NREL
NATIONAL RENEWABLE ENERGY LABORATORY



Sustainable Biofuels for Low-Carbon Maritime Transportation

Eric C.D. Tan, Abhijit Dutta, Kristiina Iisa, and Calvin Mukarakate

2022 AIChE Annual Meeting
Phoenix, AZ
November 13-18, 2022

Marine shipping sector

- One of the largest consumers of petroleum fuels, i.e., = one of the largest emitters of air pollutants
- Annual consumption: ~330 million metric tons (87 billion gal)
- > 90% world's shipped goods by marine vessels

Selection of alternative maritime fuels in the research

Category	Fuel Technology	Primary resource	Characteristics	
			Positive	Negative
Fuel oils	HFO with scrubbers	Crude oil	Low cost, reduced SOx and NOx emissions;	Carbon-heavy, high viscosity bunker fuel
Natural gases	LNG (Liquid-cooled methane/ ethane gas)	Crude oil; natural gas	Low nitrogen oxide emissions, sulfur-free; low cost	High well-to-propeller GHG output
Bio-fuels	FAME (bio-diesel)	Edible or used oils	Suitable clean alternative to MDO/MGO	Risk of acidic degradation
	HVO	Edible or used oils	High-quality drop-in diesel fuel	Higher cost; cross-sector interest
	UPO	Lignocellulosic; waste	Suitable clean alternative to HFO/IFO; high GHG reduction potential	Not commercially available
	UBO	Lignocellulosic; wet bio-mass; waste	High potential; more straightforward production process compared to UPO	Low commercialization
	FTD	Lignocellulosic; waste	Drop-in diesel fuel; very high GHG reduction potential	More impurities
	LBM (bio-LNG)	Lignocellulosic; landfill gas; waste	High GHG reduction potential	Potentially cost- competitive
Ammonia	NH3	Hydrogen	No tank-to-propeller emissions	High cost; toxic; low maturity in marine applications

Kouzelis et al (2022)

Generic technical and safety properties and emissions performances

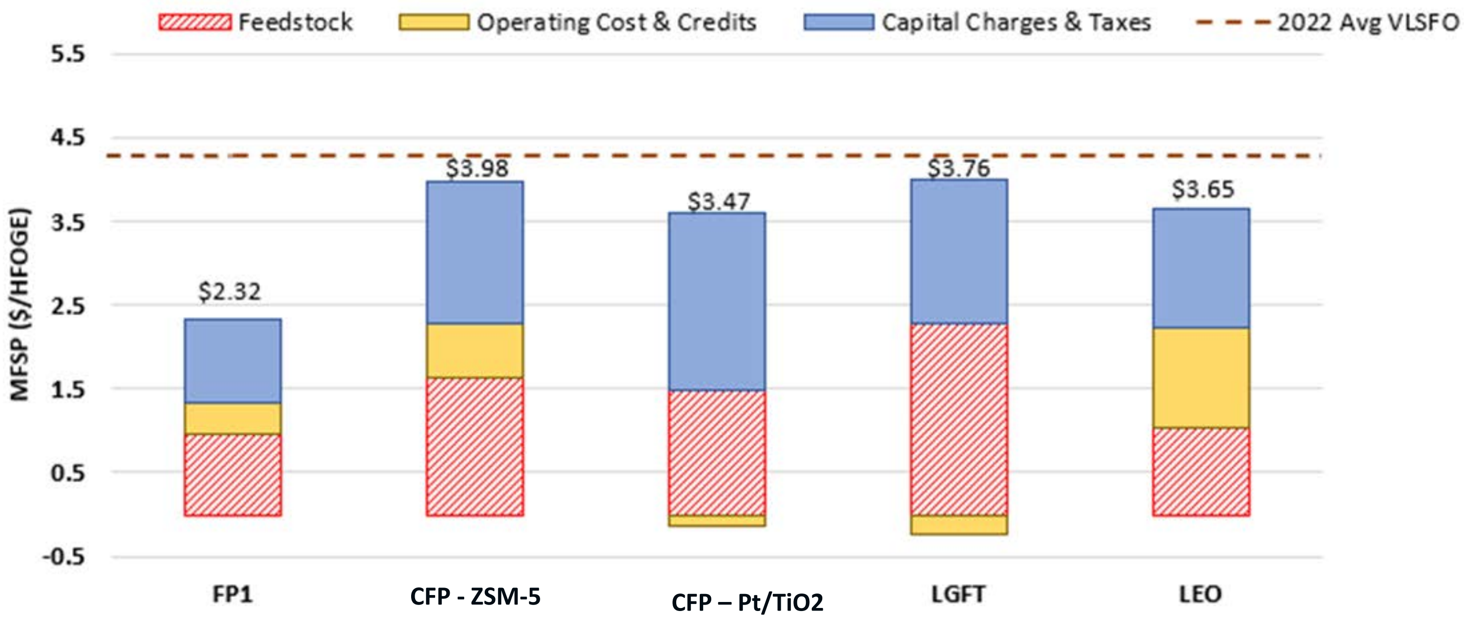
Generic technical and safety properties and emissions performances of different current and alternative maritime fuels

