

Techno-Economic Analysis and Life Cycle Assessment of Greenhouse Gas and Criteria Air Pollutant Emissions for Biobased Marine Fuels

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ABSTRACT:

Biofuels can play an essential role in the future marine fuel that is more renewable, and lower sulfur and other emissions. When used for marine propulsion, biofuels could offer a potential alternative for shippers to meet the growing demand and comply with the upcoming more stringent air emission regulations. To support this effort, we perform techno-economic analysis (TEA) and life cycle analysis (LCA) to assess the economic and environmental feasibility of various biofuel production pathways, in terms of their market competitiveness and environmental benefits concerning energy savings and air emissions reductions. The selected biofuel production pathways are 1) Fischer-Tropsch (FT) diesel from feedstocks including biomass only, and biomass cofeeding with natural gas or coal, 2) renewable diesel via hydroprocessed esters and fatty acids (HEFA) using yellow grease with and without heavy oil co-feed, and 3) bio-oil via fast pyrolysis of low ash woody feedstock. This study also develops a new version of the GREET marine fuels module for the estimation of life cycle greenhouse gas (GHG) and criteria air pollutant (CAP) emissions of conventional and biobased marine fuels. The conventional marine fuel options considered include conventional heavy fuel oil (HFO) and marine gas oil, as well as low sulfur versions of HFO and marine gas oil, and natural gas. The biofuels considered in this report are considered to be potential drop-in fuels compatible for use in marine engines. Further work is needed to confirm compatibility and to address any potential issues which could be caused by differences in their properties.

Keywords:

1. INTRODUCTION

Marine shipping is the most energy-efficient form of freight transport. It is the backbone of global trade, responsible for transporting 80 percent of the world's goods by volume and over 70 percent of global trade by value.^{1,2} Marine shipping sector heavily depends on fossil fuel and is one of the largest consumers of petroleum fuels. Heavy fuel oil (HFO) is a residual of the refinery process which contains many of the undesirable impurities separated from other refinery products and in the main fuel used by the marine shipping sector is primarily heavy fuel oil, 77% in 2013.³ Other marine fuels include marine gas oil (MGO), marine diesel oil (MDO), intermediate fuel oil (IFO), and marine fuel oil (MFO), and are categorized based on their blending properties.⁴ The annual global marine fuel consumption is projected to be around 330 million metric tons (87 billion

gallons) annually, which is higher than the world's yearly jet fuel consumption of 220 metric million tons (1.4 billion barrels).⁵ The overall demand for marine fuels is expected to double by 2030 due to the increase in global trade.^{6,7}

Moreover, ocean shipping is one of the most significant contributors to air emissions of sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulate matters (PM). Global shipping contributes 13% of human-caused emissions of sulfur oxides⁸ and 2.6% of anthropogenic carbon dioxide emissions.⁹ As a major source of pollutant emissions, the marine industry is facing several challenges related to emission regulations. The International Maritime Organization (IMO) has set emission targets to reduce global marine fuel sulfur content from current 3.5% m/m (mass by mass) to 0.5% m/m, starting on January 1, 2020 (or IMO 2020).¹⁰ Besides, in the U.S., the California Air Resources Board (CARB) and other state agencies have established regulations limiting the sulfur content of fuel used in coastal regions to 0.1% m/m.^{5,11} These regulations will require shipowners to find alternative fuel pathways. The options include low-sulfur HFO, low-sulfur MGO, installing sulfur scrubbers, or other alternative fuels/powertrains.¹⁰ In addition to sulfur emission reduction targets, the IMO has also established a framework for reducing the carbon intensity of shipping, explicitly, 40% reduction relative to 2008 levels by 2030, and 70% reduction by 2050.^{3,12}

The expected higher costs for low-sulfur marine fuels, other forthcoming emission regulations, and the additional processing associated with HFO, could provide a new market opportunity for biofuels, which have inherently low sulfur content and potential to reduce particulate matter emissions. In addition, biofuels offer the possibility to reduce net carbon dioxide emissions due to the uptake of carbon from the atmosphere during biomass growth. Biofuels can undoubtedly play an essential role in the future marine fuel that is more renewable, and lower sulfur and emissions. Techno-economic analysis (TEA) and life cycle analysis (LCA) are effective tools to assess the economic and environmental feasibility of various biofuel pathways, in terms of their market competitiveness and environmental benefits concerning air emissions reductions.

To support this effort, we evaluate the economic potential of producing renewable fuels for marine propulsion. The selected fuel production pathways for the techno-economic analysis are 1) gasification and Fischer-Tropsch (FT) for a range of feedstocks including biomass, natural gas, biomass and coal, and biomass and natural gas (Pathway 1), 2) conversion of extracted oils (yellow grease (YG) for this study) to marine fuels via hydrotreating with and without co-feeding of fossil feedstock (heavy fuel oil) (Pathway 2), and 3) fast pyrolysis (FP) of low ash woody feedstock to produce pyrolysis oil or bio-oil (Pathway 3). The biofuels considered in this report are considered to be potential drop-in fuels compatible for use in marine engines; however further work is needed to confirm compatibility and to address any potential issues which could be caused by differences in their properties.

In conjunction with the TEA study of the marine biofuels, the second objective of this paper is to estimate the life-cycle greenhouse gas (GHG) and criteria air pollutant (CAP) emissions of the biofuels. As a comparison, this study also quantifies GHG and CAP for the conventional marine fuels, namely, conventional HFO and marine gas oil, as well as low sulfur versions of HFO and marine gas oil.

2. Process Overview

2.1 Pathway 1: Gasification and Fisher-Tropsch Synthesis

The simplified block flow diagram for Pathway 1 is shown in Figure 1. The processing steps of the thermochemical conversion pathway include the conversion of feedstocks to synthesis gas via gasification, gas cleanup via reforming of tars and other hydrocarbons, syngas conditioning (compression and acid gas removal), Fisher-Tropsch synthesis (FT), hydrotreating, and product separation. For the co-feeding pathways, biomass and fossil feedstocks are assumed to be fed 50%/50% by weight. Detailed process description for BTL, GTL, and GBTL can be found in Zhang et al.¹³ For GTL, feedstock preprocessing and gasification steps are not required. Nature gas is directly sent to a reformer, which is a circulating, fluidized solid catalyst system, with reforming and regeneration operations in separate beds.¹⁴ For BTL and GBTL cases, the biomass feedstock is preprocessed, dried from the moisture level of 30% to 10%, and sent to an entrained flow gasifier operating at 1633°F and 33 psia to make raw syngas rich in CO and H₂ but also hydrocarbons such as tars and solid char. Cyclones at the exit of the gasifier separate the char and olivine (heat carrier) from the syngas. The solids flow to the char combustor, where the char is burned in the air in a fluidized bed, resulting in olivine temperatures higher than 1800°F. The hot olivine and residual ash are carried out of the combustor by the combustion gases and separated using a pair of cyclones.

