the left and after conditioning on the right.

The steel and copper specimens show significant increases in mass caused by deposits formed during the conditioning which appear insoluble in common lab solvents.

The combination of these observations leads us to believe the organic acid present in the bio-component reacted with the residual fuel oil to form additional deposits on the surface of the metal specimens.

3.3.3 HFO/BPO blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	1,0000 kg/l	N/A (*)	1,0075 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	181,7 mm²/s	N/A (*)	106,4 mm²/s	N/A (*)
TAN	ASTM D664	8,94 mg KOH/g	3,55 mg KOH/g	14,29 mg KOH/g	6,90 mg KOH/g
TSE	ISO 10307-1	0,19 %m/m	0,08 %m/m	1,17 %m/m	0,05 %m/m
Spot test	ASTM D4740	2	1	5	2
∆m Steel	In-house	51,9mg (+0,43 %m/m)		66,3mg (+0,54 %m/m)	
∆m Copper	In-house	16,7mg (+0,56%m/m)		52,5mg (+1,81%m/m)	
Volatile Acids	In-house	0,88 mg KOH/g		0,31 mg KOH/g	

(*) A sludge-like material formed deposits that made measurement of the density and viscosity by the same methods used before conditioning not possible.

Table 5 HFO/BPO B30 & B50 results

TSE results have decreased after conditioning but the blank filters for the unconditioned sample could not be properly rinsed rendering those results unreliable.

The conditioning process has a positive impact on blend stability, with the biggest effect visible on the B50 blend. Indicating that stability is influenced by the composition of the blended products and blend concentrations. Sludge formation was observed on the blank filters of the unconditioned samples resulting in less reliable results.

Figure 9 HFO / BPO metal specimens, each pair shows the specimen before conditioning on the left and after conditioning on the right

Acid number after conditioning decreased significantly and simulateously the compatibility of the blend components increases significantly as well, as indicated by the improved rating of the spot test.

The steel and copper specimens show significant increases in mass and insoluble deposits have been formed on the steel and copper specimens by the sample during the conditioning.

These observations are similar to those found on the VLSFO/BPO blends, leading us to a similar conclusion of reactions occurring between the organic acids and residual fuel oil.

3.4 Distilled Bio Pyrolysis Oil (DBPO)

3.4.1 Distilled Bio Pyrolysis Oil (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9317 kg/l	0,9492 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)
TAN	ASTM D664	N/A (**)	N/A (**)
TSE	ISO 10307-1	<0,01 %m/m	<0,01 %m/m
Spot test	ASTM D4740	1	1
∆m Steel	In-house	<0,1mg (<0.01 %m/m)	
∆m Copper	In-house	<0,1mg (<0.01 %m/m)	
Volatile Acids	In-house	<0,01 mg KOH/g	

(*) Measurement was discontinued due to risk of damage to glassware.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

Table 6 DBPO B100 results

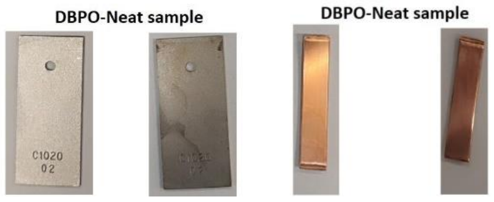

Figure 10 DBPO metal specimens, unconditioned sample on the left, conditioned sample on the right

Apart from the increased density the Distilled bio pyrolysis oil doesn't show noticeable effects from the conditioning.

