Keywords: biofuels, marine fuels, pyrolysis oil, hydrothermal liquefaction oil, biodiesel, renewable diesel

Biofuels as Heavy Fuel Oil Substitutes in the Maritime Sector: Findings and Potential Pathways

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Abstract

The United States Department of Energy has commissioned four national laboratories to evaluate the feasibility of biofuels in the maritime sector. This effort is briefly described including the overall project goals, structure, and aims. The large two-stroke crosshead engines used to power large merchant vessels were of particular interest since they can burn lower combustion quality fuels relative to four-stroke engines. This characteristic allows for consideration of pyrolysis oils and hydrothermal liquefaction (HTL) oils, which are feedstock agnostic and—without further upgrading such as hydrotreating—are more economical compared to distillate drop-in fuels. Pyrolysis and HTL oils are collectively known as bio-intermediates since they require additional processing for use in distillate fuel systems.

The key limiting feature is that these bio-intermediate fuels will cause asphaltene precipitation when blended with heavy fuel oils (HFOs) such as very low sulfur fuel oil (VLSFO) unless the bio-intermediates are upgraded to remove water and oxygenates. Economics is the key driver for scalability, and preliminary techno-economic analyses (TEAs) indicate that bio-intermediates have potentially lower costs relative to other biofuels such as biodiesel and renewable diesel; blending limits and the cost of upgrading bio-intermediates to enable blend stability needs further study to fully

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understand the economic outlook. Additionally, life cycle analyses (LCAs) of feedstocks and pathways show significant life cycle carbon reduction benefit relative to HFOs or marine diesel oils (MDOs). In addition to TEA and LCA results, we also present on the technical feasibility of these fuels. These studies have focused on the properties of biofuel blends with VLSFO that are critical to the fuel systems of maritime vessels fueled with HFOs. These properties include the compatibility with fuel system metals, viscosity, and blend stability. Aging studies with blends of VLSFO with biodiesel, HTL, and pyrolysis oils are also presented. Future efforts are being planned to conduct additional biofuel testing, including the use of biofuels as pilot fuels in zero carbon shipping options fueled with ammonia and methanol, ship-based demonstrations, and bioresource competition studies.

1. Introduction

Marine transportation is a key driver of global economies, carrying over 80% of internationally traded goods [1]. At present, marine shipping is powered almost exclusively by fossil fuels [2], leading to a significant greenhouse gas (GHG) impact: in 2022, CO_2 emissions from shipping totaled 706 Mt [3], which accounts for about 2% of the global total and if ranked as a nation would be the 6th leading emitter, ahead of the national impact of, e.g., Germany or South Korea, as shown in Figure 1; this estimate is only expected to increase over the coming decades with projected economic growth and increased maritime shipping activities.

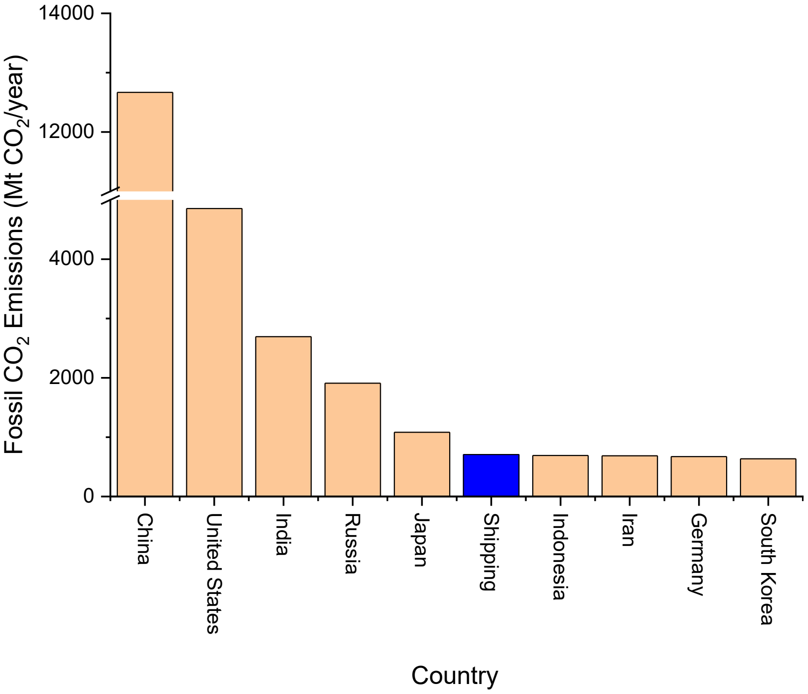

Figure 1: Annual CO_2 emissions from fossil fuel combustion ranked by country. Country data from Emissions Database for Global Atmospheric Research (EDGAR) [4]; shipping data from International Energy Agency [3].

