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Assessment of Bio-Oil and Off-Spec Biodiesel Blends for Maritime Applications

Fuels - Alternative & New Fuels

Sara Rezaee, Viswa Group

Cameron Miller, Viswa group
Aparna Balachandran, Viswa Group
Ramaratnam Visweswaran, Viswa Group

ABSTRACT

The maritime industry has begun utilizing biodiesel blends from 2022 on trial basis, with various agencies reporting positive feedback on their performance. However, a barrier to the widespread adoption of biodiesel is its high production cost. Untreated bio-oil and off-spec biodiesel offer potential as more cost-effective biofuel alternatives.

There is limited research on the suitability of bio-oil samples for maritime applications. Nonetheless, bio-oil and off-spec FAME (Fatty Acid Methyl Esters) products have the potential to serve as sustainable fuels in the maritime sector, either through the production of marine biofuel or as components of fuel blends.

To determine the feasibility of using bio-marine oil blended with conventional fuel oil in ships, the study examines the physical and chemical characteristics, storage stability and corrosivity properties of these fuels.

The characteristics of bio-oil blended with residual fuels are assessed in terms of fundamental properties such as density, viscosity, flash point, carbon residue, and water content. Stability properties are analyzed by testing total sediment existent and total sediment potential, with storage stability evaluated through accelerated stability testing.

Due to the high oxygen content in bio-oils, which may impact their energy content and ignition-combustion properties, the energy content and ignition-combustion characteristics of these blends were measured using ASTM D240 and FIA-FCA tests. Cold flow properties were analyzed through pour point and wax appearance temperature tests.

Gas chromatography-mass spectrometry (GC-MS) was employed to determine the composition of the biofuel blends, providing a detailed analysis of their constituents.

1 INTRODUCTION

The increasing adoption of Fatty Acid Methyl Ester (FAME) blended fuels in the marine industry is primarily driven by the need to reduce greenhouse gas (GHG) emissions and meet carbon intensity targets set by regulations such as the IMO's GHG strategy. FAME products first entered the marine market in 2022, with several vessels initiating trials in 2022 and commencing regular use in 2023 and 2024. Feedback on the use of biofuel blends— bio-residual and bio-distillate fuels—has been positive so far. The FAME used in these blends meets the requirements of ASTM D6751 or EN 14214, and various studies have shown that adding biodiesel to marine fuels does not negatively affect their quality. In 2024, the release of the new ISO 8217 standard introduced guidelines for testing biofuel blends, bio-residual, and bio-distillate fuels, further facilitating their integration into mainstream marine fuels infrastructure.

Kass et al. (2022) showed that adding 20 wt% biodiesel to Very Low Sulfur Fuel Oils (VLSFOs) improved several key physical and combustion properties. Their study indicated that lubrication performance was enhanced with the inclusion of as little as 5% biodiesel and that the estimated cetane number (ECN) increased with 15 wt% biodiesel. Furthermore, their research found that 20 wt% biodiesel did not promote asphaltene aggregation or precipitation [1]. Rezaee et al. (2023) reported that blending biodiesel with VLSFOs at ratios of 30%, 50%, and 70% reduced kinematic viscosity, density, MCR, sulfur content, water, ash, and metal content in the tested VLSFOs. This blending also improved the stability and ignition properties of the VLSFOs [2].

According to CIMAC WG7, engines can use FAME either as a blend component or as a 100% drop-in fuel, provided the operational guidelines set by the OEM are followed. From an operational perspective, as long as engine seals are compatible with FAME, no significant issues are expected [3]. However, there are operational considerations that must be addressed when using FAME-based fuels, including ensuring material compatibility, performing tank cleaning prior to switching to FAME products, and adjusting purifier settings [3].

Despite the generally positive feedback on the use of biodiesel blends that meet ASTM D6751 or EN14214, challenges such as the high cost and limited availability of biodiesel for marine applications have led to ongoing research into alternative fuel options. Among these alternatives are fast pyrolysis oil, tire pyrolysis oils, off-spec FAME products, and by-products from biodiesel plants.

The objective of this study is to provide an overview of the quality of various bio-oil samples and off-spec FAME products that could be suitable for marine applications.