Fuel	Energy (LHV) & Technical			Flammability & Toxicity				Emission performance (ICE)			
	Gravimetric density MJ/kg	Volumetric density MJ/l	Cetane number	Autoignition temperature in air ◦C	Flashpoint ◦C	Flammability limits in air vol%	Toxicity	CO_2	SO_X	NO_X	PM
HFO	40.5	38	>20	230	>60	0.6–7.5	–	High	Med	High	Med
MGO	40.5	37	>35	210	>60	0.6–7.5	–	High	Low	High	Low
LNG	49.1	21	130*	540	-188	5.0–15.0	NT	Med	Low	Med	Low
MeOH	20	15.8	<5	464	11–12	6.7–36.0	LAT	Med	Low	Med	Low
FAME	37.2	33.2	45–55	261	>61	0.6–7.5	–	High	Low	High	Low
HVO	44	34.4	>70	204	> 61	0.6–7.5	–	High	Low	High	Low
H_2	120	8.5	>130*	585	N/A	4.0–75.0	NT	Low	Low	High	Low
NH_3	18.6	19	120*	651	132	15.0–28.0	HT	Low	Low	High	Low

Solakivi et al (2022)

Examples of NREL TEA of sustainable biofuels for marine transportation

Comparative TEA result summary of selected alternative marine biofuels showing favorable economic feasibility to displace conventional marine fossil fuels.