3.4.2 VLSFO / DBPO blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9383 kg/l	0,9497 kg/l	0,9358 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	51,53 mm²/s	N/A (*)	28,30 mm²/s	N/A (*)
TAN	ASTM D664	0,19 mg KOH/g	0,52 mg KOH/g	0,16 mg KOH/g	N/A (**)
TSE	ISO 10307-1	0,02 %m/m	0,01 %m/m	0,02 %m/m	<0,01 %m/m
Spot test	ASTM D4740	1	1	1	1
∆m Steel	In-house		0,2mg (<0.01% m/m)		0,4mg (<0.01 %m/m)
∆m Copper	In-house		0,4mg (<0.01 %m/m)		0,1mg (<0.01 %m/m)
Volatile Acids	In-house		0,02 mg KOH/g		0,02 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of viscosity and density by the same methods used before conditioning not possible.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

Table 7 VLSFO/ DBPO results

An increase in density and viscosity can be observed but no other noticeable changes after conditioning.
Increasing the concentration of DBPO shows a negative impact on blend stability after conditioning.

3.4.3 HFO / DBPO blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9706 kg/l	N/A (*)	0,9606 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	67,6 mm²/s	N/A (*)	33,76 mm²/s	N/A (*)
TAN	ASTM D664	0,30 mg KOH/g	N/A (**)	0,25 mg KOH/g	N/A (**)
TSE	ISO 10307-1	0,01 %m/m	0,02 %m/m	0,01 %m/m	0,02 %m/m
Spot test	ASTM D4740	1	1	1	1
∆m Steel	In-house		0,3mg (<0.01 %m/m)		0,4mg (<0.01%m/m)
∆m Copper	In-house		0,4mg (<0.01 %m/m)		0,1mg (<0.01 %m/m)
Volatile Acids	In-house		0,02 mg KOH/g		0,02 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of viscosity and density by the same methods used before conditioning not possible.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

Table 8 HFO/ DBPO blend results

Sludging prevented analysis of multiple parameters after conditioning. No significant observable changes to the sample after conditioning on the analysis that could be performed.

3.5 Refined CNSL (rCNSL)

3.5.1 Refined CNSL (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9668 kg/l	0,9642 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)
TAN	ASTM D664	17,17 mg KOH/g	N/A (*)
TSE	ISO 10307-1	0,29 %m/m	0,24 %m/m
Spot test	ASTM D4740	3	3
∆m Steel	In-house		<0,1mg (<0.01 %m/m)
∆m Copper	In-house		<0,1mg (<0.01 %m/m)
Volatile Acids	In-house		0,01 mg KOH/g

(*) Measurement was discontinued due to risk of damage to glassware.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

Table 9 rCNSL B100 results

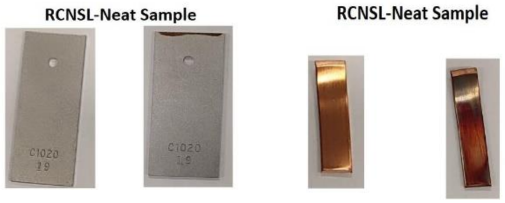

Figure 11 rCNSL metal specimens before and after conditioning

Apart from the decreased density the rCNSL (refined cashew nutshell liquid) does not show noticeable effects from the conditioning. The metal specimens show some limited local discoloration, but the sample is not to be considered corrosive.

3.5.2 VLSFO / rCNSL blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9493 kg/l	0,9517 kg/l	0,9538 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)	N/A (*)	N/A (*)
TAN	ASTM D664	5,22 mg KOH/g	N/A (**)	8,75 mg KOH/g	N/A (**)
TSE	ISO 10307-1	0,10 %m/m	0,09 %m/m	0,11 %m/m	0,12 %m/m
Spot test	ASTM D4740	2(***)	1	1(***)	2
∆m Steel	In-house		0,7mg (+0.01 %m/m)		0,4mg (<0.01 %m/m)
∆m Copper	In-house		0,4mg (<0.01 %m/m)		0,1mg (<0.01%m/m)
Volatile Acids	In-house		0,02 mg KOH/g		0,02 mg KOH/g

(*) Measurement was discontinued due to risk of damage to glassware.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

(***) Phase separation visible

Table 10 VLSFO / rCNSL results

A slight increase in density can be observed.

The metal specimens showed no observable discolouration or signs of corrosion.

