



Bio-intermediates and bio-residuals as marine fuels

Eric C.D. Tan and Brian C. Kaul

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Agenda

- Bio-intermediates and bio-residues as marine fuels
- Techno-economic Analysis (TEA)
- Future production capacity
- Marine biofuel blending
- Engine emissions impacts

Speaker Information

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Multi-lab team formed to examine marine biofuel potential opportunities

- Initial motivation driven by potential of bio-intermediates to reduce sulfur emissions from 2-stroke marine engines
- DOE Bioenergy Technologies Office (BETO) initiated a project to evaluate the viability of biofuels in the maritime sector
- Lab Roles:
 - **ORNL**: project lead & engine/emissions expertise
 - **NREL**: bio-oil production & technoeconomic analysis
 - **PNNL**: bio-crude production & technoeconomic analysis
 - **ANL**: life-cycle, scale-up analysis & engine expertise
- Multiple publications describing the opportunities for biofuels for marine shipping



ORNL/TM-2022/2373

Biofuel Viability for the Ocean-Going Marine Sector



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Article

Stability, Combustion, and Compatibility of High-Viscosity Heavy Fuel Oil Blends with a Fast Pyrolysis Bio-Oil

Michael D. Kass,* Beth L. Armstrong, Brian C. Kaul, Raynella Maggie Connatser, Samuel Lewis, James R. Keiser, Jiheon Jun, Gavin Warrington, and Dino Sulejmanovic

ENVIRONMENTAL
Science & Technology

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Article

Biofuel Options for Marine Applications: Technoeconomic and Life-Cycle Analyses

Eric C. D. Tan,* Troy R. Hawkins,* Uisung Lee, Ling Tao, Pimphan A. Meyer, Michael Wang,

ENVIRONMENTAL
Science & Technology

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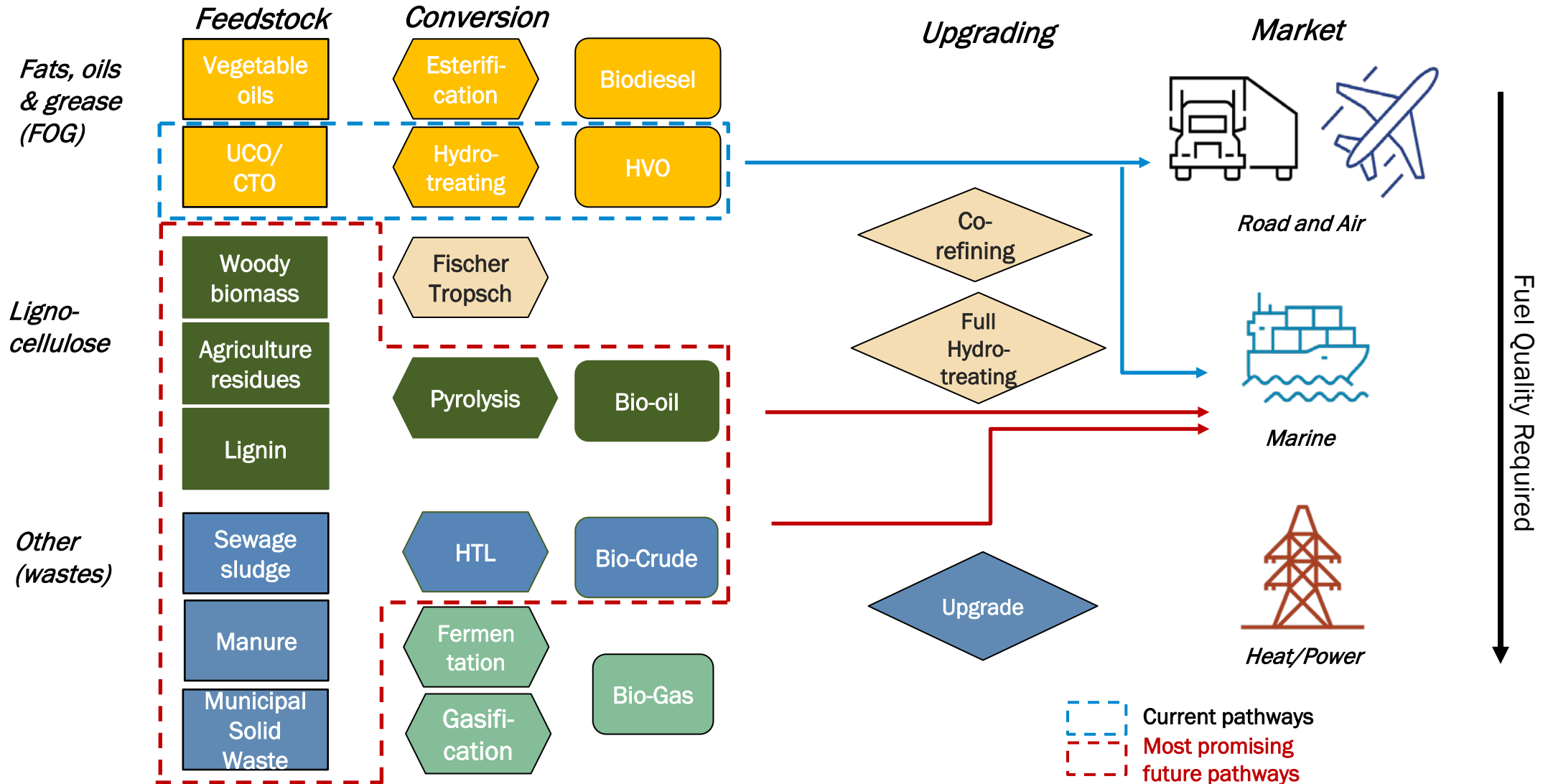
Article