Unlike national economies that include major impacts from electricity generation and industrial use, the energy use in marine shipping is exclusively the long-distance, high-load transportation use case that is among the most difficult to decarbonize. At the same time, there is a mandate from the International Maritime Organization (IMO) to cut GHG emissions from shipping by 70–80% by 2040 and reach net-zero emissions by or around 2050 [5]. This will require new low-lifecycle-carbon fuels (LLCF) and engines, and substantial efforts are underway to explore ammonia, methanol, and other novel fuels in the marine sector in pursuance of this goal. These novel fuels will have an increasing impact over time as new ships designed to operate with them come online, but with the long lifespan of ships and marine engines, much of the current fleet will still be at sea when these emissions reduction targets come due. Biofuels are thus an attractive LLCF—especially in the near term—due to their suitability as a drop-in fuel that can reduce GHG in the existing fleet. They also offer a potential path to achieve net-zero carbon when used in dual-fuel approaches, displacing petroleum-based fuel oils as the pilot fuel alongside other alternative fuels.

Biofuels including alcohols (e.g., ethanol and methanol) and fatty acid methyl ester (FAME) biodiesels have a long history in the market, typically as blending agents with gasoline or diesel fuels. These traditional biofuels will continue to play a role in the future, and the latest ISO standard for marine fuels now accounts for the use of FAME biodiesel at blends of up to 100% [6], up from the previous maximum of 7%. Methanol can also be sourced as a biofuel in addition to the synthetic e-fuel pathways being considered for green methanol. In addition to these traditional biofuels, there is growing interest in biofuels made from fast pyrolysis and hydrothermal liquefaction (HTL) processes, which can convert biomass and wet wastes, respectively, that are difficult and expensive to use for production of traditional biofuels like FAME biodiesel, bio-alcohols, or renewable diesel fuel.

Approximately two-thirds of global marine fuel usage is in ships powered by large low-speed 2-stroke engines [7], as shown in Figure 2. These engines are currently primarily operated on VLSFO and are both highly efficient and tolerant of low-quality fuels. This presents a significant opportunity for use of HTL and pyrolysis oil derived biofuels directly in these engines rather than as feedstocks to refineries to produce higher-quality fuels, saving on the energy usage and cost of upgrading them.