2 MATERIALS AND METHODS

In this research, we examined pyrolysis oils commercially available in the industry and off-spec biodiesel samples derived from biodiesel plant by-products. The off-spec biodiesel samples were primarily obtained from animal fats and used cooking oil. The following products were analyzed to assess their quality and suitability for potential marine applications:

- Wood-based pyrolysis oils (through fast pyrolysis)
- Tire pyrolysis oil (TPO)
- By-products of biodiesel plants
- Off-spec FAME products

The miscibility of pyrolysis oil with Marine Gas Oil (MGO) and residual fuel was evaluated by preparing blends and storing them at room temperature or 50°C (a typical storage condition) for one day. Samples were then collected from the top and bottom of the container, and their densities were measured to verify homogeneity. Visual inspection was also performed as an initial step to assess miscibility with distillate-based fuels.

In addition to testing for ISO 8217 parameters, further analyses were performed to characterize the chemical composition and ignition-combustion properties of these fuels. The tests included:

- Carbon-Hyrogen-Nirogen Analysis: Conducted in accordance with ASTM D5291.
- Oxygen Content Analysis: Performed using a modified ASTM D5291 method.
- Ignition and Combustion Properties: Tested following IP 541.
- Organic Chloride Content: Measured according to EN 14077.
- GC-MS Analysis: Applied to tire pyrolysis oil and off-spec biodiesel samples using a modified ASTM D7845 method.
- Free Fatty Acids: Measured as per AOCS Ca 5a-40.

- Cold Soak Filterability: Tested in line with ASTM D7501.
- Free and Total Glycerin: Measured as per ASTM D6584.
- Modified Total acid number: Modified Total Acid Number (TAN) as per National Oak Ridge Lab method [5].

This comprehensive testing framework provided a detailed characterization of the samples to evaluate their potential suitability for use in the marine industry.

3 RESULTS AND DISCUSSION

3.1 Wood-based pyrolysis oil

Commercially available wood-based pyrolysis oils (produced through fast pyrolysis and not upgraded) were tested for potential use in marine fuel applications. The composition of these bio-oil samples varies based on the feedstock and processing conditions. Typically, wood-based bio-oils have high water content and oxygenated compounds, including carboxylic acids, phenols, ketones, formaldehydes, furans, and lignin-derived structures [4].

Three wood-based pyrolysis oil samples were analyzed, and the results are summarized in Table 1, with comparisons made against ISO 8217 RMK 700 specifications. Key observations include:

Density: The density of two samples was tested, and both exceeded 1010 kg/m³, which is higher than the typical limits for marine fuels.

Water Content: All three samples exhibited high water content exceeding 25%, which is the detection limit of ASTM D95. To ensure accuracy, water content was tested using different sample quantities to verify the results.

Sediment Content: The sediment content was above 0.1% for all samples, indicating potential challenges with stability and filtration. Due to the high Total Sediment Existent (TSE) values, tests for Total Sediment Potential (TSP) and Total Sediment Accelerated (TSA) were not conducted.

Metal Content: One sample displayed exceptionally high metal content, raising concerns about its compatibility with fuel systems.

Pour Point: One sample had a pour point exceeding 30°C, which could pose challenges for cold-weather operability.

Micro Carbon Residue (MCR): One sample had an MCR value exceeding 20%, suggesting a propensity for deposit formation during combustion.

Acid Number: All samples exhibited high acid numbers, which aligns with the acidic nature of biomass-derived pyrolysis oils and is consistent with findings from previous studies. The acid number was also measured using the modified acid number method proposed by Connatser et al. (2014) [5]. They noted that the modified method provides more accurate data for low to medium-quality upgraded bio-oil, which is necessary because, according to ASTM D664, the solvent used is immiscible with hydrophilic oils or their components. This immiscibility can lead to inaccurate readings or an overestimation of the TAN [5]. By using the modified TAN technique, the AMTAN obtained is lower than the standard TAN measured by ASTM D664. The lower AMTAN is attributed to the fact that phenolic compounds are not accounted for in the AMTAN method. Despite using this method, both the AMTAN and the TAN values remain well above the acceptable limit for Acid Number set by ISO 8217.

Flash point: The flash point of one of the samples is 56°C, which is slightly below the required specification of 60°C as per ISO 8217.

The elevated water and oxygen content in these bio-oil samples contribute to their low calorific value. These components are also linked to the longer ignition delay (poor ignition properties) and a higher likelihood of corrosion in injectors and the fuel supply system [6].

These findings highlight the need for additional refining or treatment to address the identified parameters and align the samples with marine fuel specifications.