Techno-economic Analysis of Sustainable Biofuels for Marine Transportation

Shuyun Li,¹ Eric C. D. Tan,^{*,1} Abhijit Dutta, Lesley J. Snowden-Swan, Michael R. Thorson, Karthikeyan K. Ramasamy,* Andrew W. Bartling, Robert Brasington, Michael D. Kass, George G. Zaines, and Troy R. Hawkins

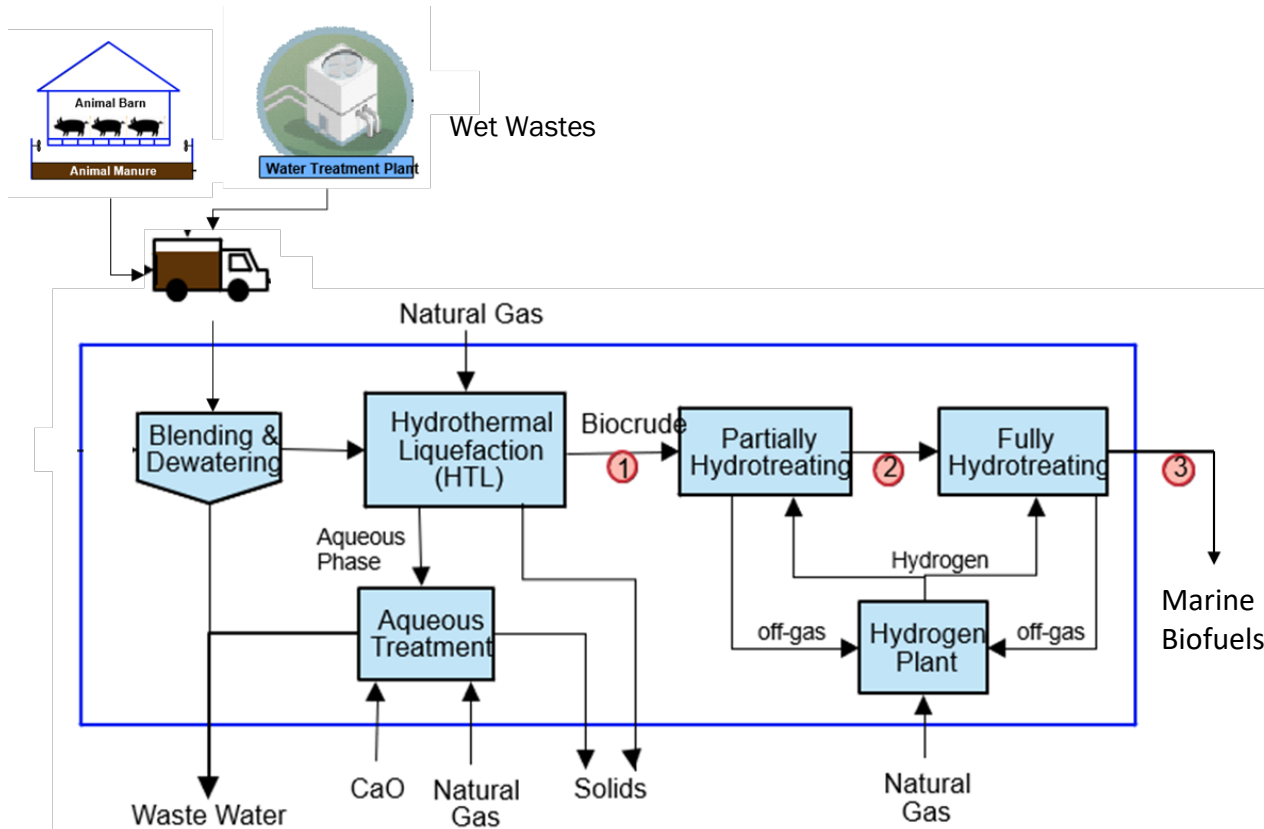
Bio-intermediates as marine fuels

Marine fuels derived from waste and low-cost feedstocks

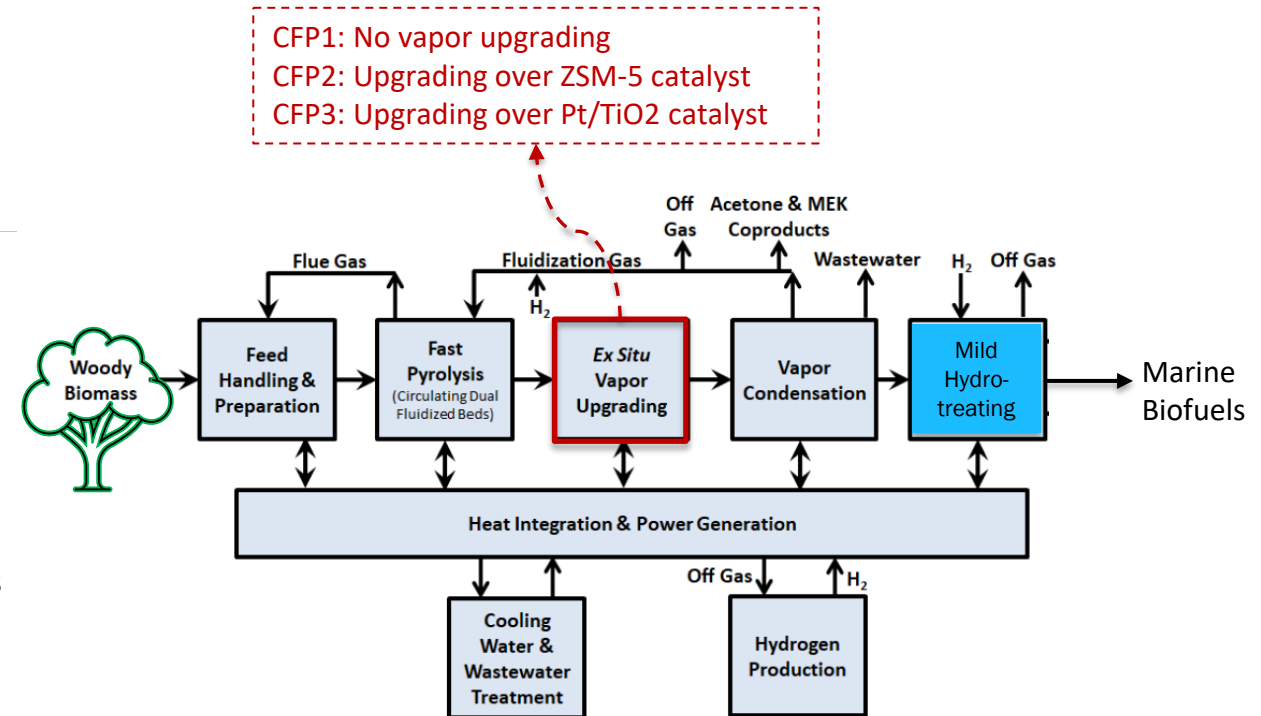


Bio-intermediates as marine fuels

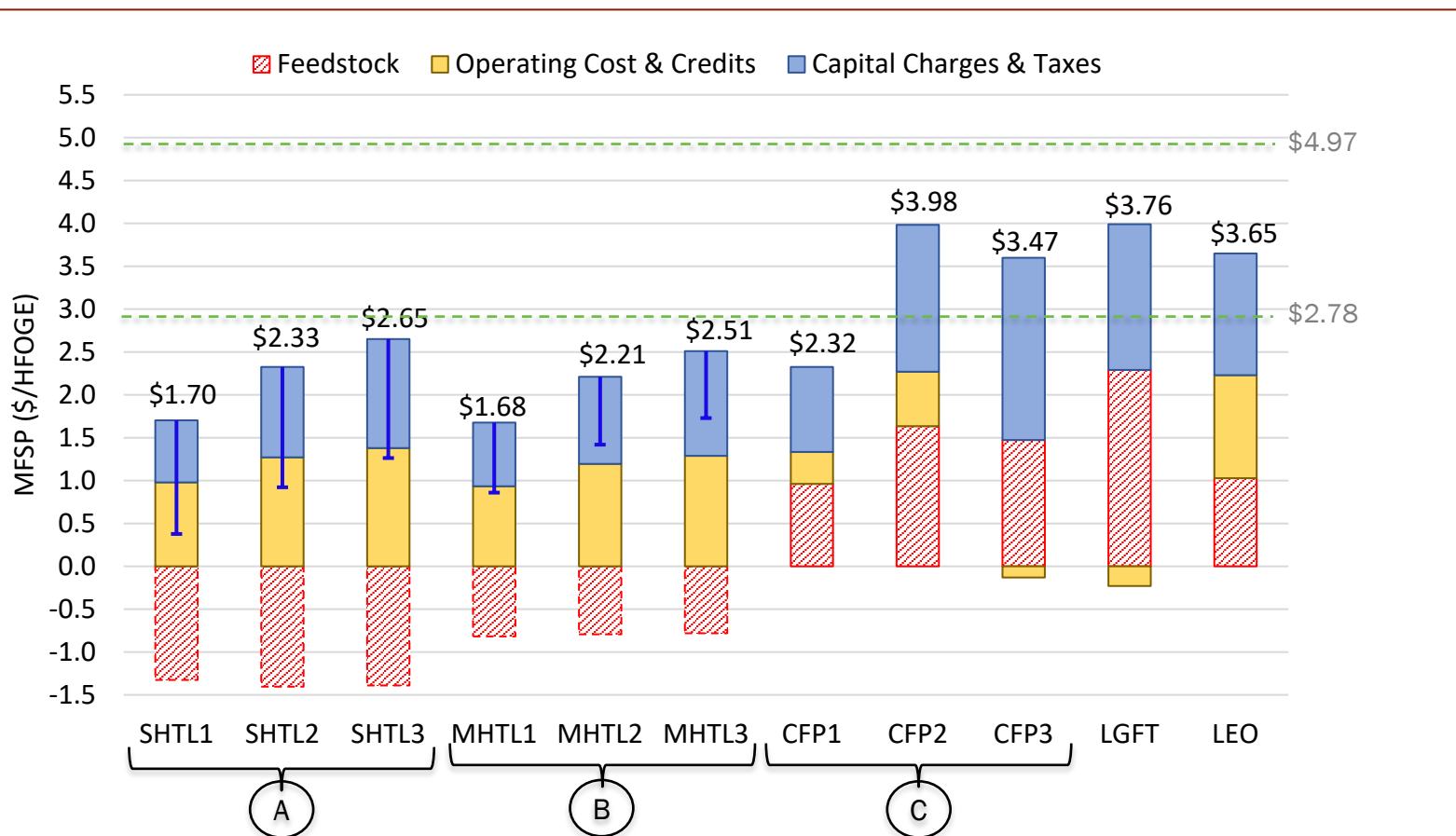
Wet Waste Hydrothermal Liquefaction (HTL)