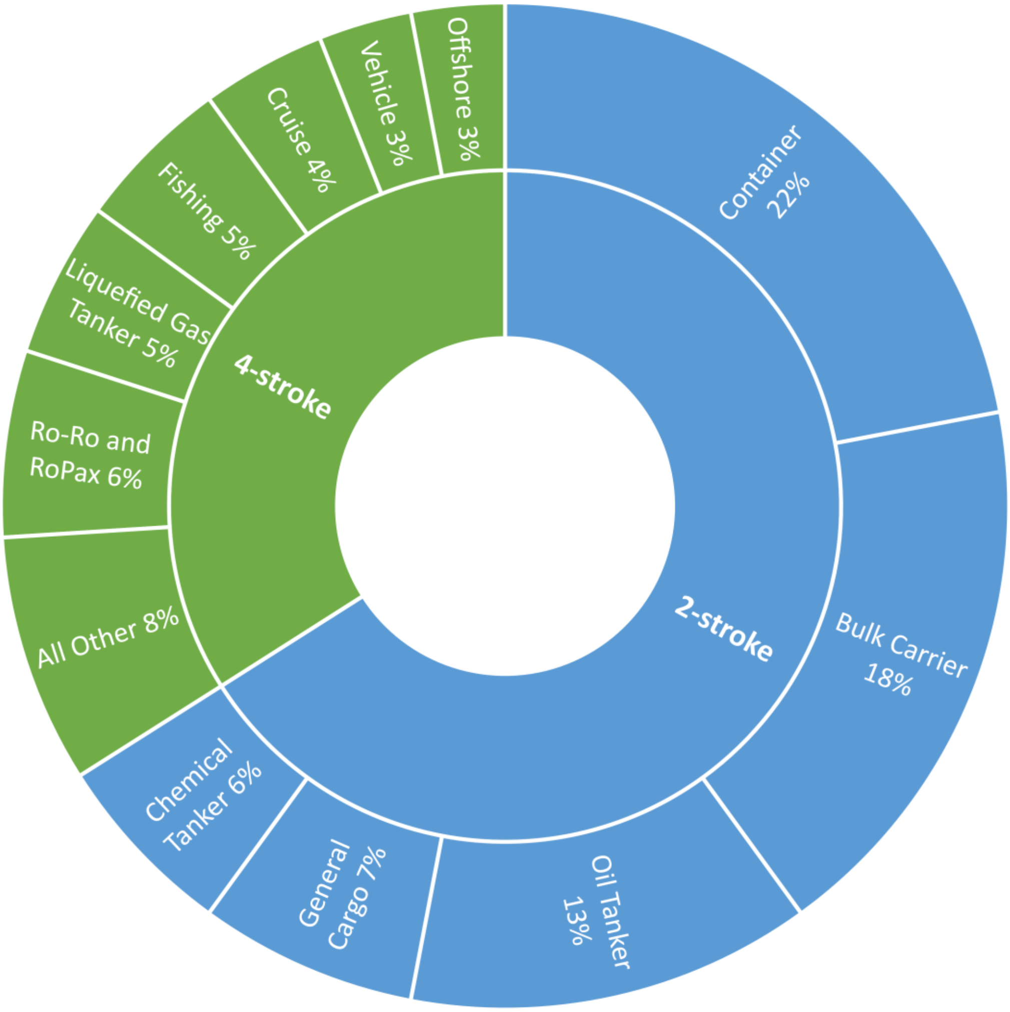

Figure 2: Fuel consumption by ship main engine type. Reproduced from Curran et al. [8]. Data from Concawe [7].

Biofuel use in the marine sector is growing rapidly, with the fuel testing company VPS reporting having tested over 500,000 Mt of biofuels (mostly FAME) in 2023, up from 230,000 Mt in 2022 [9]. A recent study by the Oil and Gas Climate Initiative (OGCI) [10] shows that while under current conditions biomass supply for the marine market is likely to be constrained by 2050, with increased legislative support there is “more than enough biomass available for marine fuel use, even accounting for sector competition.” Similarly, the 2023 Billion-Ton Report from the United States Department of Energy (DOE)’s Bioenergy Technologies Office (BETO) indicates that 1.1–1.5 billion tons of sustainable biomass production potential would exist in a mature market [11].

A key challenge that must be addressed for the adoption of new biofuels in the marine sector is blending compatibility with existing market fuels. This is important not only as a pathway to ramp up blend levels as production capacities increase, but also for switching between fuels onboard the vessel as different fuels are available in different ports. The primary concern is the presence in heavy fuel oils of asphaltenes, which are high-molecular-weight polymers in a colloidal dispersion that exist in chemical equilibrium with the surrounding fuel [7]. The solubility properties of these molecules with the surrounding liquid are important to prevent them from falling out of solution as a precipitate, which can cause filter plugging, fouling, and flow difficulties in residual fuels [12]. Regulatory emissions compliance must also be maintained, and the impact of novel fuels on emissions profiles is not yet well understood.

The DOE’s Bioenergy Technologies Office initially sponsored a study conducted jointly by Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL), Pacific Northwest National Laboratory (PNNL), and the National Renewable Energy Laboratory (NREL) to evaluate the opportunities and feasibility of using biofuels in ocean-going marine vessels. This study provided an initial favorable assessment and highlighted existing research needs [13]. Based on this initial assessment, a follow-up study was launched to conduct preliminary techno-economic analysis (TEA) and lifecycle analysis (LCA) along with key technical feasibility efforts [14]. This effort has grown into a study intended to provide the foundational information and demonstrations that will lead to future ship-based engine demonstrations of advanced biofuel blends. The scope includes determining the minimum level of upgrading and treatment necessary to successfully blend HTL and fast pyrolysis derived biofuels with heavy fuel oils, as well as updated techno-economic and lifecycle analyses of their impacts and evaluation of both the physical properties of the fuels and the impact on engine emissions in dynamometer testing. The project aims to address barriers to biofuel use in marine engines and ultimately conduct a sea trial demonstration.

2. Economic Feasibility and Greenhouse Gas Emissions Impact

In order to assess the potential opportunity for biofuels for decarbonization of the marine sector, it is important to understand both the economic feasibility of using these fuels and the potential lifecycle GHG impact of doing so. To address these questions, TEA and LCA of various pathways were conducted. This section briefly summarizes some of the results of these studies.

2.1. Techno-economic analysis

A detailed TEA was previously conducted and reported in Li *et al.* [15]. This study compared four conversion pathways: HTL of wet wastes such as sewage sludge and manure, fast pyrolysis of woody biomass, landfill gas Fischer-Tropsch synthesis, and lignin-ethanol oil from a lignocellulosic ethanol biorefinery using reductive catalytic fractionation. The fuels were modelled to have minimum fuel selling prices between $1.68 and $3.98 per HFO gallon equivalent in 2016 U.S. dollars, based on a mature plant assessment. For comparison, VLSFO ranged in price from approximately $0.50 to $1.50 per HFO gallon equivalent over the 2-year period considered in the study. While these prices are not competitive in today's market, all decarbonization solutions will be more expensive than the status quo, and the difference is small enough to consider some of these fuels as plausible options for marine transportation.