During spot test phase separation is visible before conditioning and not present after conditioning as shown in Figure 12. Because the method is developed for detecting instability by asphaltene drop out, there is no clear guideline on how to rate this spot.

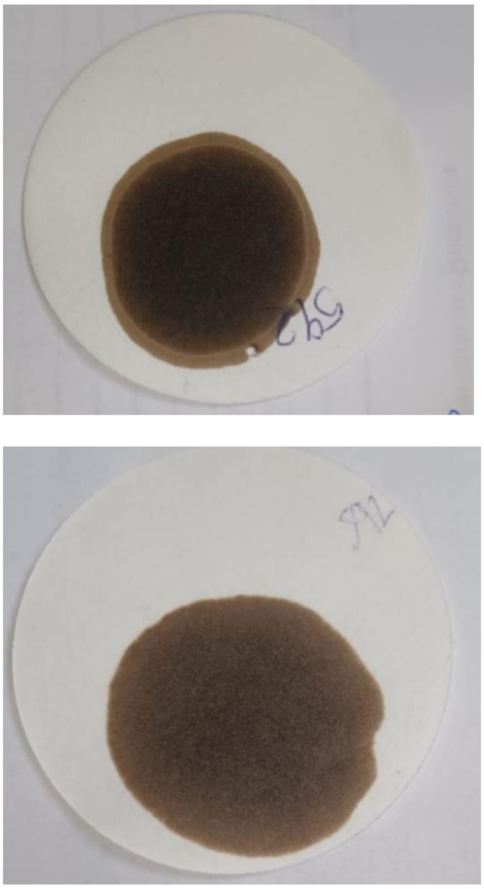

Figure 12 VLSFO/rCNSL B30 blends spot test before and after conditioning

3.5.3 HFO / rCNSL blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9834 kg/l	N/A (*)	0,9783 kg/l	0,9805 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)	N/A (*)	N/A (*)
TAN	ASTM D664	5,60 mg KOH/g	N/A (**)	8,94 mg KOH/g	N/A (**)
TSE	ISO 10307-1	0,01 %m/m	0,02 %m/m	0,01 %m/m	0,02 %m/m
Spot test	ASTM D4740	1(***)	1(***)	1(***)	1(***)
∆m Steel	In-house	-0,6mg (<0.01 %m/m)		0,4mg (<0.01 %m/m)	
∆m Copper	In-house	0,1mg (<0.01 %m/m)		0,4mg (<0.01 %m/m)	
Volatile Acids	In-house	0,02mg KOH/g		0,02mg KOH/g	

(*) Measurement was discontinued due to risk of damage to glassware.

(**) Measurement was not possible due to insufficient solubility in the required solvent.

(***) Phase separation visible

In contrast to the results for the VLSFO/rCNSL blends, the observed phase separation in the spot test was visible after conditioning as well for the HFO/rCNSL blends as shown in Figure 13. These instabilities resulted in deposits in most of the analytical equipment rendering them unavailable for further analysis and extensive cleaning procedures had to be used to be able to get the analytical equipment back to acceptable normal operating conditions. To avoid further damage to the analytical equipment analysis could not be performed.

Limited signs of local corrosion were visible on both metal specimens for the B50 blend as shown on the steel specimen in Figure 14.