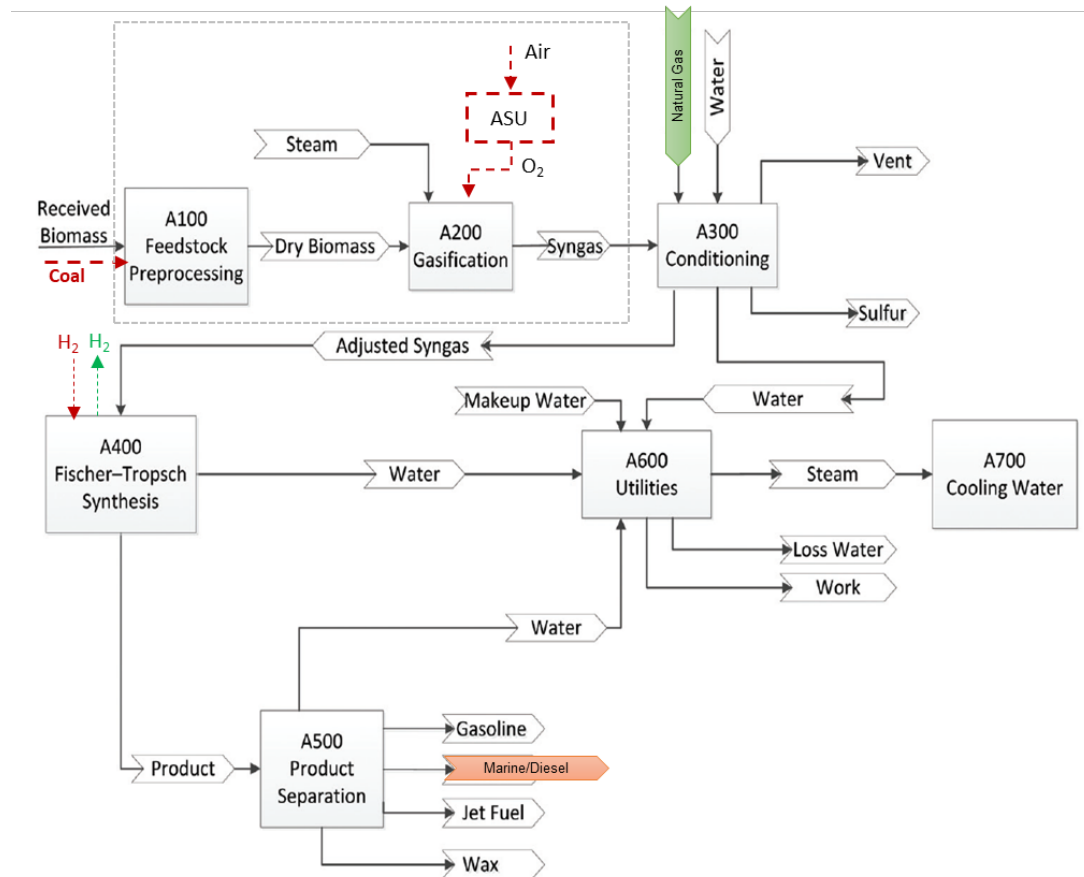


Figure 1. Process flow diagram for Fischer-Tropsch diesel production via BTG, GTL, CBTL, or GBTL.

For the CBTL case, the coal feed is mixed with water before merging with biomass. Instead of undergoing indirect gasification to make raw syngas, the confluent of biomass and coal are fed to a high-temperature entrained flow slagging gasifier (i.e., direct gasification) with conditions similar to the Shell gasifier.¹⁵ Since oxygen with high purity is required for the high-temperature gasification, an air separation unit (ASU) is required to produce nearly pure oxygen from the air. The biomass-coal direct gasification is modeled using Gibbs free energy minimization method. The oxygen flow rate to the gasifier is controlled using the desired gasifier temperature at 2470°F, which is similar to the literature.¹⁵ Both ASU and high-temperature gasification are modeled using conditions specified in Aspen Plus IGCC Model.¹⁶ It is noteworthy that as opposed to the low-temperature indirect gasification, high-temperature gasification does not favor the formation of methane and tars. Thus the raw syngas cleanup step with a reformer may be optional. The downstream processes (after gasification) are the same for all cases.

Fisher-Tropsch (FT) synthesis is considered a relatively mature conversion technology that involves the catalytic conversion of synthesis gas into a mixture of reaction products that could be refined to synthetic fuels, lubricants, and petrochemicals. One of the essential advantages that the FT process offers is its capability of producing liquid hydrocarbon fuels from synthesis gas, which are nearly free from sulfur and relatively low in aromatic content. An important aspect of this process is the adjustment of the H₂ to CO ratio, which is usually determined by the upstream gasification and reforming technologies and operating conditions. The FT reactions involve catalytic CO polymerization and hydrogenation, where the chain growth and termination of the reaction products can be described by a carbon number distribution.

The FT reactor products are condensed and separated through typical hydrocarbon separation process in a multi-cut distillation column to recover the primary products (naphtha, jet, and diesel fractions) as individual streams. Each of the primary hydrocarbon cuts is further processed to yield finished fuel blendstocks for gasoline, jet fuel, and marine/diesel. Wax produced from the synthesis reactor is sold as a co-product. However, for bunker fuels, the wax produced from the synthesis reactor can be included in the blendstock and not sent to a wax hydrocracker for upgrading. The jet and marine/diesel fractions undergo mild hydrotreating to remove any remaining heteroatom contaminants (sulfur, nitrogen, and oxygen) and improve properties for blending.

2.2 Pathway 2: Conversion of Extracted Oils (Yellow Grease) to Hydrocarbon Fuels via Hydrotreating

Figure 2 shows the schematic process flow diagram to produce renewable diesel via hydroprocessed esters and fatty acids (HEFA) using yellow grease with and without HFO co-feed. Detailed process description can be found in a recent publication.¹⁷ Briefly, yellow grease is sent to the hydroprocessing facility (first block in Figure 2), fundamentally with three reaction steps (hydrogenation, propane cleave, and decarboxylation) according to patent literature^{18,19}. The reactions take place at 400°C and 9.2 megapascals using the Pd/ γ -Al₂O₃ catalyst, resulting in the overall conversion of 91.9%. The second hydrotreating step includes hydrocracking and hydroisomerization reactions, which are operated at a temperature of 355°C, the pressure of 600 psig, a liquid hourly space velocity of 1 h⁻¹, and an H₂-to-feed ratio of 50 standard cubic feet/gal using Pt/HZSM-22/ γ -Al₂O₃ catalyst. The hydroisomerization and hydrocracking processes are followed by a fractionation process to separate the mixtures to paraffinic kerosene, paraffinic

marine/diesel, naphtha, and light gases. The hydrocracking reactions are exothermic and result in the production of lighter liquids and gas products.

2.3 Pathway 3: Fast Pyrolysis of Low Ash Woody Feedstock

Figure 3 shows the simplified process flow diagram of the bio-oil production pathway, which is designed as a standalone fast pyrolysis process with a capacity of 2,205 U.S. ton (2,000 metric tons) dry biomass per day.²⁰ As opposed to gasification, fast pyrolysis technology can be sensitive to feedstock types and compositions. For example, ash and carbon content in the feedstock showed significant impacts on the product yield and compositions; therefore, low ash feedstock is typically used for fast pyrolysis technology.²¹ Compositions and heating values of the low ash woody biomass assumed in this study are shown in Table 2. As-received biomass is initially sent to an on-site biomass dryer to reduce its moisture content from 30% to 10% before it is fed to a circulating fluidized bed pyrolyzer. Hot sand is used as a heat carrier for carrying out endothermic fast pyrolysis reaction. Biomass is converted into a mixture of vapors and char within less than two seconds. The sand and char are subsequently separated from the vapors by a series of cyclones. The hot vapors are rapidly quenched in a two-stage system with previously condensed, and cooled bio-oil and non-condensable gases are separated from the condensed bio-oil. In the first stage, most of the condensable products are removed using recirculated and indirect air-cooled bio-oil. The second stage operates at a lower temperature by indirect water cooling of the recirculating bio-oil. Most of the gases are recycled back to the pyrolysis reactor to assist fluidization. Char and a small portion of non-condensable gas are burned to heat the circulating sand. Hot flue gas from the char and gas burner is used to dry wet biomass.