Since that study, pathways for both HTL and pyrolysis oils have been updated—in particular, considering catalytic fast pyrolysis (CFP) oils, which have better blending compatibility properties than non-catalytic fast pyrolysis oils. With these updated pathways—and considering two catalyst technologies for the CFP oils (ZSM-5 zeolite and Pt-TiO_2)—minimum fuel selling prices in 2020 U.S. dollars are shown in Figure 3 and are estimated for non-hydrotreated CFP oils using conceptual scaleup of bench scale results. Here, waste pathways include feedstock credits in the form of tipping fees (fees that would have otherwise been charged for landfill disposal). For comparison, VLSFO prices for the first half of 2024 have ranged globally from $1.82 to $2.07 per HFO gallon equivalent in 2020 U.S. dollars [16]. Hence, the overall conclusion is similar: both CFP and HTL oils are expected to require a modest price premium over today's market fuel prices to be economically viable, which is plausible given existing mandates for decarbonization and is in line with proposed carbon taxes and similar incentive policies being considered.

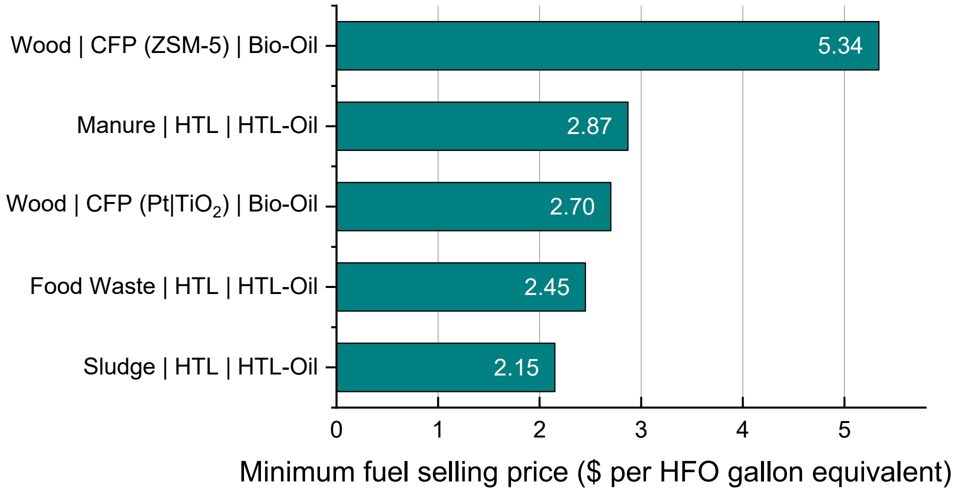

Figure 3: Updated TEA results showing minimum fuel selling price for several HTL and CFP pathways

2.2. Lifecycle GHG analysis

A comprehensive LCA of the GHG emissions impacts of a variety of biofuels for marine applications was also previously conducted and reported by Masum *et al.* [17]. This study considered eleven total biofuel pathways via four conversion processes, including HTL from wastewater sludge and manure, CFP of woody biomass, diesel produced via Fischer-Tropsch synthesis from landfill gas, and lignin ethanol oil from reductive catalytic fractionation of poplar. Results showed lifecycle GHG emissions ranging from -60–56 gCO_2e/MJ, which is a reduction of 41–163% compared to conventional VLSFOs. Waste pathways, in particular, showed net-negative carbon emissions with over 100% reduction due to offsetting the default waste management methods that would result in decomposition and methane emissions.