The second step is to verify the miscibility of the wood-based pyrolysis oil with Marine Gas Oil (MGO) and residual fuel. To conduct the miscibility test, the wood-based pyrolysis oil was mixed with residual fuel and stored at 50°C. After one day, samples were taken from both the top and the bottom of the container. The density of both layers was measured to ensure the sample remained miscible and homogenous over time. The results, shown in Table 2, clearly indicate that the densities of the top and bottom layers differ. This suggests that the wood-based pyrolysis oil did not remain miscible with residual fuels over time. The miscibility of diesel/MGO with a wood-based pyrolysis oil was evaluated visually. As shown in Figure 1, the wood-based pyrolysis oil was not miscible with MGO, resulting in a clear separation between the two phases.

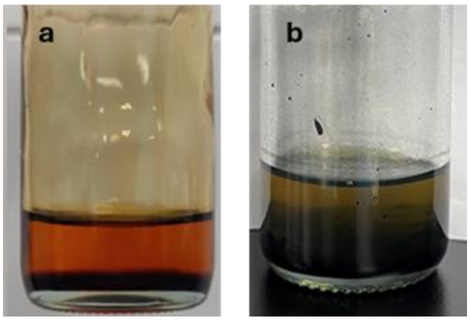

Figure 1. MGO blended with wood-based pyrolysis oil; a. Wood-based PO 2 and b. Wood-based PO 3

Table 1. Key parameters for Wood based pyrolysis oils

Test description	Units	Wood-based PO 1	Wood-based PO 2	Wood-based PO 3	Limits – RMK 700	Test method
Density @15°C	kg/m³	1225.7	1214.1	-	Max 1010.0	ISO 12185
Viscosity @ 50°C	cSt	25.1	23.8	-	Max 700.0	ISO 3104
Flash Point	°C	64	56	60	Min 60.0	ISO 2719
Pour Point	°C	<-15	<-15	39	Max 30	ISO 3016
Micro Carbon Residue	% m/m	19.1	18.9	27.9	Max 20.0	ISO 10370
Ash	% m/m	0.005	0.013	0.29	Max 0.150	ISO 6245
Water	% v/v	27.1	4.2	30	Max 0.50	ASTM D95
Sulfur	% m/m	0.04	0.04	0.12	-	ISO 8754
Total Sediment Existent	% m/m	0.6	0.8	>1.0	Report	ISO10307-1
Vanadium	mg/kg	<1	<1	8	Max 450	IP 501 (M)
Al+Si (Catfines)	mg/kg	5	12	9181	Max 60	IP 501 (M)
Sodium	mg/kg	<1	4	438	Max 100	IP 501 (M)
Calcium	mg/kg	11	21	1451	Calcium >30 and zinc >15	IP 501 (M)
Phosphorous	mg/kg	<1	2	193	or	IP 501 (M)
Zinc	mg/kg	0	<1	21	Calcium >30 and phosphorus >15	IP 501 (M)
Magnesium	mg/kg	2	6	209	-	IP 501 (M)
Potassium	mg/kg	4	9	193	-	IP 501 (M)
CCAI	-	1123	1113	-	Max 870	Calculated
Total Acid Number	mg KOH/g	Not able to measure	120	38.8	Max 2.50	ASTM D664
Modified Total Acid Number	mg KOH/g	79.4	90.5	-	Max 2.50	Modified D664
Strong Acid Number	-	0	-	0	0	ASTM D664
Net Specific Energy	MJ/kg	16.2	16.6	-	-	ASTM D240+ D5291
Gross Specific Energy	MJ/kg	17.8	18.1	14.8	-	ASTM D240
Carbon	%mass	46.4	52.6	-	-	ASTM D5291
Hydrogen	%mass	8.0	8.3	-	-	ASTM D5291
Nitrogen	%mass	0	0.0	-	-	ASTM D5291
Oxygen	%mass	45.6	39.1	-	-	ASTM D5291 (M)
Organic Chlorides	ppm	<5	<5	-	Max 50 ppm	EN 14077

M : Modified.

Table 2. Density results for the top and bottom layers of a 10% pyrolysis oil (PO) blend with VLSFO

Sample ID	Density Top Layer (kg/m3)	Density Bottom Layer (kg/m3)	Density (kg/m3) and Viscosity (cSt) of VLSFO
VLSFO1+10% Wood-based PO2	900.6	1158.6	Density = 900.6 & Viscosity = 26.4
VLSFO2+10% Wood based PO1	974.7	1010.9	Density = 908.7 & Viscosity = 33.8
VLSFO3+10% Wood based PO2	967.1	1029.8	Density = 965.9 & Viscosity = 33.8

3.2 Tire pyrolysis oil

Tire pyrolysis is a vital process for transforming solid waste into sustainable energy sources, providing significant benefits and helping to address the energy crisis [7]. This process yields three primary products: pyrolysis oil, pyrolysis gas, and pyrolysis carbon black [8]. Waste tire pyrolysis oils (TPOs) offer notable advantages as a fuel source, including high volatility, low ash content, and high heating values compared to biomass pyrolysis oil and coal [7].