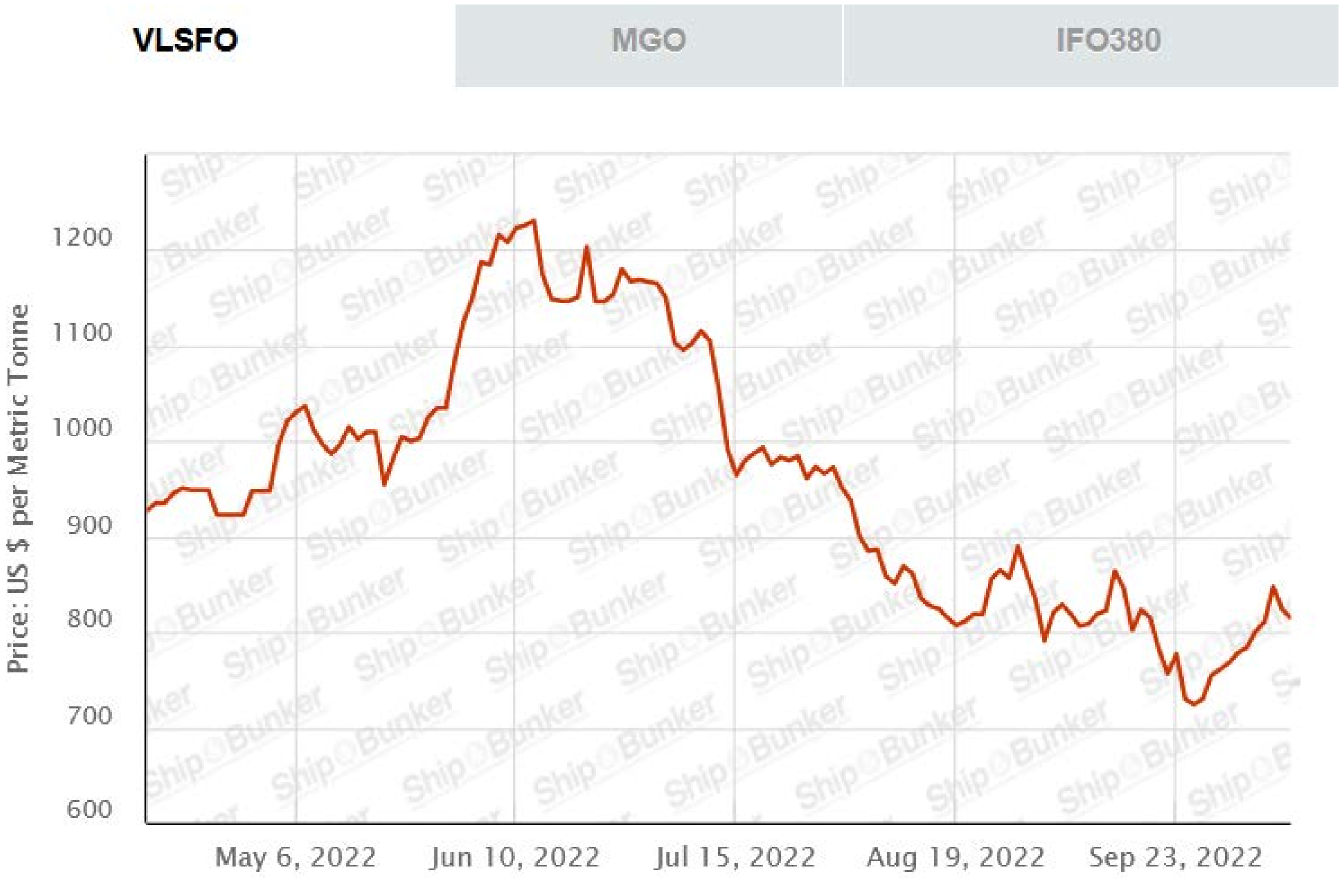


Fast pyrolysis (FP) based processes converting a 50/50 blend of forest residues and clean pine to bio-oil via three process options: fast pyrolysis without catalytic vapor upgrading (FP1), and fast pyrolysis with vapor phase upgrading over ZSM-5 zeolite catalyst (CFP – ZSM-5) and Pt/TiO_2 catalyst (CFP – Pt/TiO_2). Landfill gas-to-fuel via Fischer-Tropsch synthesis (LGFT). Lignin-ethanol oil (LEO) pathway.

Li, Tan, et al (2022) DOI:10.1021/acs.est.2c03960

https://shipandbunker.com/prices/am/nampac/us-lax-la-long-beach#VLSFO

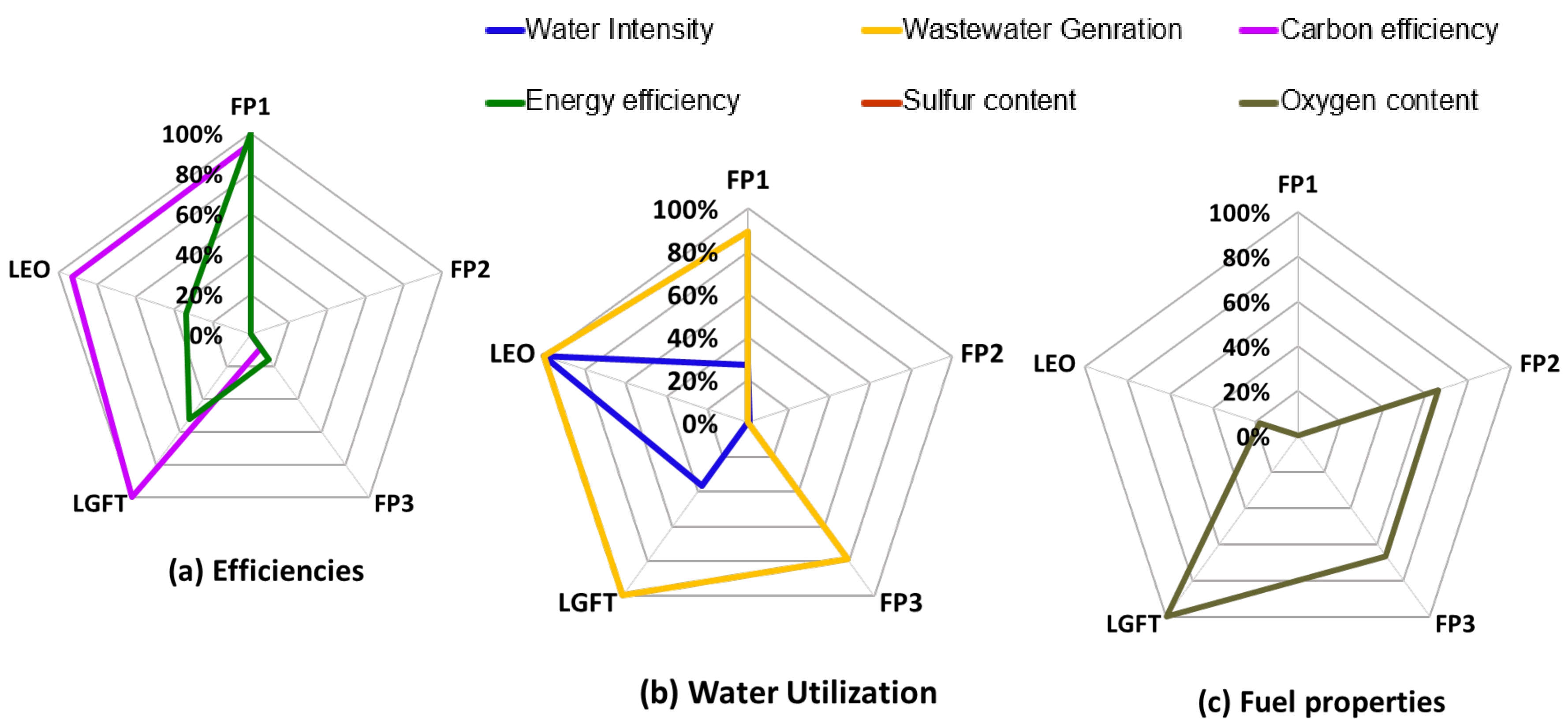
1 HFOGE = 140,353 Btu	
1 MT = 266.5 HFOGE	
$/MT	$/HFOGE
1200	4.50
1100	4.13
1000	3.75
900	3.38
800	3.00
700	2.63
600	2.25