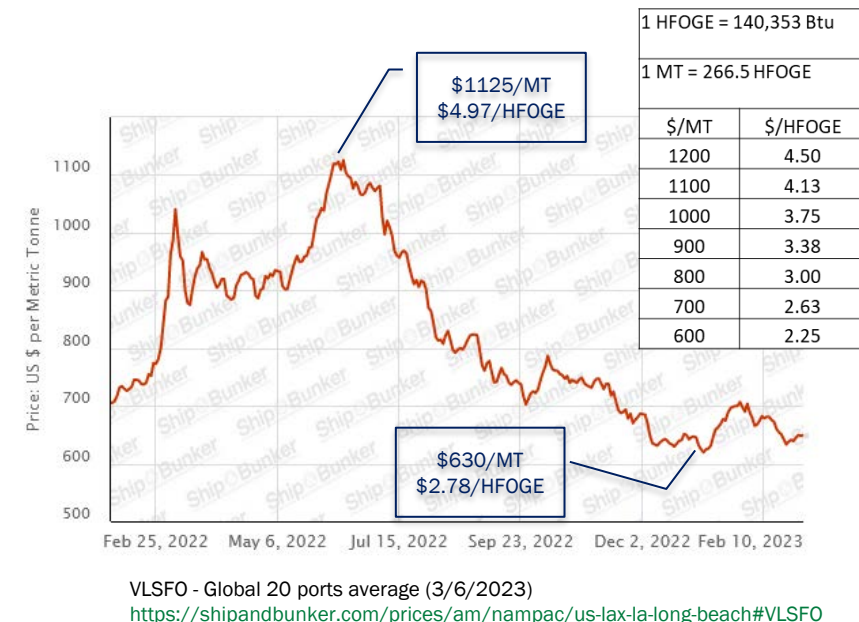
Catalytic Fast Pyrolysis (CFP)



Techno-economic analysis (TEA) shows that bio-intermediate fuel costs can approach those of VLSFO



Comparative TEA result summary (the dash feedstock costs for HTL cases represent the sensitivity cases with the potential wet waste avoided disposal fee, while the blue error bars indicate the potential decrease of MFSP for HTL pathways).

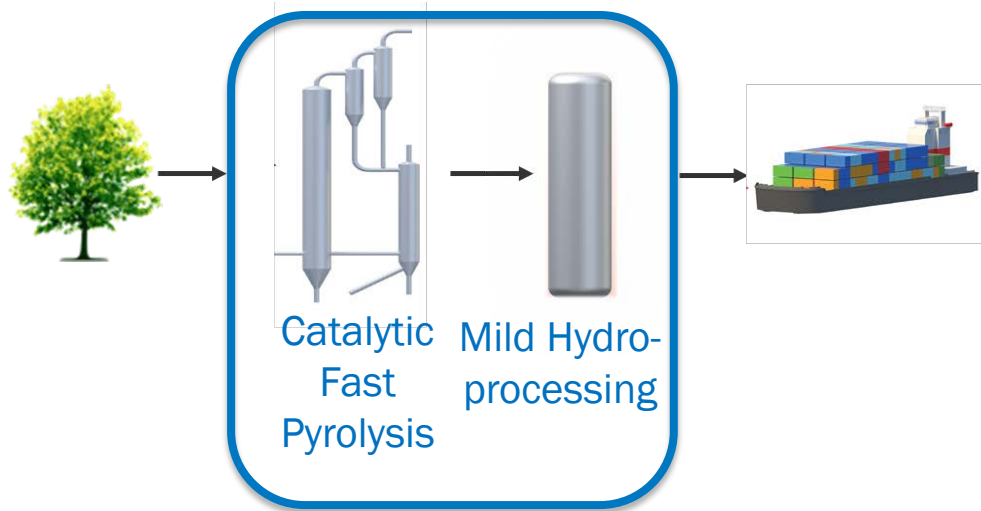


- (A) SHTL: HTL wet waste, sewage sludge
- (B) MHTL: HTL wet waste, manure
- (C) CFP: catalytic fast pyrolysis, woody biomass
- LGFT: landfill gas FT
- LEO: lignin-ethanol oil

<https://doi.org/10.1021/acs.est.2c03960>
 Environ. Sci. Technol. 2022, 56, 17206–17214

Maritime fuels via biomass pyrolysis

Goal: Determine minimum upgrading of bio-oils required to enable blending with VLSFO



Property	ISO 8217
Acid number, mg/KOH	< 2.5
Si+Al, ppm	<100
Ash, wt%	<0.15%
Water, vol%	<0.5
Density, g/cm ³	<991
Flash point, °C	≥60

Optimizing mild hydrotreating conditions



HT 1



HT 5

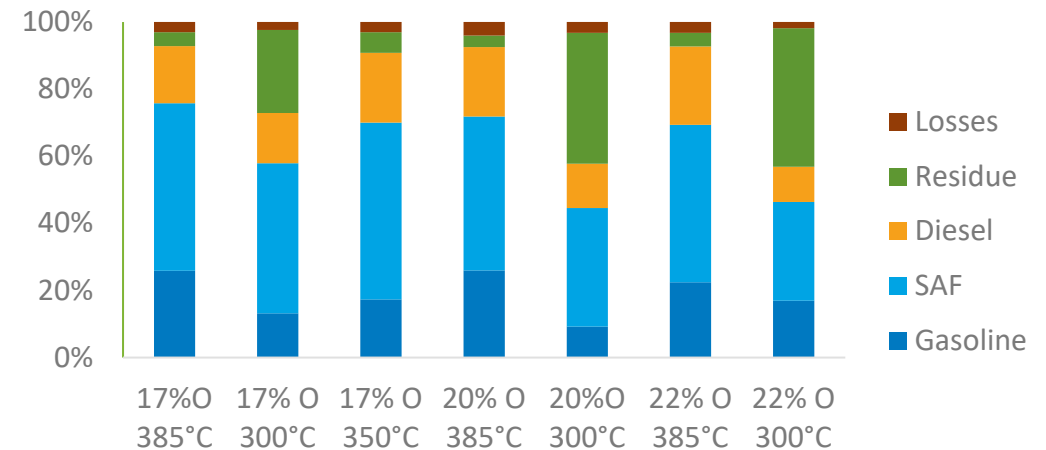


HT 2

Opportunity to Co-Produce with SAF

- Need to fully utilize bio-oil barrel
- Expensive to produce marine fuel only
- Recently completed campaign for upgrading of CFP oil to SAF via hydroprocessing