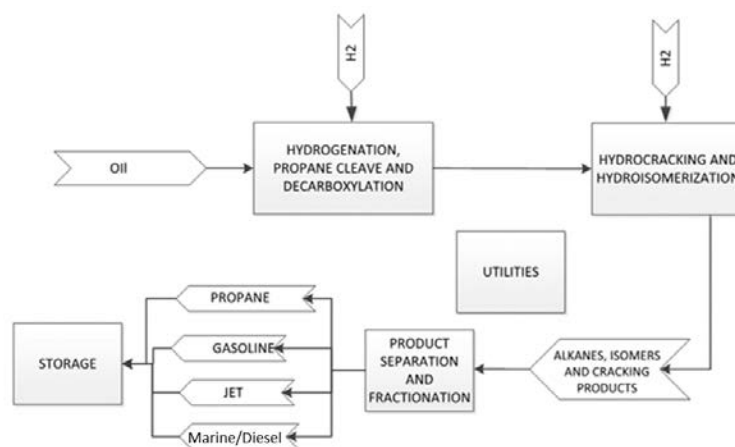


Figure 2. Schematic process flow diagram for renewable diesel production via hydroprocessed esters and fatty acids.

3. METHODS

2.1 Economic Assumptions

The TEA reported here uses n^{th} -plant economic assumptions. The important aspect associated with n^{th} -plant economics is that a successful industry has been established with many operating plants using similar process technologies. The TEA model encompasses a process model and an economic model. For a given set of conversion parameters, the process model solves mass and

energy balances for each unit operation. This data is used to size and cost process equipment and compute raw material and other operating costs. Once the capital and operating costs are determined, a discounted cash flow rate of return (DCFROR) calculation was performed to determine the minimum fuel selling price (MFSP) that meets the economic parameter using the general methodology^{22,23} and the financial parameters summarized in Table 1. The MFSP value represents the minimum selling price of fuels assuming a 30-year plant life and 40% equity financing with a 10% internal rate of return and the remaining 60% debt financed at 8% interest. The unit for the MFSP is dollars per gasoline gallon equivalent or \$/GGE. GGE is determined using the following equation, using the lower heating value (LHV) of gasoline blendstock (116,090 BTU/gal) obtained from GREET.²⁴

$$GGE = \frac{LHV \text{ of Fuel}}{LHV \text{ of Gasoline Blendstock}}$$

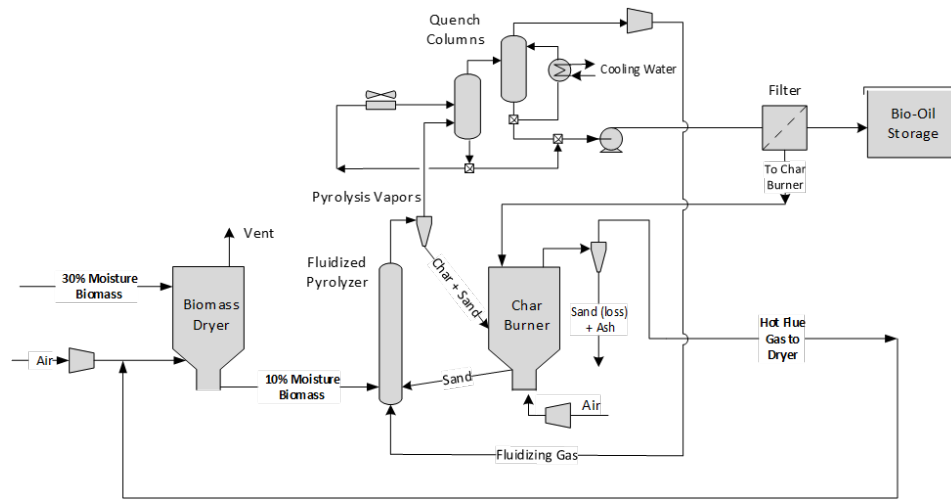


Figure 3. Simplified process flow diagram for bio-oil production by fast pyrolysis process.

Table 1. Summary of nth-Plant Assumptions for Techno-Economic Analysis²⁵

Description of Assumption	Assumed Value
Cost year	2016 US dollars
IRR on equity	10%
Plant financing by equity/debt	40%/60% of total capital investment
Plant life	30 years
Income tax rate	21%
Interest rate for debt financing	8.0% annually
Term for debt financing	10 years
Working capital cost	5.0% of fixed capital investment (excluding land purchase cost)
Depreciation schedule	7-year MACRS schedule ^a
Construction period (spending schedule)	3 years (8% Y1, 60% Y2, 32% Y3)

Plant salvage value	No value
Startup time	6 months
Revenue and costs during startup	Revenue = 50% of normal
	Variable costs = 75% of normal
	Fixed costs = 100% of normal
On-stream percentage after startup	90% (7,884 operating hours per year)

*Capital depreciation is computed according to the United States Internal Revenue Service modified accelerated cost recovery system (MACRS). Because the plant described here is not a net exporter of electricity, the steam plant and power generation equipment are not depreciated over a 20-year recovery period, according to the Internal Revenue Service. The whole plant capital is depreciated over a 7-year recovery period.

For Pathway 1, four feedstock scenarios are considered: 1) biomass-to-liquid (BTL) with 100% biomass, 2) gas-to-liquid (GTL) with 100% natural gas, 3) coal and biomass co-feed (CBTL), and 4) natural gas and biomass co-feed (GBTL). For CBTL and GBTL, the fossil-to-biomass co-feeding feedstocks is 51/49 by weight. The feedstock specifications for woody biomass and coal are shown in Table 2. Pathways 1 and 3 assume high ash and low ash woody biomass, respectively. For pathway 2, two feedstock scenarios are considered: 1) yellow grease (100%), and 2) yellow grease and heavy fuel oil co-feed (50/50 by weight). Low ash woody biomass is the feedstock for fast pyrolysis (Pathway 3). The feedstock costs are summarized in Table 3.

Table 2. Feedstock Specifications for Pathways 1 and 3

Feedstock	Woody Biomass		Bituminous Coal
	(High ash)	(Low ash)	
Component	<i>Pathway 1</i>	<i>Pathway 3</i>	<i>Pathway 1</i>
Carbon	49.81	50.94	74.55
Hydrogen	5.91	6.04	4.96
Nitrogen	0.17	0.17	1.59
Sulfur	0.09	0.03	2.44
Oxygen	41.02	41.9	6.84
Ash	3.00	0.92	9.66
Heating Value (Btu/lb)	HHV	8,449	13,326
	LHV	7,856	12,812

HHV: Higher Heating Value LHV: Lower Heating Value

Table 3. Feedstock Cost Assumption

Feedstock	Cost (2016\$)	Unit
Woody biomass (high ash) ²⁶	60.58	\$/dry ton
Woody biomass (low ash) ²⁷	91.54	\$/dry ton
Bituminous coal ²⁸	29.52	\$/ton
Natural gas ²⁹	0.13	\$/lb
Yellow grease ¹⁷	0.28	\$/lb
Heavy oil ³⁰	0.26	\$/lb

2.2 LCA Methodology and Assumptions

These pathways are evaluated using a new version of the GREET marine fuels module developed for this project. This new module includes several new marine biofuel pathways as well as updated pathways for conventional marine fuels and natural gas as a marine fuel. We updated the combustion emission factors using the best available data.