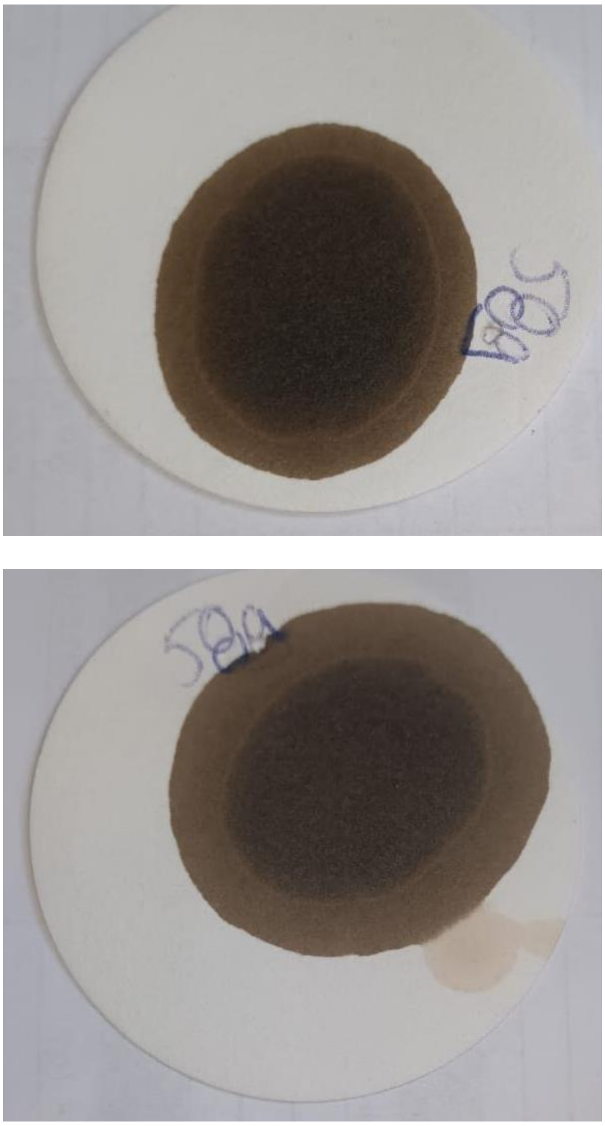

Figure 13 HFO/rCNSL B50 spot tests

Figure 14 HFO/rCNSL Steel specimen before (left) and after (right) conditioning

3.6 MR1-100

3.6.1 MR1-100 (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9203 kg/l	0,9285 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)
TAN	ASTM D664	0,36 mg KOH/g	1,89 mg KOH/g
TSE	ISO 10307-1	<0,01 %m/m	<0,01 %m/m
Spot test	ASTM D4740	1	1
∆m Steel	In-house		<0,1mg (<0.01 %m/m)
∆m Copper	In-house		<0,1mg (<0.01 %m/m)
Volatile Acids	In-house		0,63 mg KOH/g

(*) Measurement was discontinued due to risk of damage to glassware.

Table 11 MR1-100 B100 results

After conditioning the sample of MR1-100 shows a decrease in density and an increase in Total Acid Number with a notable quantity of volatile acids also being released. No change in the intensity of the spot test was observed and no effect on the metal specimens was recorded either.

3.6.2 VLSFO / MR1-100 blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9351 kg/l	0,9461 kg/l	0,9308 kg/l	0,9425 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)	N/A (*)	N/A (*)
TAN	ASTM D664	0,24 mg KOH/g	1,84 mg KOH/g	0,28 mg KOH/g	1,51 mg KOH/g
TSE	ISO 10307-1	0,10 %m/m	0,09 %m/m	0,11 %m/m	0,12 %m/m
Spot test	ASTM D4740	2	2	1	2
∆m Steel	In-house		0,3mg (<0.01 %m/m)		0,1mg (<0.01 %m/m)
∆m Copper	In-house		0,1mg (<0.01 %m/m)		0,1mg (<0.01%m/m)
Volatile Acids	In-house		0,26 mg KOH/g		0,08 mg KOH/g

(*) Measurement was discontinued due to risk of damage to glassware.