Table 3 summarizes the characteristics of tire pyrolysis oil (TPO) from various manufacturers. The ISO 8217 parameters for TPOs vary among the manufacturers. Due to limited sample quantities, a full ISO 8217 test could not be conducted for all three samples. The parameters tested, as shown in the table, generally align with RMB30 specifications, with the exceptions of flash point and CCAI. Additionally, the acid numbers for TPO 1 and TPO 2 exceed the ISO limit, while TPO 3 complies with the standard. Testing for Total Sediment Potential (TSP) was not possible due to the low flash point and the presence of low boiling point components.

The energy content of the tested TPOs is comparable to that of VLSFOs. However, the TPOs contain approximately 2% oxygen, attributed to oxygenated compounds such as free fatty acids and aromatic acids. This oxygen content is significantly higher than that of regular VLSFOs, which typically contain less than 0.5% oxygen.

GCMS analysis identified several chemical compounds in TPO 1 and TPO 2. Both samples showed elevated levels of nitrogen-based compounds, along with considerable amounts of aromatic acids. Additionally, free fatty acids were present in varying concentrations in these samples. Free fatty acids are corrosive, and they are more susceptible to oxidation in comparison to naphthenic acids.

The combustion quality of TPO2 was evaluated using an FIA-100 FCA fuel combustion analyzer to determine its estimated cetane number (ECN). TPO2 exhibited an ECN value of 3.5, indicating poor ignition properties. This value is lower compared to the average ECN of VLSFOs and high sulfur fuel oils (HSFOs). The miscibility of all three TPOs blended with MGO and VLSFOs was tested at a ratio of 10% TPO and 90% residual fuels and MGO over a period of 8 weeks at room temperature. The blends remained miscible for at least 8 weeks of storage at room temperature.

In conclusion, TPOs may be considered a potential feedstock for blending with residual fuels. For TPO samples with a low flash point, the blend, under ideal conditions (where residual fuels have a flash point greater than 130°C), may only be able to tolerate 5-10% of the TPO sample to meet the flash point specifications outlined in ISO 8217. However, TPOs exhibit high acidity and contain free fatty acids and aromatic acids. Due to the presence of these compounds, these samples are prone to oxidation and polymerization over time. Consequently, a comprehensive storage stability study is necessary to assess the long-term stability of the sample. Additionally, the poor ignition quality of the sample should be carefully considered.

3.3 Off-spec FAME products

In this part of the study, off-spec FAME samples were assessed as potential alternatives to compliant FAME for marine applications. The off-spec samples evaluated included:

- Off-spec FAME 1: Unfiltered FAME containing sterol glycosides, leading to noncompliance due to hazy appearance and poor cold flow properties.
- Off-spec FAME 2: Non-compliant due to issues with cold soak filterability.
- Off-spec FAME 3: Off-spec due to mono-, di-, and triglyceride content.
- Off-spec FAME 4: Non-compliant with oxidation stability standards.

Table 5 summarizes key characteristics of these samples. However, due to limited sample availability, comprehensive testing of all properties was not feasible.