The scope of this study includes the well-to-hull emissions of each fuel option. Supply chain emissions are included for petroleum extraction and refining, biofuel feedstock growth, harvesting, and conversion, as well as natural gas extraction and liquefaction. Use phase emissions are based on the best available emissions factors, however, in several cases, conventional diesel emissions are used as a proxy for emissions from biobased diesel. The infrastructure associated with fuel production and distribution, as well as fuel-specific handling requirements is outside the scope of this study. The findings of this study are meant to gauge the potential emissions benefits associated with the use of biofuels for marine transportation and to identify tradeoffs amongst fuel options.

2.2.1 LCA System Boundary

In this study, a total of nine fuel types is considered (Table 4). For heavy fuel oil (HFO) that is the most typical marine fuel, we considered two additional HFO with low sulfur contents (0.5% and 0.1%) along with conventional HFO with a sulfur content of 2.7%. Marine gas oil (MGO), a distillate fuel, which has relatively lower sulfur content (1.0%) than the baseline HFO is considered with two additional MGOs with low sulfur contents (0.5% and 0.1%). Marine diesel oil (MDO) is considered as a mixture of HFO and MGO, which generate three types of MDO with different sulfur contents. By default, we assume to mix 50% HFO and 50% MGO by weight. Liquefied natural gas (LNG) has emerged to comply with regulations by IMO and MARPOL because of its clean combustion profile and recent competitive LNG price. Other than these conventional fossil-based marine fuels, we analyzed alternative fuel production pathways: 1) Fisher-Tropsch diesel (FTD) via Pathway 1 using four different feedstocks (natural gas [NG], biomass, biomass/NG, and biomass/coal), 2) renewable diesel via Pathway 2 using yellow grease with and without HFO, and 3) pyrolysis oil via Pathway 3 from woody biomass. We also include straight vegetable oil or SVO (soy oil) and biodiesel as alternative marine fuels.

Table 4. Fuel Production Pathways Evaluated in This Study

Pathways	Note
HFO (2.7% sulfur)	Residual oil in GREET
HFO (0.5% sulfur)	Residual oil in GREET + Desulfurization
HFO (0.1% sulfur)	Residual oil in GREET + Desulfurization
MGO (1.0% sulfur)	Unfinished oil in GREET
MGO (0.5 % sulfur)	Unfinished oil in GREET+ Desulfurization
MGO (0.1 % sulfur)	Unfinished oil in GREET+ Desulfurization
MDO (1.92% sulfur)	Mixture of HFO 2.7%S and MGO 1.0%S
MDO (0.5% sulfur)	Mixture of HFO 0.5%S and MGO 0.5%S
MDO (0.1% sulfur)	Mixture of HFO 0.1%S and MGO 0.1%S
LNG	LNG in GREET
FT-Diesel (NG)	Newly added (this study, Pathway 1, GTL)
FT-Diesel (biomass)	Newly added (this study, Pathway 1, BTL)
FT-Diesel (biomass/NG)	Newly added (this study, Pathway 1, GBTL)
FT-Diesel (biomass/coal)	Newly added (this study, Pathway 1, CBTL)
Pyrolysis oil (woody biomass)	Newly added (this study, Pathway 3)

Renewable diesel (yellow grease/HFO)	Newly added (this study, Pathway 2)
Renewable diesel (yellow grease)	Newly added (this study, Pathway 2)
Straight Vegetable Oil (SVO)	Soy oil in GREET
Biodiesel	Biodiesel in GREET

To compare the life cycle GHG and CAP emissions for these marine fuels, it is essential to have a consistent system boundary with reliable datasets. The Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET®) model³¹ is a tool with significant datasets enabling a systematic LCA of various transportation fuels. This model includes all processes associated with feedstock recovery, feedstock transportation, fuel production, fuel transportation, and fuel combustion. Since the analysis covers from feedstock recovery (well) to pump (WTP) and pump-to-hull (fuel combustion) (PTH), we call the life cycle of marine fuels as well-to-hull (WTH).³² WTP of petroleum products (HFO, MGO, and MDO) include crude oil recovery, crude oil transportation, crude oil refining for HFO and MGO production, and fuel transportation. All the parameters for these processes are from GREET,³¹ which are mainly based on the studies by Elgowainy et al.³³ and Forman et al.³⁴ For LNG production, WTP covers both conventional NG and shale gas recovery, NG processing, transportation, and liquefaction which are documented in the earlier papers.^{35,36} For the parameters of the new fuel production processes (FTD, pyrolysis oil, and renewable diesel), we documented inputs and outputs of the processes in the following sections. For SVO, we used parameters of soy oil production in GREET, and biodiesel is assumed to be 100% from soybean via transesterification. In case there are products other than marine fuels, energy allocation is used. For global warming potential (GWP) values, the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC) was used.³⁷ All fuel specifications are presented in Table 5.

Table 5. Fuel Specifications

	Units	HFO (2.7% sulfur)	HFO (0.5% sulfur)	HFO (0.1% sulfur)	MDO (1.92% sulfur)	MDO (0.5% sulfur)	MDO (0.1% sulfur)	MGO (1.0% sulfur)	MGO (0.5% sulfur)	MGO (0.1% sulfur)
Lower heating value	MJ/kg	39.5	39.5	39.5	41.0	41.0	41.0	42.8	42.8	42.8
Density	kg/L	0.99	1.0	1.0	0.91	0.91	0.91	0.84	0.84	0.84
C ratio	% by wt.	87	90	90	87	87	87	87	87	87
S ratio	% by wt.	2.70	0.50	0.10	1.92	0.50	0.10	1.00	0.50	0.10
Biogenic carbon share	% by wt.	0%	0%	0%	0%	0%	0%	0%	0%	0%

	Units	FT-Diesel (NG)	Liquefied Natural Gas (LNG)	FT-Diesel (Biomass & Coal)	Renewable diesel (Yellow grease & HFO)	FT-Diesel (Biomass & NG)	Straight Vegetable Oil (SVO)	Pyrolysis oil (Woody biomass)	FT-Diesel (Biomass)	Renewable diesel (Yellow grease)	Biodiesel
Lower heating value	MJ/kg	43.2	48.63	43.2	44.0	43.2	37.2	15	43.2	44.0	37.5
Density	kg/L	0.8	0.43	0.8	0.78	0.8			0.80	0.78	0.89
C ratio	% by wt.	90	75	90	87	90	78	41	85	87	78

S ratio	% by wt.	0.00	0.00	0.00	1.51	0.00	0.00	0.00	0.00	0.00	0.00
Biogenic carbon share	% by wt.	0%	0%	49%	50%	49%	100%	100%	100%	100%	100%

2.2.2 Production of HFO and MGO with Low Sulfur Content

Residual oil and unfinished oil in GREET are used for HFO (2.7% sulfur) and MGO (1.0% sulfur), respectively. In order for the production of low sulfur marine fuels via desulfurization, additional processes with hydrogen inputs are required. Due to limited information to perform simulations to estimate additional inputs and allocated emissions, we used a regression equation to estimate hydrogen inputs. McKetta³⁸ summarized hydrogen requirements for desulfurization of atmospheric tower bottoms, which shows desulfurizing 3.8% sulfur feed to 1.0%, 0.3%, and 0.1% require 497, 650, 725 scf/bbl, respectively. These can be converted into 0.245, 0.320, and 0.357 MJ H₂ for MJ of fuel production. With these and the baseline 3.8% sulfur fuel, we generated a regression equation (2nd order polynomial) among sulfur input, sulfur output, and hydrogen requirement (Figure 4). Estimated additional hydrogen requirements for HFO from 2.7% sulfur to 0.5% sulfur and 0.1% sulfur become 15,664 and 19,448 J H₂/MJ of fuel, respectively. Similarly, for MGO from 1.0% sulfur to 0.5% sulfur and 0.1% sulfur, hydrogen requirements are estimated at 4,325 and 8,109 J H₂/MJ of fuel, respectively. These hydrogen inputs were added along with other inputs for fuel production to estimate all upstream energy use and emissions. For MDO, we assumed it is a mixture of 50 vol.% HFO and 50 vol.% MGO; all related parameters were averaged between HFO and MGO on an energy input basis.