Table 12 VLSFO/MR1-100 blends results

3.6.3 HFO/MR1-100 blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9682 kg/l	0,9784 kg/l	0,9542 kg/l	0,9648 kg/l
Viscosity @ 50°C	EN ISO 3104	N/A (*)	N/A (*)	N/A (*)	N/A (*)
TAN	ASTM D664	0,37 mg KOH/g	0,83 mg KOH/g	0,37 mg KOH/g	2,54 mg KOH/g
TSE	ISO 10307-1	0,01 %m/m	<0,01 %m/m	0,01 %m/m	<0,01 %m/m
Spot test	ASTM D4740	1	1	1	1
∆m Steel	In-house		0,4mg (<0.01 %m/m)		0,8mg (<0.01 %m/m)
∆m Copper	In-house		0,1mg (<0.01 %m/m)		0,1mg (<0.01 %m/m)
Volatile Acids	In-house		0,03 mg KOH/g		0,07 mg KOH/g

(*) Measurement was discontinued due to risk of damage to glassware.

An increase in density of both blends can be noticed after the conditioning period as well as significant increases in Total Acid Number and the formation of volatile acids, similar to what was observed for the B100 MR1-100.

3.7 FAME Distillation Residue (FDR)

3.7.1 FDR (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,9730 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	132,3 mm²/s	N/A (*)
TAN	ASTM D664	3,16 mg KOH/g	N/A (**)
TSE	ISO 10307-1	N/A (***)	N/A (***)
Spot test	ASTM D4740	2	2
∆m Steel	In-house		0,1mg (<0.01 %m/m)
∆m Copper	In-house		0,6mg (+0.02 %m/m)
Volatile Acids	In-house		0,37 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of viscosity and density by the same methods used before conditioning not possible.

(**) Measurement was not possible due to insufficient solubility in the required solvent

(***) Filtration time exceeded.

After conditioning the sample of FAME Distillation Residue could no longer be subjected to most of the attempted analytical techniques. The sample formed a sludge which was not soluble in common lab solvents.

3.7.2 VLSFO / FDR blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9459 kg/l	0,9527 kg/l	0,9487 kg/l	0,9559 kg/l
Viscosity @ 50°C	EN ISO 3104	123,0 mm²/s	186,2 mm²/s	105,5 mm²/s	N/A (*)
TAN	ASTM D664	1,87 mg KOH/g	3,68 mg KOH/g	3,25 mg KOH/g	N/A (**)
TSE	ISO 10307-1	0,06 %m/m	0,07 %m/m	0,12 %m/m	0,12 %m/m
Spot test	ASTM D4740	1	3	2	3
∆m Steel	In-house	0,2mg (<0.01 %m/m)		0,3mg (<0.01 %m/m)	
∆m Copper	In-house	0,2mg (0.01 %m/m)		0,8mg (0.03%m/m)	
Volatile Acids	In-house	0,04 mg KOH/g		0,06 mg KOH/g	

(*) A sludge-like material formed deposits that made measurement of viscosity by the same methods used before conditioning not possible.

(**) Measurement was not possible due to insufficient solubility in the required solvent

Table 13 VLSFO/FDR Results

A significant increase in Total Acid Number can be noticed after conditioning for the B30 blend as well as an increase in viscosity and Spot rating.

3.7.3 HFO/FDR blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9801 kg/l	0,9874 kg/l	0,9730 kg/l	N/A (*)
Viscosity @ 50°C	EN ISO 3104	186,1 mm²/S	N/A (*)	132,3 mm²/s	N/A (*)
TAN	ASTM D664	2,03 mg KOH/g	4,08 mg KOH/g	3,16 mg KOH/g	3,91 mg KOH/g
TSE	ISO 10307-1	0,03 %m/m	0,04 %m/m	0,15 %m/m	0,15 %m/m
Spot test	ASTM D4740	2	2	2	3
∆m Steel	In-house	0,3mg (<0.01 %m/m)		<0,1mg (<0.01 %m/m)	
∆m Copper	In-house	0,1mg (<0.01 %m/m)		0,2mg (0.01 %m/m)	
Volatile Acids	In-house	0,03 mg KOH/g		0,03 mg KOH/g	

(*) A sludge-like material formed deposits that made measurement of viscosity and density by the same methods used before conditioning not possible.

Table 14 HFO/FDR results

Similarly to the VLSFO blends a significant increase in Total Acid Number can be observed.