Table 3. Key parameters for Tire pyrolysis oils

Test description	Units	TPO 1	TPO 2	TPO 3	Limits - RMB 30	Test method
Density @15°C	kg/m³	-	936.0	912.8	Max 960.0	ISO 12185
Viscosity @ 50°C	cSt	-	2.91	2.85	Max 30.00	ISO 3104
Flash Point	°C	56	<30	<30	Min 60.0	ISO 2719
Pour Point	°C	-	<-21	-18	Max 0 (Winter)	ISO 3016
Micro Carbon Residue	% m/m	-	1.95	0.74	Max 10.00	ISO 10370
Ash	% m/m	-	0.004	0.010	Max 0.070	ISO 6245
Water	% v/v	0.13	0.05	0.09	Max 0.50	ASTM D6304
Sulfur	% m/m	-	0.89	0.79	Statutory Requirements	ISO 8754
Total Sediment Potential	% m/m	NA	NA	NA	Max 0.10	ISO 10307-2
Total Sediment Existent	% m/m	0.01	-	0.01	Report	ISO 10307-1
Vanadium	mg/kg	<1	<1	2	Max 150	IP 501 (M)
Al+Si (Catfines)	mg/kg	10	15	4	Max 40	IP 501 (M)
Sodium	mg/kg	<1	<1	2	Max 100	IP 501 (M)
Calcium	mg/kg	<1	<1	2	Calcium >30 and zinc >15 or Calcium >30 and phosphorus >15	IP 501 (M)
Phosphorous	mg/kg	<1	2	1		IP 501 (M)
Zinc	mg/kg	2	<1	2		IP 501 (M)
Magnesium	mg/kg	<1	1	1	-	IP 501 (M)
CCAI	-	-	889	867	Max 860	Calculated
Total Acid Number	mg KOH/g	10.4	5.73	1.02	Max 2.50	ASTM D664
Strong Acid Number	mg KOH/g	0	0	0	0	ASTM D664
Net Specific Energy	MJ/kg	-	40.54	-	-	ASTM D240 +D5291
Gross Specific Energy	MJ/kg	-	42.55	43.07	-	ASTM D240
FAME Content	%m/m	<0.5	<0.5	<0.5	-	ASTM D7963
Carbon	%mass	86.4	86.29	-	-	ASTM D5291
Hydrogen	%mass	11.1	10.18	-	-	ASTM D5291
Nitrogen	%mass	0.6	0.48	-	-	ASTM D5291
Oxygen	%mass	1.9	2.15	-	-	ASTM D5291 (M)
Organic Chlorides	ppm	10.8	20	46	Max 50 ppm	EN 14077

M: Modified

Table 4. Fuel ignition and combustion parameters for TPO2

Description	TPO2	Units
Estimated Cetane Number (ECN)	3.9	-
Ignition Delay	10.17	ms
Main Combustion Delay	12.84	ms
End of Main Combustion	34.06	ms
End of Combustion	41.43	ms
Pre-Combustion Period	2.67	ms
Main Combustion Period	21.23	ms
After Burning Period	7.37	ms
Maximum ROHR (Rate of heat release)	0.44	Bar/ms
Position of max ROHR	19.16	ms
Accumulated ROHR	5.96	(arb. Unit)
Maximum Pressure Increase	6.08	bar

Table 5. Key parameters for off-spec FAME samples

Test description	Units	Off-spec FAME 1	Off-spec FAME 2	Off-spec FAME 3	Off-spec FAME 4	Test Method
Density @15°C	kg/m³	876.43	870.7	908.6	880.2	ISO 12185
Viscosity @ 40°C	cSt	4.2	5.5	11.8	4.8	ISO 3104
Flash Point	°C	>100	>70	>70	>70	ISO 2719
Pour Point	°C	15	-	-3	-12	ISO 3016
Micro Carbon Residue (10% Dist. Residue)	% m/m	0.05	0.04	0.23	0.04	ISO 10370
Ash	% m/m	0.0001	0.0001	0.0001	0.0001	ISO 6245
Water	% v/v	0.04	0.04	0.05	0.09	ASTM D6304
Sulfur	% m/m	0.02	0.39	0.20	0.003	ISO 8754
Vanadium	mg/kg	<1	<1	<1	<1	IP 501 (M)
Al+Si (Catfines)	mg/kg	2	<1	<1	<1	IP 501 (M)
Sodium	mg/kg	2	<1	<1	<1	IP 501 (M)
Aluminum	mg/kg	1	<1	<1	<1	IP 501 (M)
Silicon	mg/kg	1	<1	<1	<1	IP 501 (M)
Iron	mg/kg	1	<1	2	<1	IP 501 (M)
Nickel	mg/kg	<1	<1	1	<1	IP 501 (M)
Calcium	mg/kg	3	<1	<1	<1	IP 501 (M)
Phosphorous	mg/kg	2	<1	<1	<1	IP 501 (M)
Zinc	mg/kg	<1	<1	<1	<1	IP 501 (M)
Potassium	mg/kg	<1	<1	<1	<1	IP 501 (M)
Lead	mg/kg	<1	<1	<1	<1	IP 501 (M)
Magnesium	mg/kg	<1	<1	<1	<1	IP 501 (M)
Total Acid Number	mg KOH/g	0.2	0.5	0.2	0.25	ASTM D664
Net Specific Energy	MJ/kg	37.2	-	36.9	37.3	ASTM D240 + D5291
Gross Specific Energy	MJ/kg	39.8	-	39.4	39.7	ASTM D240
Cetane Index	-	48.7	49.8	38.5	49.0	ISO 4264
Visual Appearance	-	Not clear and bright	Not clear and bright	Not clear and bright	Clear and bright	-
Cloud Point	°C	14.8	-2	-3.4	-1.3	ASTM D5771
Cold Filter Plug Point	°C	12	-	-8.0	-5.0	ASTM D6371
HFRR Lubricity	µm	200	180	210	200	ISO 12156-1
Oxidation Stability	hr	-	10.0	3.7	0.6	EN 15751
FAME Content	%v/v	95.9	98.5	61.8	97.9	EN14078 (M)
Total Sediment Existent (TSE)	%	0.01	0.02	0.05	0.01	ISO 10307-1
Cold Soak Filterability	sec	-	1211	220	-	ASTM D7501
Monoglycerides	mass%	0.1	0.15	0.20	0.37	ASTM D6584/ Cd 11C-93
Diglycerides	mass%	-	0.07	0.29	0.04	ASTM D6584/ Cd 11C-93
Triglycerides	mass%	-	0.01	25.9	0.1	ASTM D6584/ Cd 11C-93
Total Glycerin	mass%	-	0.05	2.83	0.11	ASTM D6584