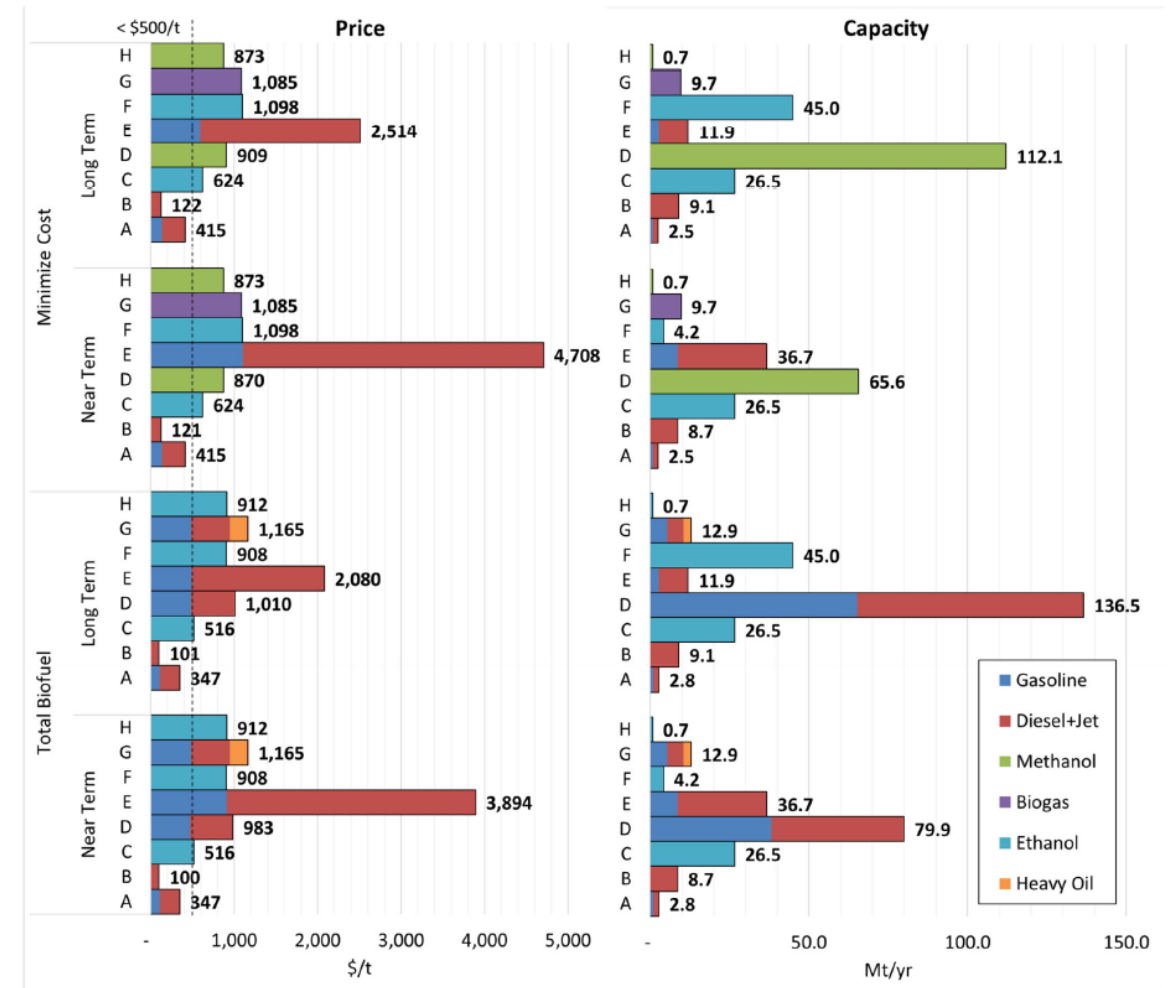
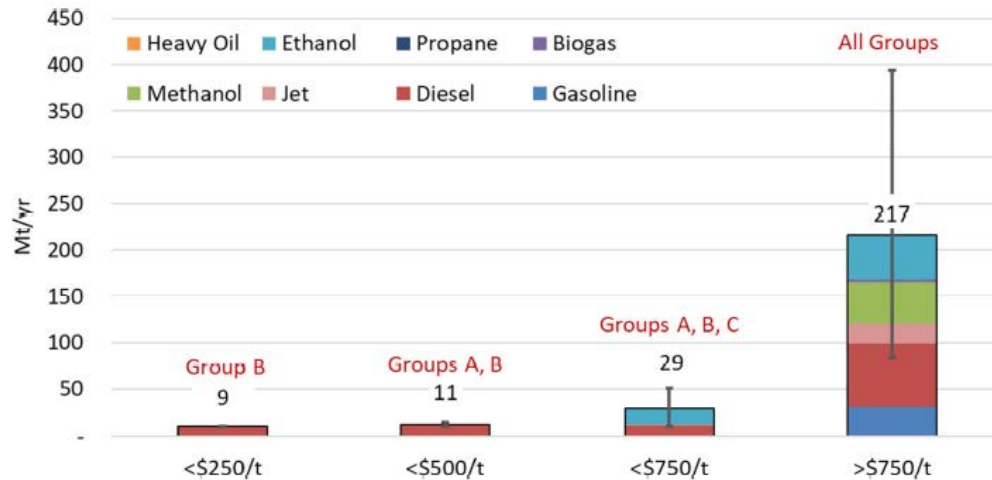
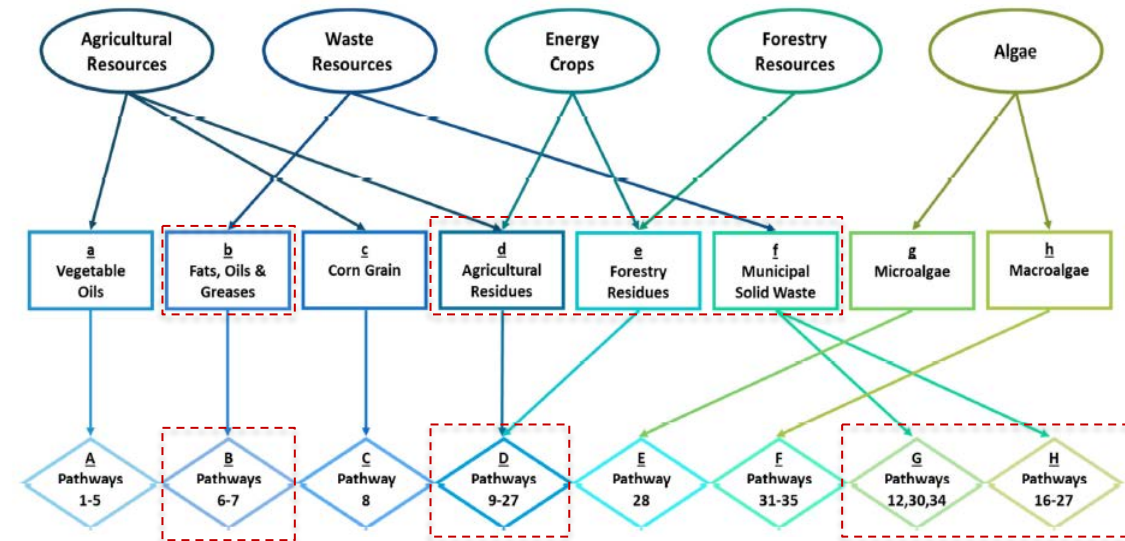
Distillation of Hydrotreated CFP Oils