3.8 Rapeseed Methyl Ester (RME)

3.8.1 RME (B100)

Analysis	Method	Before Conditioning	After Conditioning
Density @ 15°C	EN ISO 12185	0,8824 kg/l	0,9169 kg/l
Viscosity @ 50°C	EN ISO 3104	4,429 mm²/s	N/A (*)
TAN	ASTM D664	0,37 mg KOH/g	3,38 mg KOH/g
TSE	ISO 10307-1	<0,01 %m/m	< 0,01 %m/m
Spot test	ASTM D4740	1	1
∆m Steel	In-house		0,6mg (<0.01 %m/m)
∆m Copper	In-house		0,2mg (+0.01 %m/m)
Volatile Acids	In-house		0,61 mg KOH/g

(*) A sludge-like material formed deposits that made measurement of viscosity by the same methods used before conditioning not possible.

Table 15 RME B100 results

After conditioning the sample of RME shows a strongly increased Total Acid Number and a significant amount of volatile acids were also measured.Slight discolouration was noted on both samples but not enough to be considered corrosion.

3.8.2 VLSFO / RME blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9232 kg/l	0,9343 kg/l	0,9110 kg/l	0,9250 kg/l
Viscosity @ 50°C	EN ISO 3104	28,84 mm²/s	45,82 mm²/s	13,14 mm²/s	19,94 mm²/s
TAN	ASTM D664	0,27 mg KOH/g	1,31 mg KOH/g	0,30 mg KOH/g	2,95 mg KOH/g
TSE	ISO 10307-1	0,03 %m/m	0,20 %m/m	0,02 %m/m	0,05 %m/m
Spot test	ASTM D4740	1	3	1	3
∆m Steel	In-house		1,0mg (0.01 %m/m)		0,2mg (<0.01 %m/m)
∆m Copper	In-house		0,2mg (0.01 %m/m)		0,2mg (0.01%m/m)
Volatile Acids	In-house		0,18 mg KOH/g		0,35 mg KOH/g

Table 16 VLSFO/RME results

Figure 15 VLSFO/RME B30 metal specimens after conditioning

A significant increase in Total Acid Number can be noticed after conditioning for the B30 and B50 blend as well as an increase in viscosity.

Conditioning the samples results in the formation of organic acids, these organic acids have a clear impact on stability of the blend as can be seen from the TSE results. Fame concentration has a positive impact on stability of the blend, when fame reacts to form its oxidation byproducts the solubility goes down which results in instability of the blend. Making oxidation stability an important parameter to consider.

Discolouration can be observed on both the copper and steel specimens as shown in Figure 15

3.8.3 HFO/RME blends

		B30		B50	
Analysis	Method	Before Cond.	After Cond.	Before Cond.	After Cond.
Density @ 15°C	EN ISO 12185	0,9556 kg/l	0,9652 kg/l	0,9336 kg/l	0,9434 kg/l
Viscosity @ 50°C	EN ISO 3104	37,38 mm²/s	64,66 mm²/s	14,60 mm²/s	21,80 mm²/s
TAN	ASTM D664	0,40 mg KOH/g	0,84 mg KOH/g	0,40 mg KOH/g	1,05 mg KOH/g
TSE	ISO 10307-1	0,02 %m/m	0,60 %m/m	0,01 %m/m	0,45 %m/m
Spot test	ASTM D4740	1	5	1	5
∆m Steel	In-house		1,6mg (0.01 %m/m)		3,0mg (0.02 %m/m)
∆m Copper	In-house		0,1mg (<0.01 %m/m)		0,4mg (0.01 %m/m)
Volatile Acids	In-house		0,05 mg KOH/g		0,14 mg KOH/g

Table 17 HFO/RME results

As with the VLSFO blends a significant increase in Total Acid Number and viscosity can be observed. The metal specimens shown in Figure 16 display a stronger discolouration than with the VLSFO/RME blend as well as an increase in mass on the steel specimen. This indicates corrosion.