Free Glycerin	mass%	0.005	0.003	0.001	0.001	ASTM D6584
Free Fatty Acids	Oleic acid, %	0.25	0.22	11.2	0.24	AOCS Ca 5a-40
Carbon	%mass	76.15	-	76.3	76.6	ASTM D5291
Hydrogen	%mass	12.23	-	11.6	11.6	ASTM D5291
Nitrogen	%mass	0	-	0	0	ASTM D5291
Oxygen	%mass	11.73	-	12.1	11.8	ASTM D5291 (M)

M: Modified

Sample 1, which is unfiltered biodiesel, exhibited poor cold flow properties compared to diesel fuels due to the presence of sterol glycosides. These compounds are relatively insoluble in biodiesel and tend to precipitate over time, negatively impacting cold-weather operability. Given it's hazy appearance and non-compliance with cold flow specifications for distillate-based fuels, Sample 1 was blended with very low sulfur fuel oil (VLSFO) at a 30:70 (FAME:VLSFO) ratio. Testing of the blend against ISO 8217 specifications revealed no significant issues with basic properties. Further evaluations included long-term stability, sediment content, acidity changes over time, ignition-combustion properties and microbial contamination. Over a 60-day storage period at 50°C, no significant changes were observed in sediment formation or acidity levels. The results of these blending studies are summarized in Table 6.

Sample 2 was off-spec due to non-compliance with hazy appearance and cold soak filterability properties as per the ASTM D6751 specification. The maximum acceptable limit under ASTM D6751 is 360 seconds, while the result for off-spec FAME 2 was 1211 seconds. All other tested parameters for this sample were within normal limits. To assess its potential for marine fuel applications, this sample was blended with very low sulfur fuel oil (VLSFO) at a 30:70 (Off-spec FAME:VLSFO) ratio. The blend was evaluated against ISO 8217 specifications, and no issues were observed regarding its basic properties. Furthermore, long-term tests indicated no significant changes in acidity or sediment content over time, demonstrating the blend's stability during storage.

Sample 3 was off-spec due to hazy appearance and elevated levels of tri- and diglycerides and non-compliant FAME content according to the ASTM D6751 specification. The maximum allowable total glycerol under ASTM D6751 is 0.24%, whereas Sample 3 had a total glycerol content of 2.8%. To evaluate its suitability for marine applications, the sample was blended with very low sulfur fuel oil (VLSFO) at a 30:70 (Off-spec FAME:VLSFO) ratio. The blend met ISO 8217 specifications initially. However, after 60 days of storage at 50°C, the blend exhibited a 60% increase in acidity and a 50% increase in sediment content, indicating potential long-term stability issues. Additionally, the blend tested for a steel corrosion test (Figure 2), which revealed severe rust formation, highlighting concerns about its corrosiveness.

Figure 2. Steel corrosion test as per ASTM D665 for 30:70 Off-spec FAME 3:VLSFO versus clean rod (Left rod).

Sample 4 was off-spec due to poor oxidation stability, with a measured oxidation stability of 0.6 hours compared to the minimum requirement of 3 hours specified in ASTM D6751. The sample was blended with very low sulfur fuel oil (VLSFO) at a 30:70 (Off-spec FAME:VLSFO) ratio and tested against ISO 8217 specifications. The blend demonstrated no issues with ISO 8217 parameters, and no significant changes were observed in acidity or sediment content over time, indicating acceptable stability under the test conditions.