Assessed on 10/12/2022

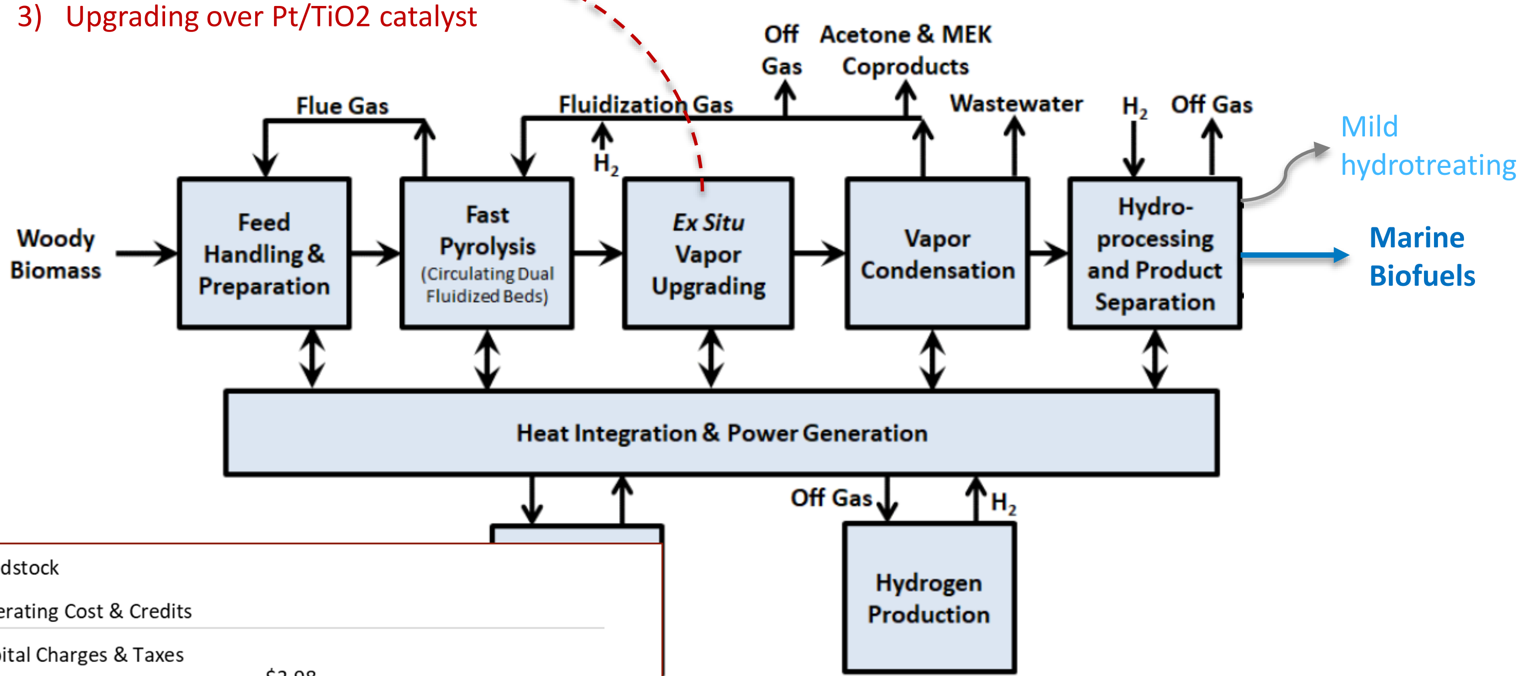
Examples of NREL sustainable biofuels for marine transportation