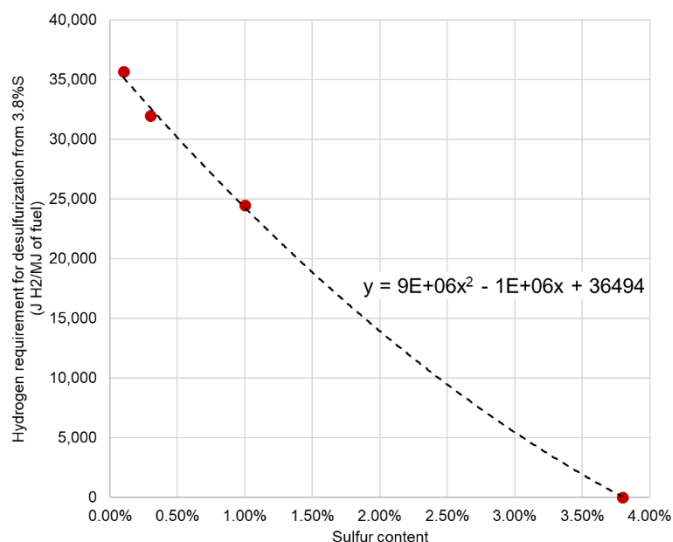


Figure 4. Hydrogen requirement for desulfurization from atmospheric tower bottoms with a sulfur content of 3.8%.

2.2.3 Life-Cycle Inventory

The life cycle inventory (LCI) data are obtained from the material and energy flows of the conversion steps that capture the impacts of input raw materials, and outputs such as fuel yields, wastes, and coproducts as predicted by the process model, and are shown in Table 6 for Pathway

1, Table 7 for Pathway 2, and Table 8 for Pathway 3. The input/output inventories provide the necessary information required for performing the life cycle GHG and CAP emissions.

Table 6. Inputs and Outputs of Fischer-Tropsch Diesel Production via Pathway 1

	Units	Feedstock			
		Biomass	NG	Biomass +NG	Biomass +Coal
Energy inputs					
Woody residue	MJ	1.97	0	0.434	0.644
	dry g	108	0	23.8	35.3
Natural Gas	MJ	0.00	1.52	1.24	0
Coal	MJ	0.00	0	0	0.836
Diesel	J	1,528	924	1,245	1,535
Natural Gas (process fuel)	J	0.00	0.00	0.00	0.00
Hydrogen	J	0.00	0	0	563,589
Electricity	J	0.00	0	7	1
Water	L	0.173	0.058	0.055	0.348
Chemicals/Catalysts					
Magnesium Oxide (MgO)	mg	13.35	0.00	2.94	4.36
Olivine	mg	306.49	0.00	67.51	0.00
Tar Reformer Catalyst	mg	13.20	4.97	5.57	14.40
Zinc Oxide (ZnO) Catalyst	mg	3.44	1.96	2.24	1.92
FT Synthesis Catalyst (Co based)	mg	2.51	0.87	1.34	1.36
Hydrotreating Catalyst (sulfided CoMo or NiMo)	mg	3.24	1.84	2.58	2.65
LO-CAT Chemicals	mg	74.34	0.00	16.24	728.42
Amine Make-Up	mg	0.02	3.72	5.35	53.19
Boiler Chemicals	mg	0.41	0.24	0.11	2.74
Cooling Tower Chems	mg	2.49	0.97	1.12	1.59
Products					
Marine/Diesel	MJ	0.18	0.11	0.14	0.18
Jet	MJ	0.40	0.23	0.31	0.38
Naphtha	MJ	0.31	0.20	0.27	0.33
Wax	MJ	0.12	0.07	0.09	0.11
Hydrogen	MJ	0.00	0.40	0.19	0.00
Mass ratio					
Fossil	%	0%	100%	51%	51%
Biomass	%	100%	0%	49%	49%

Table 7. Inputs and Outputs of Renewable Diesel Production Using yellow grease with and without HFO co-feed via Pathway 2

	Units	Yellow grease	Yellow grease with HFO
Energy Inputs			
Feedstock (Yellow Grease)	MJ	1.21	0.51
	g	30.4	12.9
HFO (co-feed)	MJ	0.00	0.51
Hydrogen	J	77,146	50,835
Natural Gas	J	79,109	85,602
Electricity	J	11,193	8,467
Catalysts			
Hydrotreating catalyst	mg	3.17	2.97
Isomerization/Hydrocracking catalyst	mg	0.52	0.53
Water	L	0.21	0.20
Products			
Marine/Diesel	MJ	0.01	0.18

Jet	MJ	0.69	0.48
Gasoline	MJ	0.22	0.26
Propane	MJ	0.08	0.08

Table 8. Inputs and Outputs of Pyrolysis Oil Production via Pathway 3

		Units	Low ash-feedstock case	High ash-feedstock case
Inputs				
	Feedstock (Woody biomass)	MJ	1.49	1.61
		g	80.7	88.0
	Electricity	J	31,062	42,788
	Cooling tower chemicals	mg	0.128	0.137
Product				
	Pyrolysis oil	MJ	1.00	1.00

2.2.4 Emissions from Fuel Use

Among the fuel supply chain stages, combustion emissions contribute the most life-cycle emissions. Combustion emissions are dependent on fuel properties, engine characteristics, and control technologies.^{39,40} Table 9 summarizes the emission factors used in this study and the corresponding data sources. It shows emission factors vary by engine types as well as fuel types. We include five major engine types (Slow-Speed Diesel [SSD], Medium-Speed Diesel [MSD], Steam Turbine [ST], Gas Turbine [GT], and LNG) and three auxiliary engine types (MSD, High-Speed Diesel [HSD], and LNG). Due to strict regulations on NO_x, the emission factors of NO_x are highly dependent on regulations. SO_x emissions are estimated based on the sulfur content of fuels, assuming 97.75% of sulfur is emitted as Sox, and the rest (2.247%) becomes sulfate in PM₁₀ emissions. The emission factors of PM₁₀ in Table 9 represent base PM without considering PM from sulfur in marine fuels. Note that the emission factors of PM_{2.5} are calculated as 92% of those of PM₁₀.⁴¹ CO₂ emissions are estimated based on carbon balance assuming all carbon in fuels are emitted as VOC, CO, CH₄, and CO₂. Due to limited information for the emission factors of other fuels (diesel, SVO, and pyrolysis oil), we used the same emission factors of MGO/MDO. The emission factors of LNG show that overall LNG vessels would generate lower CAP emissions compared to petroleum-based fuels except for CH₄ emissions (CH₄ slip).⁴⁰