A microbial contamination test was conducted on all four blends. After 60 days of storage at 50°C, no microbial contamination was observed.

Table 6. Off-spec FAME blended with VLSFOs characteristics

Testing parameters	30% Off-spec FAME 1 +70% VLSFO 1	30% Off-spec FAME 2 +70% VLSFO 1	30% Off-spec FAME 3 +70% VLSFO 1	30% Off-spec FAME 4 +70% VLSFO 1
ISO 8217	√	√	√	√
Cold Flow Properties	√	√	√	√
Ignition Properties by FIA	**√ (greater than 20)**	**√ (greater than 20)**	**√ (greater than 20)**	**√ (greater than 20)**
Long Term Stability Study (60 days)	√	√	x (50% increase in sediment)	√
Acidity Changes over Time (60 days)	√	√	x (60% increase in acidity)	√
Microbial Contamination (60 days)	Negative	Negative	Negative	Negative

3.4 By products of biodiesel plants

In this section, three by-products from biodiesel production plants (BDP) were evaluated for potential marine applications:

BDP1: This refers to the natural impurities present in animal fats used for transesterification. These impurities are unable to form methyl esters during the reaction process.

BDP2: Known as the FAME distillation bottom or biodiesel distillation residue, often referred to as Biodiesel Heavy Atmospheric (BHA) residue. This material consists of saturated and unsaturated fatty acid methyl esters with carbon chain lengths ranging from C6 to C24. In addition to methyl esters, the residue may contain residual glycerol, waxes, triglycerides, and partial glycerides, also within the C6-C24 carbon range. Trace amounts of hetero elements or heavy metals may also be present.

BDP3: Material Organic Non-Glycerol (MONG) is another by-product of biodiesel production. MONG consists of Fatty Acid Methyl Esters, Fatty Acid Ethyl Esters, Free Fatty Acids, and Glycerides. The composition of MONG varies depending on the feedstock used in the biodiesel production process [9].

Table 7 summarizes the tested ISO 8217 parameters and additional characteristics for these three samples.

Based on the test results, BDP1 has a high acid number due to its elevated free fatty acid concentration, which makes up 30% of the sample. The FAME content is 49.4%, while the remaining 20.6% likely consists of mono-, di-, and triglycerides, along with sterol glycosides. The sample also has a high water content of 1% and a sediment content of 0.6%. Among these off-spec parameters, the acid number is the limiting factor for blending. To meet the ISO 8217 acid number specification, this sample would need to be blended at a very low ratio (below 4%) with VLSFOs.

BDP2 is off-spec with an acid number of 3.7 mg KOH/g fuel, exceeding the ISO 8217 limit of 2.5 mg KOH/g fuel. It is also non-compliant with respect to ash, phosphorus, and calcium content.

Blending BDP2 is limited to ratios below 25% to meet the ISO 8217 ash content specification. A blend of 25% BDP2 and 75% VLSFO was tested for ISO 8217 compliance and monitored for changes in acidity and sediment content over 60 days at a storage temperature of 50°C. Although the blend remained within ISO 8217 specifications, the acid number increased by up to 35%, and sediment content rose by 45%, raising concerns about its stability during extended storage.

BDP3 is off-spec with respect to acid number, measuring 37.4 mg KOH/g fuel, which exceeds the ISO 8217 limit of 2.5 mg KOH/g. To use this stream in a blend that meets ISO 8217 specifications, the BDP3 content should be limited to less than 6%. During a 60-day storage period at 50°C, this blend (6% BDP3 + 94% VLSFO) experienced a 30% increase in acid number and a 40% increase in sediment content raising concerns about its stability during extended storage.