The earlier LCA was also updated with the new CFP and HTL pathways. The GREET lifecycle assessment model was used to conduct the GHG emissions estimation [18]. Figure 4 shows the updated results, with lifecycle GHG emissions ranging from approximately -81–16 gCO_2e/MJ; again, waste pathways show net-negative carbon emissions. This analysis only includes biomass production (farming), landing processing (which includes cutting down shorter limbs, cutting logs to transportable lengths, and sometimes debarking on site), transportation, receiving & handling, and storage, and transportation from the farming site to the biorefinery. In Figure 4, Natural gas, Electricity, and Diesel are categories representing energy inputs consumed during the conversion process. The Material & Chemicals and Catalysts categories are inputs considered in the conversion process to produce the biofuel. The T&D category relates to the emissions from transporting fuel to distribution sites and, in case of the HTL pathways, emissions due to transporting HTL-biosolids to the carbon sequestration site 100 km away. The Combustion category captures end-use emissions of products and includes CO_2 (which is biogenic in this case), CH_4, N_2O, volatile organic compounds (VOC), black carbon (BC), and organic carbon (OC). The C Sequestration category captures credits from the biosolids generated in the process of conversion: these were viewed as potential means of carbon sequestration, and hence credits were applied. Displacement credits are due to electricity and sulfur production that displaces U.S.-based grid electricity and conventional sulfur. Counterfactual credits are generated by avoiding the conventional waste management practices and diverting the waste for fuel generation. Conventional waste management results in the decomposition of waste materials and therefore methane emissions from sludge, manure, and food waste to the air. Finally, the LCA provides the numbers of the life cycle assessment from farming through end use of the product. In all cases, a significant benefit is seen, with reductions of 83–188% compared to petroleum-based marine fuels (see marine diesel oil, MDO, 0.1% sulfur).

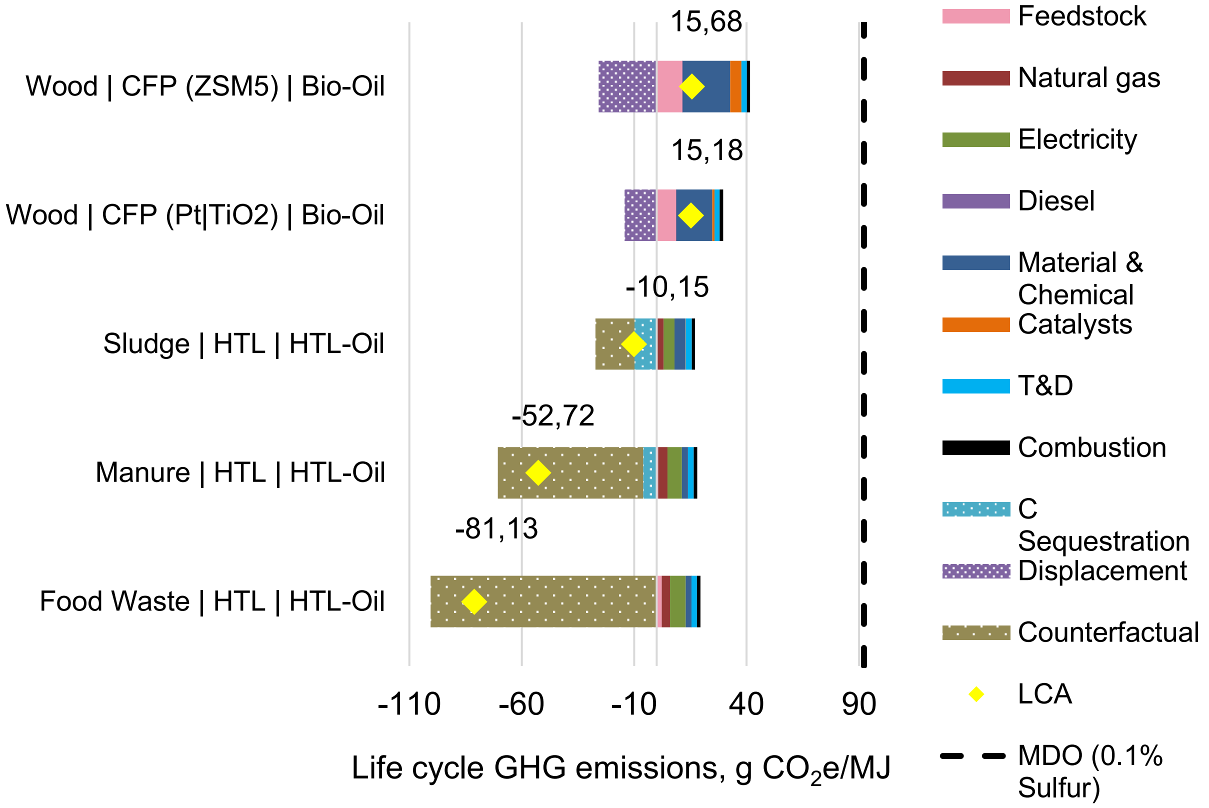

Figure 4: Updated LCA results showing lifecycle GHG emissions for several HTL and CFP pathways

3. End-use Technical Feasibility

In addition to understanding the economic feasibility and GHG impact of potential biofuels, it is also important to understand the impacts of new biofuels in end-use situations in order to enable their use. This includes effects of the physical properties of the fuels (viscosity, fuel system materials compatibility, blending compatibility, etc.) that will have a direct impact on infrastructure and ship hardware as well as impacts on engine combustion and regulated emissions, including NO_x. This section briefly summarizes the results of studies into these effects.