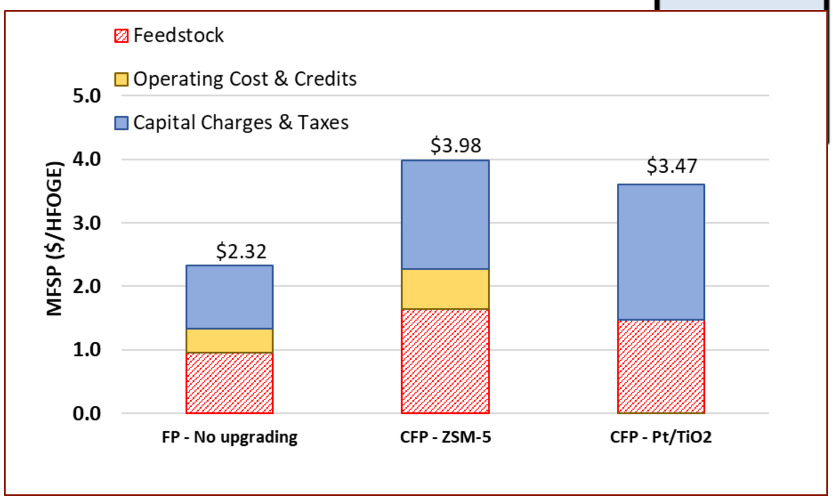
Sustainability metrics results summary. 100% and 0% represent the best and worst case among all the pathways, respectively.



Fast Pyrolysis Oil to Marine Biofuels

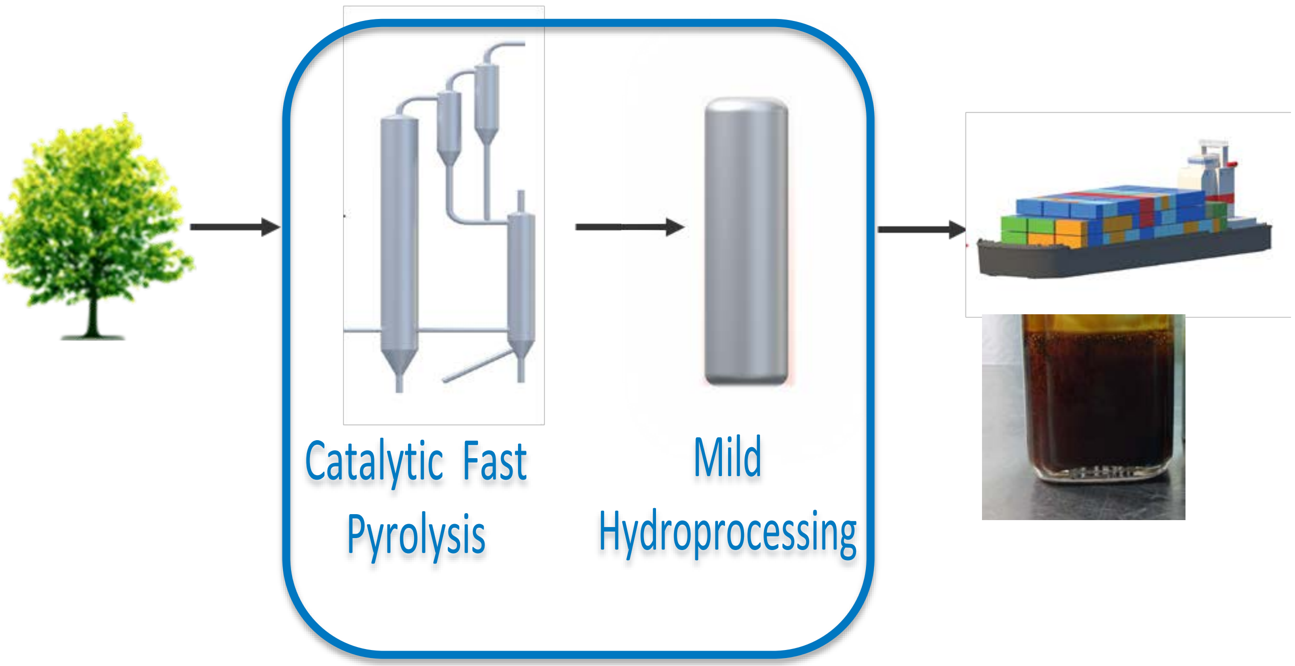
1) No vapor upgrading
2) Upgrading over ZSM-5 catalyst
3) Upgrading over Pt/TiO2 catalyst