Table 7. Key parameters for by products of biodiesel plants

Test description	Units	BDP1	BDP2	BDP3	Test method
Density @15°C	kg/m³	888.5	920.2	898.4	ISO 12185
Viscosity @ 40°C	cSt	6.62	16.62	34.72	ISO 3104
Flash Point	°C	31	>70	>70	ISO 2719
Pour Point	°C	18	3	-3	ISO 3016
Micro Carbon Residue	% m/m	0.8	2.5	3.4	ISO 10370
Ash	% m/m	0.012	0.55	0.001	ISO 6245
Water	% v/v	1.01	0.2	0.24	ASTM D6304
Sulfur	% m/m	0.03	0.04	0.02	ISO 8754
Vanadium	mg/kg	0	<1	<1	IP 501 (M)
Al+Si (Catfines)	mg/kg	3	30	<1	IP 501 (M)
Sodium	mg/kg	41	76	1	IP 501 (M)
Aluminum	mg/kg	1	22	<1	IP 501 (M)
Silicon	mg/kg	2	<10	<1	IP 501 (M)
Iron	mg/kg	59	-	<1	IP 501 (M)
Nickel	mg/kg	<1	-	<1	IP 501 (M)
Calcium	mg/kg	<1	73	<1	IP 501 (M)
Phosphorous	mg/kg	<1	275	<1	IP 501 (M)
Zinc	mg/kg	<1	<1	<1	IP 501 (M)
Potassium	mg/kg	<1	-	<1	IP 501 (M)
Lead	mg/kg	2	-	<1	IP 501 (M)
Magnesium	mg/kg	<1	-	<1	IP 501 (M)
Total Acid Number	mg KOH/g	66	3.7	37.4	ASTM D664
Net Specific Energy	MJ/kg	35.96	36.22	37.1	ASTM D240 + D5291
Gross Specific Energy	MJ/kg	38.47	38.84	39.6	ASTM D240
HFRR Lubricity	µm	NA	260	240	ISO 12156-1
FAME Content	%	49.4	59.2	78.7	ASTM D7963
Total Sediment Existent (TSE)	%	0.6	0.06	0.01	ISO 10307-1
Total Sediment Potential (TSP)	%	-	0.08	0.01	ISO 10307-2 (Procedure A)
Free Fatty Acids	%	30.1	3.4	1.0	AOCS Ca 5a-40
Free Glycerin	%	0.2133	-	-	GCMS- Direct Liquid Injection
Monoglycerides	%	0.45	-	-	GCMS- Direct Liquid Injection
Carbon	%mass	75.65	-	76.3	ASTM D5291
Hydrogen	%mass	12.11	-	11.9	ASTM D5291
Nitrogen	%mass	0	-	0	ASTM D5291
Oxygen	%mass	12.2	-	11.8	ASTM D5291 (M)
Organic Chlorides	ppm	<5	<5	<5	EN 14077

M: Modified

4 CONCLUSION

This study provides an overview of some streams that may be considered as blending options with residual fuels. However, a more detailed and comprehensive study over an extended storage period is required to fully evaluate the suitability of these streams for marine applications.

At this stage, generalizing the conclusions is not feasible due to the limited number of samples tested and the fact that the production process can significantly affect the quality of the blends. However, based on the study conducted on three wood-based pyrolysis oil (not upgraded) samples, we observed that these oils tend to have high acid numbers and high water content, which can lead to miscibility issues when blending with both VLSFO and MGO samples. Blending agents can help maintain miscibility, but their very low flash points result in a final blend with a flash point lower than 60°C, making it non-compliant with ISO 8217.

In the case of TPO samples, the chemical composition and characteristics vary depending on the production process. Some TPOs show high acid numbers, low flash points, and poor ignition and combustion properties, further emphasizing the complexity of blending these materials.

This study assessed the suitability of off-spec FAME samples blended with VLSFO for marine fuel applications. Sample 1, despite poor cold flow properties due to sterol glycosides, showed good stability when blended with VLSFO, meeting ISO 8217 specifications with no significant changes over 60 days. Sample 2, with cold soak filterability issues, also performed well in terms of basic properties and long-term stability. Sample 3, containing high levels of tri- and diglycerides, exhibited stability issues, with a notable increase in acidity and sediment content, as well as medium corrosion after 60 days. Sample 4, though off-spec for oxidation stability, met ISO 8217 parameters when blended with VLSFO, showing acceptable stability. Overall, while off-spec FAME samples have potential for marine applications, further long-term testing is necessary to ensure consistent performance.

The by-products of biodiesel production, including BDP1, BDP2, and BDP3, present varying challenges for fuel compatibility with ISO 8217 standards. BDP1, with its high acid number and free fatty acid concentration, requires blending at very low ratios with VLSFOs to meet quality specifications. BDP2, although suitable for blending at lower ratios, showed some changes in acidity and sediment content over a 60-day storage period, remaining within ISO 8217 specifications. BDP3, on the other hand, exceeds the ISO 8217 acid number limit and requires blending at less than 6% to comply. During a 60-day storage period, it experienced increases in acid number and sediment content, highlighting the need for monitoring when using BDP3 in fuel blends.

Further investigation over a longer duration would help better understand the long-term stability and performance of these by-products in marine fuel applications.

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