3.1. Physical properties and compatibility

In order to be effectively used for GHG reduction in the existing fleet, novel biofuels must be compatible with infrastructure and fuel system components. To enable transition away from petroleum-derived fuels, the new fuels must also have good blend compatibility with existing market fuels. Viscosity is also a key property, as VLSFO requires heating to meet particular viscosity targets for pumping and fuel injection. These effects have been studied in both neat biofuels and blends.

The most important factor for blend compatibility with existing market fuels is avoiding asphaltene precipitation. CFP oils have shown good blend stability up to at least 50% mass concentration in some instances [19], while HTL oils are more challenging, with precipitation occurring at blend levels as low as 5%. Initial results indicate commercially available additives can allow blending of HTL oils beyond 20% [14], and hydrotreating can also be used to improve the blending properties of CFP, FP, and HTL oils.

Raw (unprocessed) pyrolysis oils (also known as bio-oil) have relatively high concentrations of organic acids and water. They are corrosive to carbon steels, though type 430F and type 316 stainless steels perform reasonably well [20, 21]. Compatibility with fuel system elastomers and plastics has also been evaluated, with raw pyrolysis oils causing significant elastomer swell for most relevant elastomers relative to diesel fuel [22]. Hydrotreating and co-processing with petroleum-derived oils can reduce the acid content and abate the corrosion concerns [20]. Synergistically, this is the same processing needed to ensure blend compatibility with petroleum-based heavy fuel oils.

Biofuels generally have a beneficial impact on viscosity in blends with VLSFO, with a nonlinear impact even at low blend levels, as shown in Figure 5 for HTL and FAME biodiesel blends, where both exponential curve fits have an R^2 of 0.998. The significant reduction in viscosity implies a reduction in heating energy input to achieve operational viscosity targets for fuel injection.

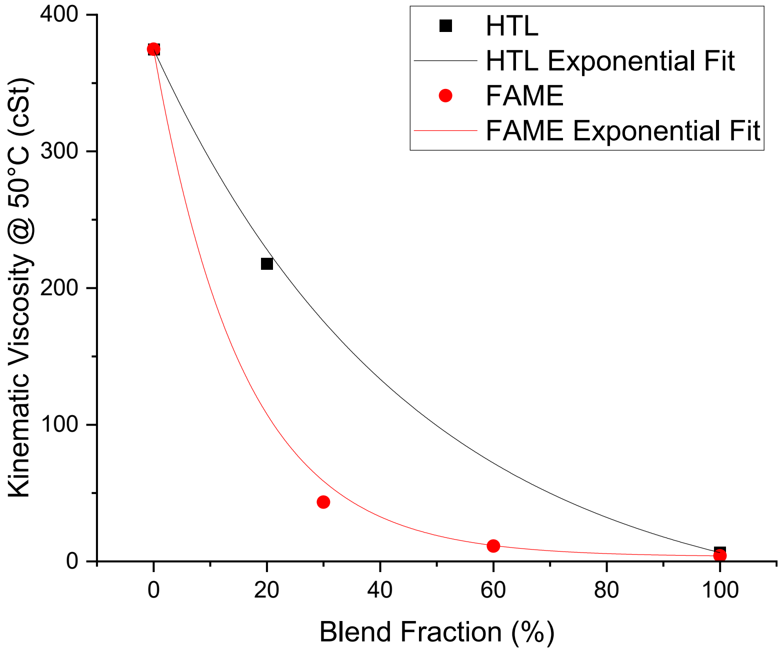

Figure 5: Viscosity blending effects of HTL and FAME biofuels with VLSFO

Polymerization is also a concern with pyrolysis-derived bio-oils, as this can cause issues in the fuel system. If polymerization occurs at relatively low temperatures, filter plugging and similar obstructions can occur; more critically, the higher temperatures experienced in fuel injector tips during engine operation can cause injector fouling and loss of power. An initial study of viscosity aging effects with 10% blends of HTL and CFP oils into VLSFO shows that CFP oils are prone to this, as illustrated in Figure 6: even when aged at 50 °C for extended periods, a notable increase in viscosity is observed for the 10% CFP blend; when aged at 90 °C , the 10% CFP viscosity rapidly surpasses that of the base VLSFO and continues to increase with time. A more detailed viscosity aging analysis will be reported in future publications. Avoidance of polymerization is in pyrolysis-derived bio-oils is an area of active research, with various additives and processing methods being evaluated for their effectiveness in avoiding this effect. The HTL blend did not show signs of polymerization, with aging stability approximately the same as that of the base VLSFO.