Maritime Fuels via Biomass Pyrolysis

Goal: Determine minimum upgrading of bio-oils required to enable blending with very-low sulfur fuel oil (VLSFO)



Property	ISO 8217
Acid number, mg/KOH	< 2.5
Si+Al, ppm	<100
Ash, wt%	<0.15%
Water, vol%	<0.5
Density, g/cm³	<991
Flash point, °C	≥60

- ***Measure fuel properties***

Properties of Hydrotreated Samples

	ISO 8217	Feed	HT 1	HT 2	HT 3	HT 4	HT 5
Pressure, psi			1000	1500	1500	1500	1500
Temperature			200	350	300	300	300
H_2: oil, L/L			3000	4200	4200	4200	3000
WHSV			0.78	0.12	0.12	0.17	0.24
Oil O, wt% db		22%	17-18	0	0.02	3	5
Acid number	≤2.5	28	25	0	0	0	
Density, g/cm^3	991	1130	1060	845	884	968	988
Ash	≤0.1	0.1	0.1	0.1	0.1	0.1	0.1
H_2O, wt%	≤0.5	4.5		0.3	0.6	2.2	3.4
Flash point, °C	≥60	48		<7	<7	<7	<7

- Samples 2-4 passed acid number test but failed flash point and water content
  - Will distill to separate lights

Properties of Hydrotreated Samples

- Hydrotreated Catalytic Fast Pyrolysis (CFP) oil
- Hydrotreating at temperatures ≥300°C produced fuel with acceptable properties with respect to acidity, density, ash content
  - Acid number 0 mg KOH/g (< 2.5) mg KOH/g)
  - O content 0-3%
  - Density < 990 g/cm3
  - Ash ≤ 0.1 wt%
- Flash point too low (<7°C vs. ≥60°C)
  - Will distill lights off to increase flash point
  - Beneficial use of lights: gasoline or chemicals (BTX)

Two of the hydrotreated products (HT 2 and HT3) met four of the key specifications as a neat marine fuel (acid number, density, ash and water contents), and an additional two met three of the specifications (acid number, density, ash). By blending with petroleum products, it may not be necessary to meet the specifications, and blending of the hydrotreated products HT4-5 at levels of 10%-20% may be acceptable for water content.

Next step
TEA

HT 1

$/gal ?

HT 5

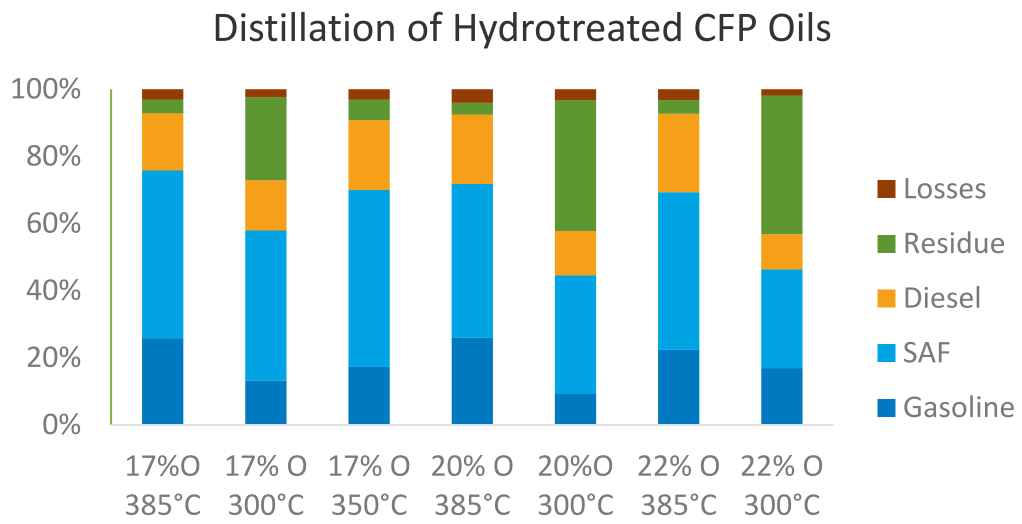
$/gal ?

HT 2

$/gal ?