Diesel and Residue could be used for marine

- 20-40% (50%) to marine
- (30%-) 50% to SAF

Potential future production capacity projection

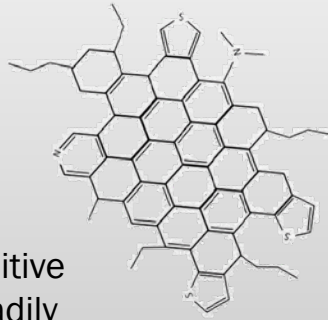


Tan et al. (2022) *Biofuels, Bioprod. Bioref.* <https://doi.org/10.1002/bbb.2350>

Blend stability is a key factor for introduction of bio-oils and bio-intermediates

Asphaltenes in marine fuel oils

- Colloidal dispersion of large polyaromatic molecules in chemical equilibrium with the surrounding fuel oil
- Asphaltene dispersion is highly sensitive to changes in fuel chemistry: will readily precipitate (fall out of solution) if solubility is altered
- ASTM 4740 spot tests are used to evaluate blend stability to avoid asphaltene precipitation when new fuel is bunkered



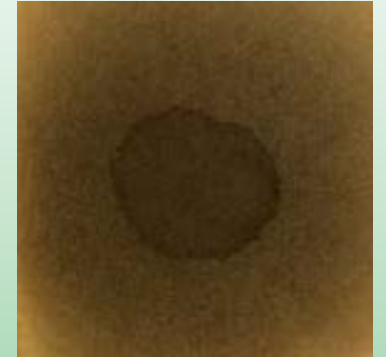
We just paved the fuel tank!



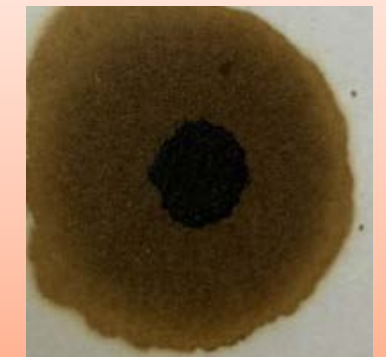
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2.0

Biodiesel + VLSFO
Slight ring appearance
No filter plugging



Diesel + VLSFO
Heavy dark center spot
Filter plugging



Solid asphaltene sludge
(i.e. asphalt) in fuel tanks

Additives, hydrotreating, and/or catalytic stabilization may enable blend stability

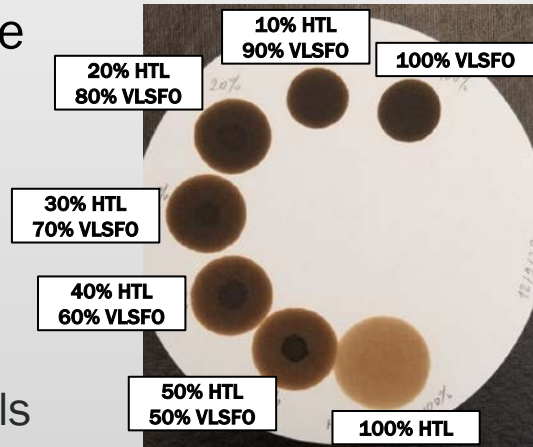
Bio-intermediates are not inherently miscible with VLSFO



Additives, hydrotreating, and/or catalytic stabilization may enable blend stability

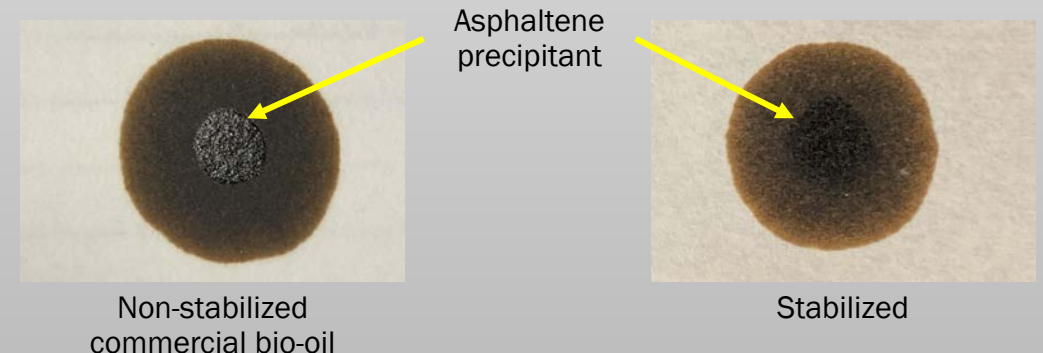
Hydrothermal Liquefaction (HTL) Bio-crudes