Table 9. Emission Factors (g/kWh operation)

		Emission Regulation Tier	Main engine					Aux. engine		
			SSD	MSD	ST	GT	LNG	MSD	HSD	LNG
VOC (HC) ^a		-	0.6	0.5	0.1	0.1	0.5	0.4	0.4	0
CO ^a		-	1.4	1.1	0.2	0.2	1.30	1.1	0.9	1.3
NO _x	HFO ^a	0	18.1	14	2.1	6.1	-	14.7	11.6	-
		1	17	13				13	10.4	
		2	15.3	11.2				11.2	8.2	
		3	3.4	2.6				2	2.6	
	MGO/MDO ^a	0	17	13.2	2.0	5.7	10.9	13.8		

		1	16	12.2				9.8	12.2	
		2	14.4	10.5				7.7	10.5	
		3	3.4	2.6				2	2.6	
	LNG ^c	-	-	-	-	-	1.82	-	-	1.82
PM10 [*]	HFO ^a	-	0.576	0.576	0.93	0.06	-	0.576	0.576	-
	MGO/MDO ^a	-	0.155	0.155	0.16	0.01	-	0.155	0.155	-
	LNG ^c	-	-	-	-	-	0.04	-	-	0.04
CH ₄	HFO/MDO ^b	-	0.012	0.01	0.002	0.002	-	0.008	0.008	
	LNG ^c	-	-	-	-	-	5.05	0.008	0.008	5.05
N ₂ O ^b	HFO/MDO ^b	-	0.031	0.034	0.049	0.049		0.036	0.036	-
	LNG ^c	-	-	-	-	-	0.015	-	-	0.015

SSD: Slow-Speed Diesel, MSD: Medium-Speed Diesel, ST: Steam Turbine, GT: Gas Turbine, HSD: High-Speed Diesel

* PM10 does not include PM converted from sulfur. It is estimated that 2.247% of sulfur in fuels is converted into additional PM10.

References: ^a Billings [personal communication], ^b IMO 2014³⁹, ^c Thomson et al.⁴⁰

2.2.5 Fuel Consumption

Marine fuel consumption presented as brake-specific fuel consumption (BSFC) or specific fuel oil consumption (SFOC) also varies by fuel and engine types. The information is important to estimate the energy use for a trip. Additionally, since SO_x and CO₂ emissions are estimated based on sulfur and carbon balances, respectively, fuel consumption values are used to estimate SO_x and CO₂ emissions. We used SFOC data from the IMO 2014 report³⁹ (Table 10). The fuel consumption values (g fuel/kWh operation) of MGO/MDO were converted into energy consumption (Btu/kWh operation); the same energy consumption values are used for diesel fuels.

Table 10. Specific Fuel Oil Consumption by Engine and Fuel Types (g fuels/kWh operation)³⁹

Main engine	HFO	MGO/MDO	LNG
SSD	195.0	185.0	
MSD	215.0	205.0	
ST	305.0	300.0	
GT	305.0	300.0	
LNG			166.0
Aux engine	HFO	MGO/MDO	
HSD	227.0	217.0	
MSD	227.0	217.0	
LNG			166.0

2.3.6 Trip Characteristics

Various marine vessels are operated to serve different purposes, which incurs different trip profiles. In order to evaluate the WTH emissions of trips, vessel types and corresponding trip characteristics should be defined. Adom et al.³² characterized trips for three vessel types (bulk, container-large, and tanker VLCC [Very Large Crude Carriers]) in different regions (Pacific,

Atlantic, Gulf of Mexico, Great Lakes, and California waters). The trips consist of several segments (hotel, reduced-speed zones [RSZ], cruise), and trip information such as distance, speed, time in mode, load factor, and payload for each segment was characterized.³² In this study, we used the trip information by Adom et al.³² to evaluate the WTH GHG and CAP emissions for each trip. Note that we can select different fuels for each trip segment in GREET, which is useful to manage emission profiles.

3. RESULTS AND DISCUSSION

3.1 Process Performance

The process designs feature an annual production capacity of 50 MM GGE of liquid hydrocarbon fuels and 90% on-stream time (7,884 annual operating hours). The capacity is attained by adjusting the feedstock flowrates. The product yields and distributions are summarized in Table 11. The liquid fuel products include naphtha-, jet-, and marine/diesel-range hydrocarbons. All fuel products are reported in GGE. For Pathway 1, the product distribution is similar for all scenarios, roughly 20% for marine/diesel, 37% for jet, and 43% for naphtha. Note that the current FT process is modeled based on the Anderson-Schulz-Flory (ASF) value of 0.84 and with assumed targeted syngas H₂/CO ratio of 2.1, which gives the maximum yield of the reaction product slate, in terms of GGE.²³ Varying the ASF value will have a direct effect on the product distribution, which in turn will also have a direct impact on the MFSP. Additionally, as the marine fuels typically are distillate and residual bunker fuel, the FT crude hydrocarbon separation process can be easily tailored to meet the desired properties for blending. Moreover, marine biofuels do not need intensive refining, and the production cost attributed to the separation process can be relatively lower.

The liquid fuel products for Pathway 2 also include naphtha-, jet-, and marine/diesel-range hydrocarbons (Table 11). The product distribution for the yellow grease only scenario (YG) is roughly 1% for marine/diesel, 75% for jet, and 24% for naphtha. The product distribution for the case with heavy fuel oil co-feed (YG + HFO) is roughly 20% for marine/diesel, 52% for jet, and 28% for naphtha. It is noteworthy that the hydrocarbon product distribution, including increasing the marine/diesel slate, can be manipulated at the product separation and fractionation step. The current process is modeled with the focus on producing jet fuel that meets the jet fuel specifications (e.g., high flash point and good cold flow properties), and these are accomplished with the hydrocracking and isomerization steps. The current processes can be further optimized for marine fuel-range hydrocarbon production. Additionally, co-feeding yellow grease with heavy oil provides another process parameter for achieving the targeted product distribution, which can be tailored by varying the ratio of the two co-feeding feedstocks.

For Pathway 3, the condensed bio-oil is the only hydrocarbon product (Table 11). Considered as a potential drop-in fuel compatible for use in marine engines, bio-oil is not further upgraded via hydrotreating to transportation fuels (diesel- and naphtha-range blendstocks). Further work is needed to confirm compatibility and to address any potential issues which could be caused by differences in their properties. Substantial capital and operating expenditures are avoided as hydrotreating is a multi-step process involving a stabilizer, a low-temperature hydrotreater, and a high-temperature hydrotreater, and even a hydrocracker, and requiring a substantial amount of hydrogen.²⁰

Table 11. Fuel Production Summary

Fuel Production (MM GGE/yr)	Pathway 1				Pathway 2		Pathway 3
	BTL	GTL	GBTL	CBTL	YG & YG	HFO	FP
Marine/Diesel	10.28	9.94	9.91	10.11	0.45	9.99	50.00*
Jet	17.34	18.38	18.47	18.50	37.67	26.05	--
Naphtha	22.37	21.68	21.62	21.39	11.88	13.96	--
Total	50.00	50.00	50.00	50.00	50.00	50.00	50.00

* Fast pyrolysis bio-oil

3.2 Total Capital Investment

The capital costs for the three pathways are presented in Table 12, Table 13, and Table 14. The capital costs for each plant area are based on data from various sources, including NREL design reports and publications.^{13,17,20,42} The purchased costs for the equipment and installation factors are used to determine the installed equipment cost. The indirect costs (non-manufacturing fixed-capital investment costs) are estimated using factors based on the total direct cost (TDC). The factors used in this study are adopted from Tan et al.⁴² as percentages of total purchased equipment costs (TPEC), TDC, and fixed capital investment (FCI), which is equal to the sum of TDC and total indirect costs. With the calculated total installed cost (TIC) and assumptions for indirect costs and working capital, the FCI and total capital investment (TCI) can be determined. For Pathway 1, the TCI for the four feedstock scenarios increases in the order: GTL (\$422MM) < GBTL (\$455MM) < BTL (\$633MM) < CBTL (\$717MM) (Table 12). CBTL exhibits the highest TCI and is mainly attributed to the requirement of ASU and more expensive of the high-temperature slagging gasifier. BTL and GBTL do not need an ASU to produce pure oxygen for the less expensive low temperature entrained flow gasifier.