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



Diesel and Residue could be used for marine

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

Heavy fraction → marine

Light fraction → BTX or gasoline

Aqueous

Adoption of biofuels for marine shipping decarbonization

A long-term price and scalability assessment

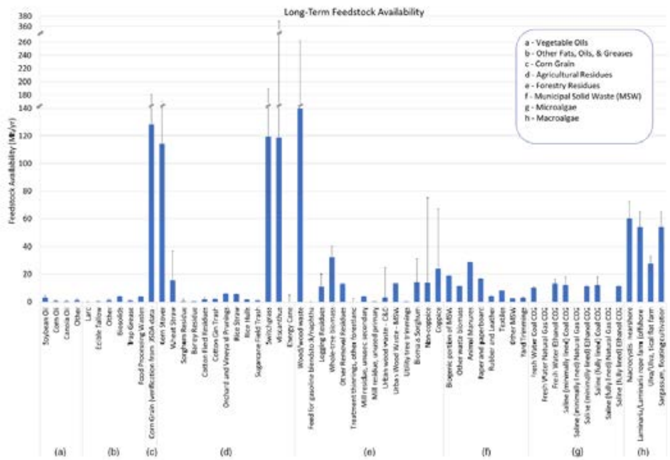


Figure 2. Summary of long-term feedstock availability by feedstock type. The feedstock types are grouped with lower case letters (a–h). Error bars indicate the maximum and minimum feedstock availability for each feedstock.