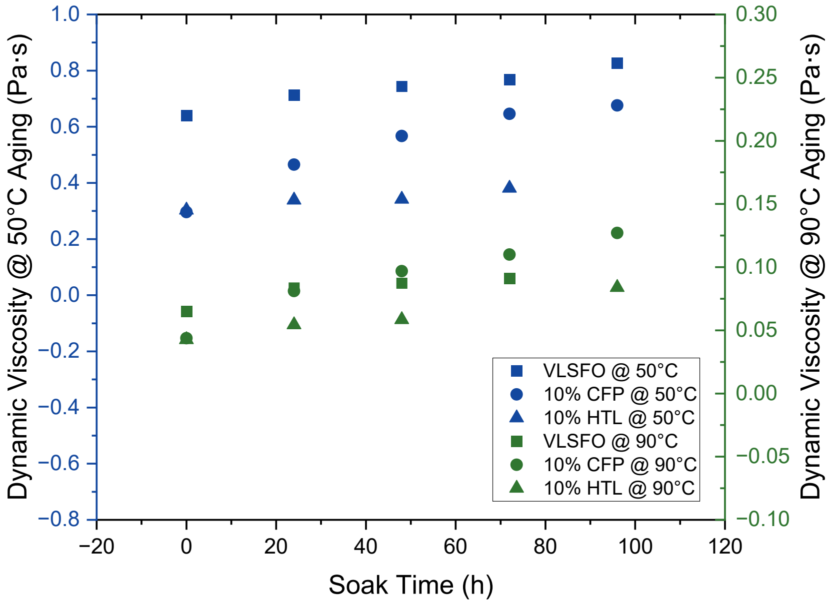

Figure 6: Viscosity aging effects at 50 °C and 90 °C for VLSFO and 10% blends of CFP and HTL oils

3.2. Engine combustion and emissions impacts

A number of studies have been completed examining the impact of FAME biodiesel on NO_x and particulate matter (PM)/black carbon (BC) emissions. The results are generally consistent in that NO_x increases and BC decreases with increasing biodiesel content, though for blend levels < 30%, the NO_x increase is typically within testing repeatability [23–25]; for higher blend levels, adjusting the fuel injection timing can compensate for the increase in NO_x emissions [26]. There is less historical experience with the use of HTL and CFP bio-oils and blends, and thus a lack of data in the literature on their emissions impacts.

An initial study within this project tested 10% blends of both CFP and HTL bio-oils splash-blended into a VLSFO in the Enterprise single-cylinder marine diesel research engine. This is a reduced-scale 2-stroke crosshead research engine designed to replicate many of the key features of full-scale low-speed 2-stroke marine diesel engines with significantly reduced fuel and lubricant requirements. Table 1 lists the primary specifications of the engine, which is designed with a high-swirl flow field two hydraulic electronic unit injector (HEUI) fuel injectors with an asymmetrical spray pattern, as illustrated in Figure 7. The engine is approximately 1:10 scale relative to typical low-speed 2-stroke marine engines, and while boundary conditions are duplicated to the greatest extent possible, time-scales and rotational speeds do vary. In order to maintain a realistic mean piston speed (which sets the boundary condition for the cylinder lubricant at the piston ring/liner interface), the rotational speed scales inversely with the stroke. This means that while thermodynamic conditions in the cylinder can be matched, the time-scales will be reduced relative to the full-scale engines. Emissions impacts from fuel changes will be directionally correct, but either model-based scaling studies or full-scale testing would be necessary to precisely quantify expected emissions from a full-scale engine. A detailed description of the engine design can be found in Kaul, *et al.* [27].

Table 1. Enterprise engine specifications

Cylinder bore	107.95 mm
Piston stroke	432 mm
Stroke/bore ratio	4:1
Displacement	3.95 l
Geometric compression ratio	13:1
Mean piston speed	8 m/s @ 556 rpm

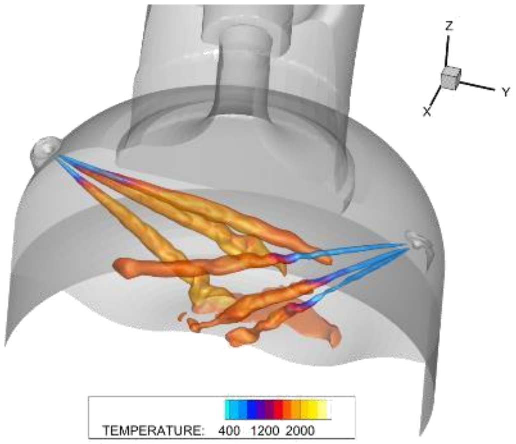

Figure 7: CFD simulation of combustion in the Enterprise engine, showing fuel injection spray patterns.