Table 12. Summary of Capital Cost for Pathway 1

in MMS	BTL	GTL	GBTL	CBTL
Feedstock Handling*	1.67	--	1.18	2.90
Air Separation Unit	--	--	--	36.84
Gasification	51.59	--	25.59	94.66
Syngas Cleanup & Conditioning	109.52	55.19	53.83	88.75
Fisher-Tropsch synthesis	159.14	147.72	145.36	143.06
Product Separation	5.34	5.56	4.50	4.55
Steam System & Power Generation	31.96	30.53	27.86	39.32
Cooling Tower & Others	5.21	2.68	3.42	3.67
Total Installed Equipment Cost (TIC)	362.75	241.68	260.57	410.86
Total Direct Costs (TDC)	375.77	250.02	269.74	425.58
Total Indirect Costs	225.46	150.01	161.84	255.35
Fixed Capital Investment (FCI)	601.24	400.03	431.59	680.92
Land Purchase Costs	1.85	1.85	1.85	1.85
Working Capital	30.06	20.00	21.58	34.05
Total Capital Investment (TCI)	633.15	421.88	455.01	716.82

*Feedstock Handling not included in this calculation

The capital costs for each plant area for Pathway 2 are based on data from the recent study by Tao et al.¹⁷ Fuel upgrading area, which includes hydrogenation, propane cleave, and decarboxylation, as well as hydrocracking and hydroisomerization, exhibits the highest capital expenditure for both scenarios for Pathway 2. The total installed costs for the case with yellow grease only (YG) and the case with yellow grease and heavy fuel oil co-feed (YG + HFO) are similar, at \$130.73 MM and \$134.15 MM, respectively.

The capital costs estimation for Pathway 3 were performed based on published data.²⁰ The fast pyrolysis reactor system includes pyrolyzer (circulating bed type), quench, product separation system, and auxiliaries. Costs of the bio-oil product filtration, char combustion system and utility system (tanks, cooling tower, and plant air) were not included in the pyrolyzer system. The capital cost evaluation results are summarized in Table 14. Installed equipment of the fast pyrolysis reactor system is approximately 90% of the total installed equipment cost (TIC). Installed equipment cost of the bio-oil filtration is about 5% of the TIC. In addition, the installed equipment costs for char combustor and utility system were less than 5% of the TIC. Total direct cost (TDC), total indirect cost, fixed capital investment, land, working capital, and total capital investment were estimated based on the TIC of MM\$137.83 and are also shown in Table 14. The assumptions of TDC, FCI, and TCI estimation were consistent with other pathways in this study.

Table 13. Summary of Capital Cost for Pathway 2

in MMS	YG	YG + HFO
Fuel Upgrading	118.20	120.40
Product Separation	3.96	4.14
Storage	6.24	7.27
Utilities	2.33	2.33
Total Installed Equipment Cost (TIC)	130.73	134.15
Total Direct Costs (TDC)	152.11	155.94
Total Indirect Costs	91.27	93.57
Fixed Capital Investment (FCI)	243.38	249.51
Land Purchase Costs	1.85	1.85
Working Capital	12.17	12.48
Total Capital Investment	257.40	263.83

Table 14. Summary of Capital Cost for Pathway 3

In MMS	FP
Fast pyrolysis reactor system (Including pyrolyzer, quench, product separation, and auxiliaries)	122.71
Bio-oil filters	6.49
Compressor for char combustor	3.2
Utility	5.43

Total Installed Equipment Cost (TIC)	137.83
Total Direct Costs (TDC)	147.13
Total Indirect Costs	88.28
Fixed Capital Investment (FCI)	235.41
Land Purchase Costs	1.71
Working Capital	11.77
Total Capital Investment (TCI)	248.89

3.3 Operation Costs and Co-product Credits

The operating costs are presented in Table 15 for Pathway 1, Table 16 for Pathway 2, and Figure 6 for Pathway 3. Operating costs include variable and fixed operating costs. Variable operating costs, including the annualized costs for catalysts, olivine, and waste disposal are determined based on raw materials, waste-handling charges, and by-product credits incurred only during the process operation. Fixed operating costs are generally incurred in full whether the plant is producing at full capacity. These costs include labor and various overhead items. Many of the assumptions on fixed operating costs follow earlier publications.^{20,26,29} General overhead equals 90% of total salaries, maintenance equals 3% of FCI, and insurance and taxes equal 0.7% FCI. For Pathway 1, the fixed operating costs range from \$0.42/GGE (GTL) to \$0.62/GGE (CBTL) (Table 15). Similarly, the total operating costs vary from \$0.84/GGE (GTL) to \$1.99/GGE (CBTL). For GTL, the co-product credits are largely attributed to excess hydrogen (owing to the inherent high hydrogen-to-carbon ratio of natural gas). Conversely, hydrogen import is required for the CBTL case.

Table 15. Annual Operating Costs for Pathway 1

\$/GGE	BTL	GTL	GBTL	CBTL
Biomass Feedstock	1.00	--	0.27	0.32
Natural Gas	--	1.97	1.14	--
Coal	--	--	--	0.14
Catalysts	0.15	0.10	0.09	0.14
Olivine	0.01	--	0.003	--
Makeup Hydrogen	--	--	--	0.90
Other Raw Materials	0.04	0.02	0.02	0.26
Waste Disposal	0.03	2.0E-04	0.01	0.03
Electricity	--	--	0.01	--
Co-product credits	-0.45	-1.66	-0.80	-0.43
Total Variable Operating Cost	0.79	0.43	0.74	1.36
Fixed Operating Costs	0.56	0.42	0.44	0.62
Total Operating Costs	1.35	0.84	1.18	1.99

The annual operating costs for Pathway 2 are presented in Table 16. The total operating costs for the case with yellow grease only (YG) and the case with yellow grease and heavy fuel oil co-feed (YG + HFO) are \$3.00/GGE and \$2.48/GGE, respectively. The feedstock costs represent the most significant contribution (~82%) to the operating costs. The lower operating cost for the HFO co-

feed case is largely attributed to the lower HFO cost (\$0.56/kg vs. \$0.61/kg for the yellow grease) and the lower hydrogen cost.