- Additives used to improve blend stability
 - Blend stability up to ~40% HTL oil addition
 - HTL oils have inherently less water and acidity than CFP oils
 - Hot water wash used to remove inorganics to improve mild hydrotreating process and meet ISO 8217 specifications
- Prior efforts have demonstrated that HTL oils:
 - Are compatible with fuel system infrastructure metals
 - Exhibit suitable combustion quality results for blend levels up to at least 10%



Pyrolysis Bio-oils

- Catalytic Fast Pyrolysis (CFP) showed better miscibility than non catalytic oils
- Hydrotreating screening studies led to CFP oils meeting many key ISO 8217 criteria
 - Identified hydrotreatment process 1500 psi and 300°C
 - Flash point was below spec; blending with VLSFO may mitigate
 - TEA updated to reflect hydrotreatment process
- Blend stability studies suggested that stabilized CFP oils less prone to asphaltene precipitation



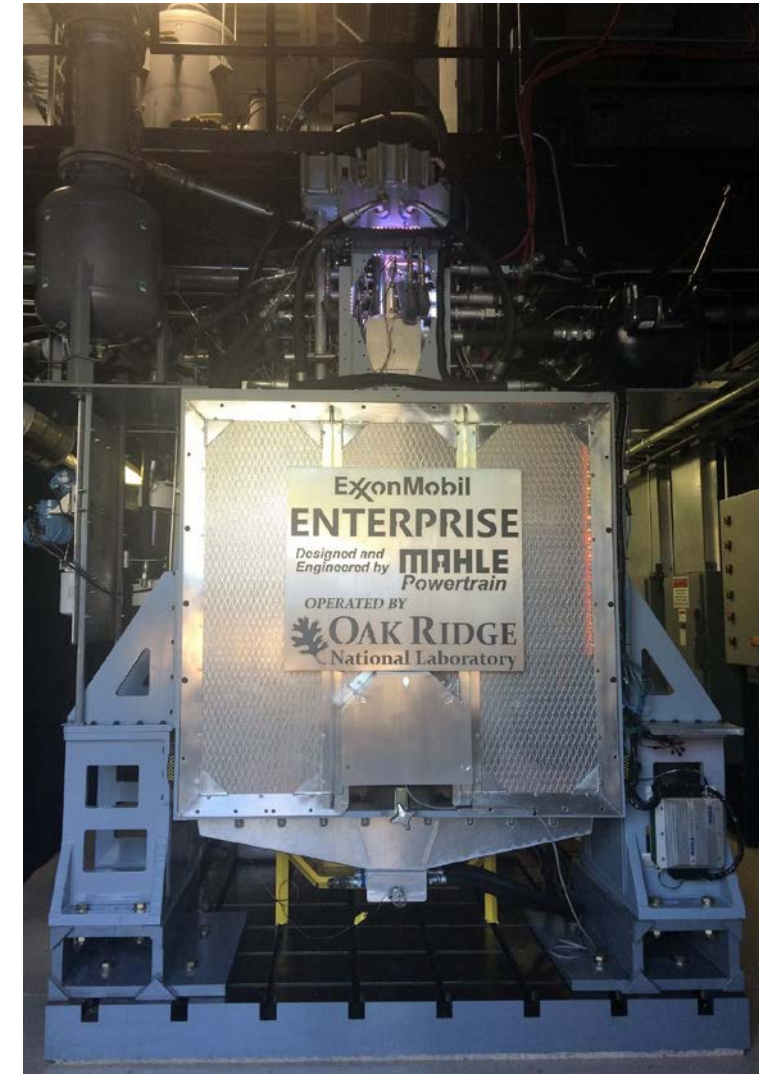
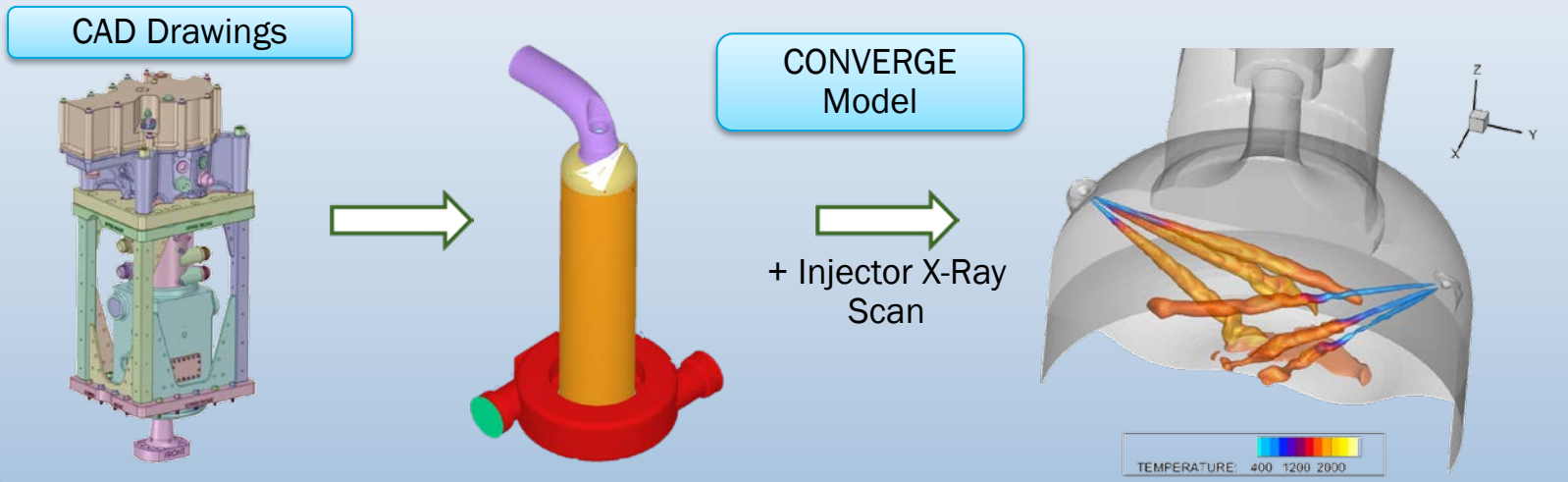
Also important to meet non-GHG emissions standards