Figure 16 HFO/RME B50 metal specimens before and after corrosion

4 CONCLUSIONS

This study investigated the stability, compatibility, and corrosion behavior of B30 and B50 biobased blends with VLSFO and HFO fuels under oxidative conditions at 130°C. The key findings are summarized as follows:

Bio Pyrolysis Oil (BPO):

BPO exhibited significant deposit formation, as evidenced by increased Total Sediment Existent (TSE) and sludge formation. This behavior is attributed to the high acid content of the raw CNSL-based product, in particular the anacardic acids it contains, which appear to undergo reactions during conditioning, leading to the observed reduced acid numbers and improved compatibility of the remaining fuel.

Corrosion testing showed significant mass increases on steel specimens due to deposit adhesion, indicating material challenges in applications involving carbon steel when using a fuel containing this type of biological blend component.

Distilled Bio Pyrolysis Oil (DBPO):

DBPO demonstrated superior stability and compatibility when compared to the undistilled BPO, with negligible sedimentation and corrosion effects across both VLSFO and HFO blends. Its low acid content confirms that high anacardic acid levels in the BPO are a primary factor in the observed instability.

Refined CNSL (rCNSL):

rCNSL showed moderate stability, with lower TSE values than those of BPO but higher than those of DBPO. Phase separation observed in spot tests before conditioning was resolved after oxidation, although compatibility and sedimentation performance remained suboptimal compared to DBPO.

MR1-100:

MR1-100 blends showed an increase in density and Total Acid Number (TAN) after conditioning, along with the formation of volatile acids. However, Total Sediments Existent (TSE) values remained low, with the B30 blend of VLSFO staying within the acceptable specification limit of 0.10 %m/m. However, the B50 blend of VLSFO exceeded this limit, indicating instability at higher biobased product concentrations. In contrast, both HFO blends performed well within the specification, demonstrating better stability in comparison to the VLSFO blends. No significant deposit formation or corrosion effects were observed on the metal specimens.

These findings suggest that MR1-100 demonstrates good overall stability and material compatibility, making it a viable component for blending in marine fuels. However, this is especially true for HFO blends, where Total Sediments Existent (TSE) values remained well within acceptable limits, showcasing stability even at higher blend ratios. For VLSFO blends, caution is required as B50 blends exceeded the TSE specification limit of 0.10 %m/m, indicating potential instability at higher concentrations of MR1-100.

FAME Distillation Residue (FDR):

FDR exhibited significant challenges post-conditioning, particularly in its neat form (B100). The sample formed a sludge that was insoluble in common solvents, making further analysis impossible. Highlighting its bad thermal oxidative properties.

Blends with VLSFO and HFO displayed noticeable increases in viscosity and Total Acid Number (TAN) after conditioning. With Total Sediment Existent (TSE) values exceeding 0.10 %m/m for both B50 blends of VLSFO and HFO, significant stability issues at higher blend concentrations can be observed. While B30 blends remained within acceptable limits, these results emphasize the need for careful monitoring and potential adjustments when using higher concentrations of FDR in marine fuel blends. While some blends caused minor corrosion effects on copper specimens, emphasizing the need for further evaluation of material compatibility.

FDR exhibited significant stability and thermal oxidative challenges. The high Total Acid Number (TAN) and its increase with blend concentration exacerbate these issues. Additionally, sludge formation post-conditioning highlighted severe stability concerns, making further refinement necessary to address these challenges effectively.

RME

The RME blends showed an increase in density, TAN and viscosity after thermal oxidative conditioning.

After the conditioning process a significant increase of volatile acids can be observed showing the instability of RME against thermal oxidative processes.

After the conditioning process instability of the blends are observed in all blend concentrations for VLSFO and HFO. These are confirmed with the spot test and TSE results showing increased results.