Samples of mildly hydrotreated CFP and HTL oils produced by NREL and PNNL were blended at 10% by volume into a base VLSFO and run in the engine at several steady-state speed/load operating conditions (shown in Table 2) with no changes to the engine calibration. NO_x emissions were measured using a Fourier transform infrared analyzer (FTIR), and PM emissions concentrations were measured using an AVL Micro Soot Sensor. Results showed no notable impact for the 10% blend levels tested, as indicated in Figure 8. There was similarly no notable impact to combustion phasing or duration for these low-level blends, though prior operation on this engine with high-level bio-diesel blends has shown a strong correlation between combustion phasing and NO_x emissions like that observed in the literature. Operation with higher blend levels (or potentially neat bio-fuels) is planned in the upcoming months, with larger fuel quantities becoming available from commercial vendors.

Table 2. Engine operating conditions

Operating condition	**Speed, rpm (% rated)**	**BMEP, bar**
Full steaming	545 (98%)	14.1
Slow steaming	400 (72%)	9.8
Maneuvering	280 (50%)	3.9

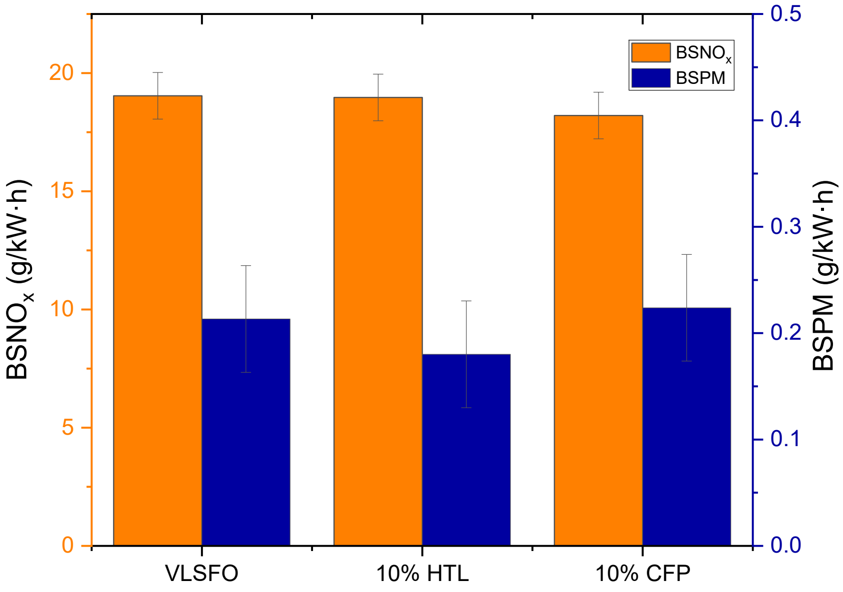

Figure 8: Brake-specific NO$_x$ (BSNO$_x$) and brake-specific PM (BSPM) emissions at full steaming operation for VLSFO and 10% blends of HTL and CFP fuels in the Enterprise research engine. Error bars represent the standard deviation of 8 repeats of the baseline VLSFO fuel.

4. Future Plans

Research to address remaining barriers to engine demonstrations, both in the laboratory and the field, is ongoing. High blend levels (potentially up to 100%) of mildly hydrotreated CFP and HTL bio-oils will be tested in the upcoming year to evaluate the blending compatibility and thermal stability (i.e., resistance to polymerization) of blends exceeding 50% biofuel, and mitigation measures, including additives to prevent polymerization will be explored to address remaining challenges. High blend levels will be tested in the Enterprise research engine to gain further confidence of suitability for engine operation as well as data on emissions impacts. In parallel with these efforts, planning is underway for a ship-borne demonstration, including fuel sourcing and partnerships with operators to enable sea trials.

5. Conclusion

The U.S. Department of Energy's Bioenergy Technologies Office (BETO) has sponsored a project comprising four national laboratories to evaluate the opportunities for the use of biofuels to decarbonize marine transportation, with a particular focus on HTL and CFP oils for the displacement of heavy fuel oils in ocean-going vessels. This project spans from TEA and LCA evaluations of the high-level impacts and economics to end-use challenges, including material compatibility, blend stability, and engine emissions impacts. Results to date show significant potential, with a few remaining challenges to implementation that are the subject of ongoing studies. Fuels are being systematically evaluated for suitability for engine testing and eventual sea trials, and barriers are being identified and addressed.

Acknowledgments

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