Platform for evaluation: ExxonMobil “Enterprise” research engine at ORNL

Enterprise Research Engine Specifications

- 1/10 scale: Intermediate scale between bench tests and field deployment
 - 108 mm bore x 432 mm stroke (4:1 s/b ratio)
 - 565 rpm rated speed (linear mean piston speed matches full-scale engines)
- Compression ignition, 2-stroke, uniflow scavenged combustion system
- Crosshead configuration
- High-swirl combustion system with dual HEUI fuel injectors
- ~12 feet tall ~16,000 pounds

Digital Twin for Simulation Studies



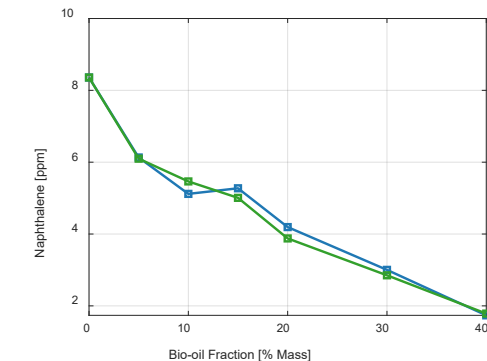
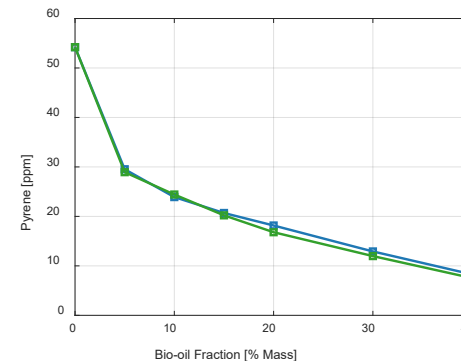
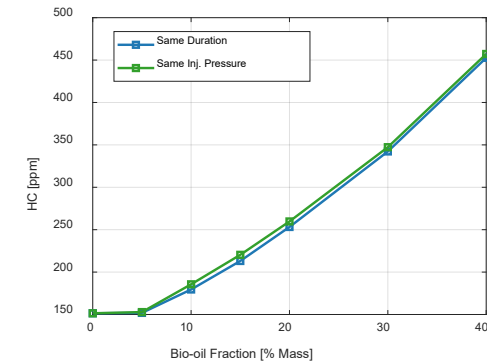
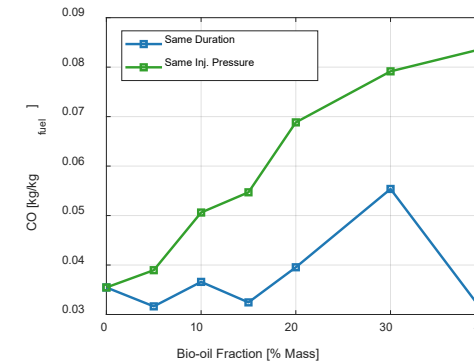
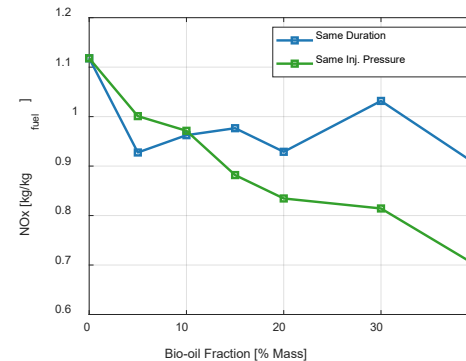
Initial simulation results are favorable, but emissions modeling is limited

Results are directionally promising

- NO_x emissions similar when combustion duration is maintained
 - Bio-diesel typically increases NO_x emissions; not clear whether this effect will be the same for bio-oils
- Increase in CO and HC emissions
- Significant reduction in pyrene and naphthalene, which are important soot precursors

Combustion simulations require complex chemical kinetics mechanisms; an existing pyrolysis bio-oil mechanism for oil heating was used here, but may not fully capture engine combustion chemistry for these oils

Need data from engine operations to really quantify emissions impacts, particularly with bio-intermediates where well-characterized models are lacking



Chuahy et al. (2022) *Fuel*. <https://doi.org/10.1016/j.fuel.2022.123977>

Experimental evaluation of bio-fuels will determine impact on combustion and emissions of NO_x and black carbon (soot)

Enterprise Engine Instrumentation

In-cylinder pressure sampled every 0.2° CA for combustion diagnostics

CO₂, CO (NDIR)

NO_x (HCLD)

O₂ (Paramagnetic)

HC (HFID)

Other gaseous emissions (FTIR)

Particulate Mass (AVL MicroSoot Sensor)



500-gallon heavy fuel oil supply system

Fuel Quantity Requirements

Fuel consumption is on the order of 10–20 gallons over a 6-hour operating shift, allowing evaluation of relatively small batches of fuel: recently implemented small-batch heated fuel system to allow operation from drum quantities of heavy fuel oils



55-gallon heavy fuel oil supply system

Planning to begin evaluations of bio-fuel performance & emissions impacts later this year

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Questions?



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