General Observations:

Several samples formed persistent deposits on the analytical equipment and glassware during testing. These deposits were particularly difficult to remove and often hindered the measurement of density and viscosity after conditioning. In some cases, even pre-conditioning measurements were affected. This behavior underscores the challenges in stability for certain blends, as such deposits indicate a high tendency for sedimentation and the formation of insoluble components during thermal oxidation which could interfere with the smooth operation of fuel systems and engine components that come into contact with these fuels.

Volatile acids were consistently detected in conditioned samples highlighting oxidative degradation processes. With DBPO and rCNSL serving as an exception highlighting their relatively higher stability and compatibility compared to their unrefined predecessors.

Acid number of the pure biobased product as well as acid number of the blend are of big importance when evaluating stability and sludge & deposit formation. The specification of 2,5 mg KOH / g in the ISO 8217 specification [2] seems to be confirmed as a good limit to maintain especially regarding the stability of the bio-residual blends. Biobased blend components contain different organic acid than those usually found in fossil fuels and identifying these and assessing their influence could be a worthwhile topic for a future study.

Spot tests effectively identified phase separation and compatibility issues, correlating well with sedimentation, acidity and stability data. We find these serve as an essential and quick tool to assess the viability of bio-residual fuel blends.

The steel specimen used in the thermal oxidation provided additional insights, indicating that some products adhere strongly to steel, potentially complicating material compatibility in real-world applications. Polymerisation products and soap formation is likely to be the cause of this, but further investigation is required to confirm this hypothesis.

Suggested future steps:

1. Investigate soap formation under marine conditions to evaluate the impact of organic acids and (sea-)water.
2. Study on the impact of different organic acids on the stability of the residual fuel blends.
3. The impact of different residual fuel compositions on biobased blending stability.
4. Analyze polar extracts and molar mass distribution to better understand their contributions to sedimentation and compatibility.
5. Explore the use of additives such as antioxidants or metal deactivators to enhance the stability of CNSL-based blends.
6. Explore different types of biobased materials for blending.
7. Performance based testing on promising biobased products to imitate in the field conditions.

We believe that performing (some of) the additional suggested research could help pave the way to a science-based approach for assessing the suitability of biobased fuel blending components in the marine industry. While updating the scope of standards such as ISO 8217 might be too far reaching, it could help establish an analytical framework or guideline that investigates the blending compatibility of existing and novel renewable components.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

CNSL: Cashew Nut Shell Liquid, a byproduct oil from cashew nut processing.

BPO: Bio Pyrolysis Oil, consists of 100% CNSL subjected to pyrolysis treatment.

DBPO: Distilled Bio Pyrolysis Oil a distillate of BPO

rCNSL: Refined Cashew Nut Shell Liquid

FDR: FAME Distillation Residue, a leftover material that remains after the purification and distillation of raw biodiesel.

FAME: Fatty Acid Methyl Esters, also known as biodiesel. A renewable fuel made from vegetable oils, animal fats, or used cooking oil by the process of transesterification.

MR1-100: A proprietary blend component for fuel oils derived from Used Cooking Oil, which is commercially available on the market.

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7 REFERENCES AND BIBLIOGRAPHY

[1] REGULATION (EU) 2023/1805 of the European Parliament and of the council of 13 September 2023

[2] ISO 8217:2024 Products form petroleum, synthetic and renewable sources – Fuels – specifications of marine fuels

ISO 4259-2:2017 Petroleum and related products – precision of measurement methods and results – part 2 Interpretation and application of precision data in relation to methods of test

CIMAC WG7 guideline No. 02:2016 “the interpretation of Marine Fuel Analysis Test Results”

EN ISO 12185:2024 Crude petroleum, petroleum products and related products - Determination of density - Laboratory density meter with an oscillating U tube sensor

ISO 3104:2023 Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity

ISO 10307-1:2009 Petroleum products — Total sediment in residual fuel oils — Part 1: Determination by hot filtration

ASTM D664-24 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration

ASTM D4740-24 Standard Test Method for Cleanliness and Compatibility of Residual Fuels by Spot Test

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