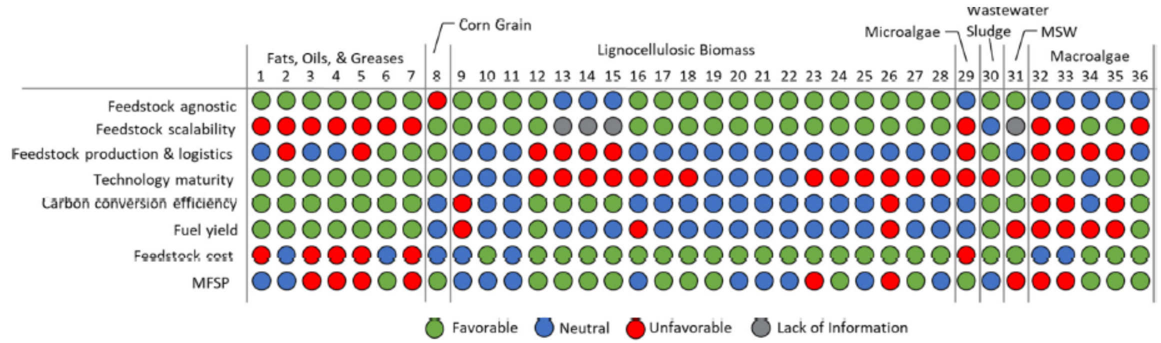


Figure 3. Conversion pathway screening assessment

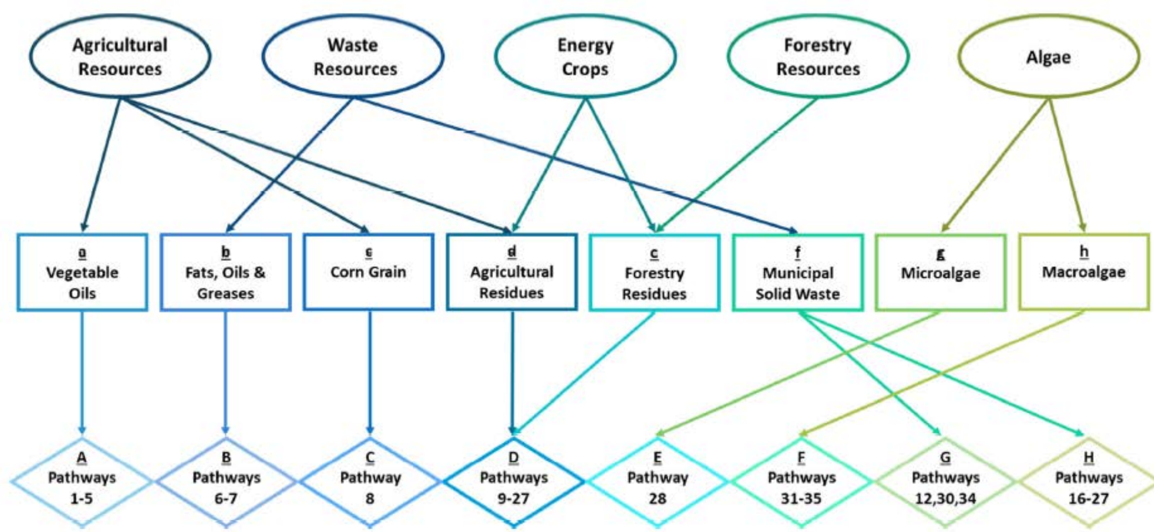
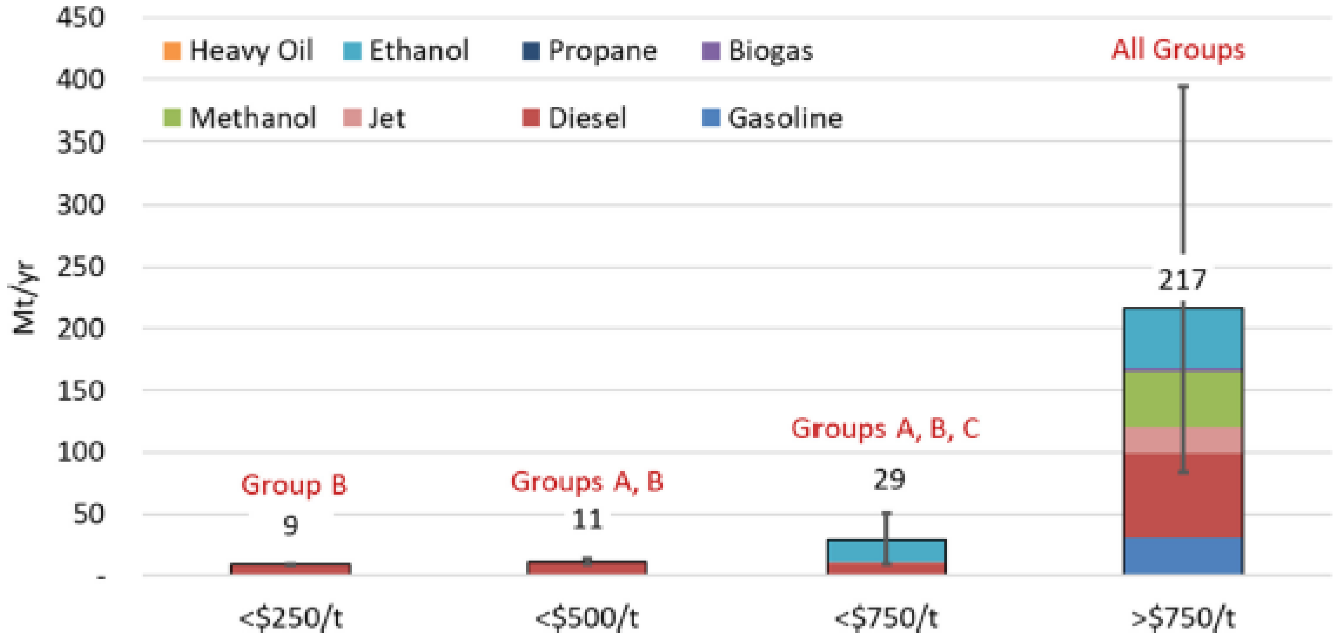


Figure 4. Schematic representation mapping feedstock groups (a–h) with conversion pathways (1–34) for production capacity and price projections. Technology groups are designated with upper case letters (A–H)

Tan et al (2022) https://doi.org/10.1002/bbb.2350

Adoption of biofuels for marine shipping decarbonization



A long-term price and scalability assessment

Figure 11. Consolidated long-term projected biofuel capacity and product slate at various price ranges

At a price range up to $500/t, biodiesel is the main product, and the annual capacity (12 Mt) is limited to feedstock availability constraints.

Biodiesel and corn ethanol are the main biofuels at a price range up to $750/t.

At a higher price point (above $750/t), the biofuel types and annual capacities increase substantially (218 Mt per year). Biofuels above this price include gasoline-, jet-, and diesel-range blendstocks, as well as bio-methanol, bio-propane, and biogas.

Tan et al (2022) https://doi.org/10.1002/bbb.2350

Questions?

Speaker information:
Eric C. D. Tan, Ph.D.
Senior Research Engineer
Catalytic Carbon Transformation and Scale-up Center
National Renewable Energy Laboratory (NREL)
303-384-7933
eric.tan@nrel.gov
www.nrel.gov

Acknowledgements

DOE's Bioenergy Technologies Office (BETO)
http://www.eere.energy.gov/biomass

Josh Messner
BETO Technical Manager

NREL/PR-5100-84535

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.