Table 16. Annual Operating Costs for Pathway 2

\$/GGE	YG	YG + HFO
Yellow Grease	2.47	1.05
Heavy Fuel Oil	--	0.97
Hydrogenation catalyst	0.12	0.11
Isomerization/cracking catalyst	0.02	0.02
Hydrogen	0.14	0.09
Waste Disposal	0.03	0.01
Other Chemicals	0.09	0.08
Co-Product Credit	-0.01	-0.01
Total Variable Operating Cost	2.85	2.33
Fixed Operating Costs	0.15	0.15
Total Operating Costs	3.00	2.48

The total operating cost for Pathway 3 is \$1.34/GGE, with the distribution shown in Figure 5. Variable costs (feedstock, chemical, utilities, and waste disposal) are about 80% of the total operating cost, while fixed costs (labors) are about 20% of the total operating cost. Woody biomass feedstock is the most expensive variable cost at \$1.00/GGE or 75% of the total operating cost.

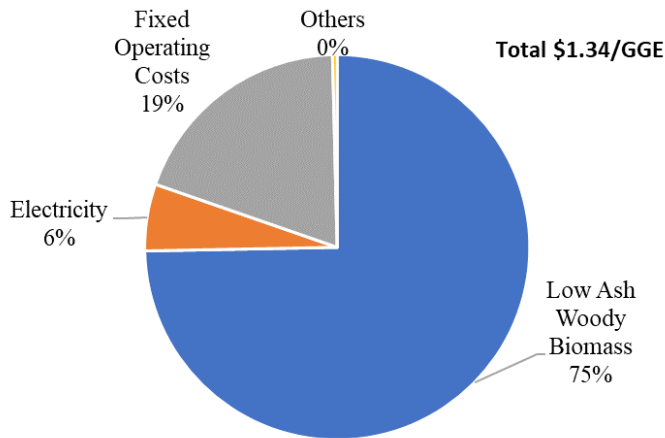


Figure 5. Operation cost distribution for Pathway 3.

3.4 Minimum Fuel Selling Price

The MFSPs are obtained by performing the discounted cash flow analysis—via iterating the selling cost of fuel until the net present value of the project is zero. This analysis requires that the discount rate, depreciation method, income tax rates, plant life, and construction start-up duration be

specified. The fuel products (naphtha, jet, and marine/diesel blendstocks) are combined and referred to as a single-fuel product for simplicity. All MFSP calculations are performed and reported on a combined product basis. The cost contributions to the MFSP (Figure 6) are divided into capital charges and taxes, operating costs and co-product credits, and feedstock costs (biomass, natural gas, and coal). The MFSPs for the evaluated scenarios for Pathway 1 increase in the order: \$1.95/GGE (GTL) < \$2.37/GGE (GBTL) < \$2.99/GGE (BTL) < \$3.79/GGE (CBTL).

MFSPs for the two feed scenarios for Pathway 2 are determined to be \$3.50/GGE for the case with yellow grease only (YG) and \$2.95/GGE for the case with heavy oil co-feed (YG + HFO). Feedstock costs respectively contribute about 71% and 68% to the MFSPs. Under the nth plant assumptions, the MFSP for the fast pyrolysis marine bio-oil (Pathway 3) is determined to be \$1.95/GGE. Like Pathway 2, feedstock cost is the most significant cost contributor to the MFSP, and it is over 50% of the MFSP. Capital related costs (capital depreciation, income tax, and return on investment) and operating costs (variable costs and labors) are about 32% and 17% of the MFSP, respectively.

GTL and FP show the lowest MFSPs (\$1.95/GGE), attributing to a combination of favorable yields and lower operating costs for the former, and high carbon conversion efficiency (47%)²⁰ for the later. Conversely, CBTL has the highest MFSP (\$3.99/GGE) as a result of the higher capital expenditure associated with the air separation unit and the high-temperature slagging gasifier, as well as hydrogen cost. GBTL and YG+HO exhibit relatively favorable MFSPs. Co-feeding biomass with the fossil feedstock (NG or HFO) is an practical synergistic approach to improve liquid fuel yields while simultaneously lowering greenhouse gas (GHG) emissions.

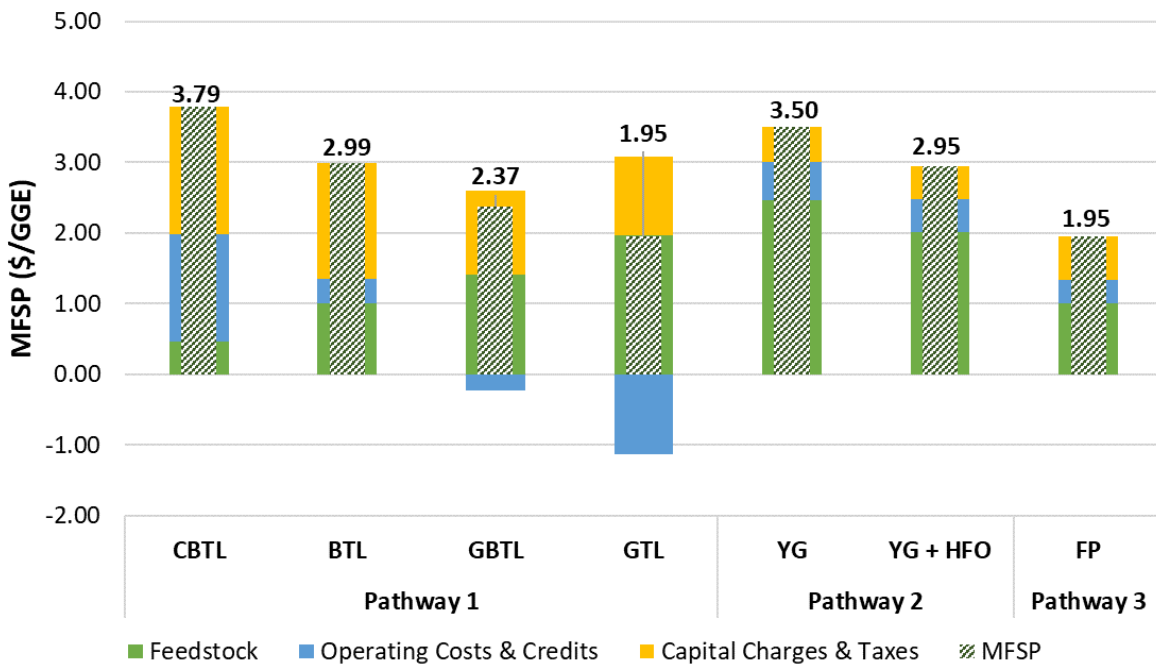


Figure 6. TEA result summary.

3.5 Assessment of Economic Viability of Biofuels for Marine Propulsion

The choice of adoption of which option for ships to comply with the low sulfur regulations is primarily dependent on the vessel owners' economic decisions. Fuel costs already represent more than 50 percent of total operating expenses before complying with the IMO 2020, making shippers difficult to absorb any additional operating expenses and stay operational.⁴³ The current TEA evaluations provide an important baseline analysis for establishing the feasibility of biofuel adoption for operating vessels. Figure 7 shows the rough projection of maximum biofuel prices, as a function of biofuel blending ratio, determined using the price premium for 0.5% sulfur bunker fuel over the current global standard of 3.5%, roughly \$30/metric ton.⁴⁴ The isolines are for three HFO price scenarios: \$1.50, \$2.00, and \$2.50 per gallon. HFO accounts for more than 75% of the total marine shipping consumption⁵ and is used for baseline comparison. The low sulfur (0.5%) fuel price is the sum of the high sulfur (3.5%) fuel price and the fuel premium (about \$0.11/gal). For example, if the high sulfur HFO price is \$2.50/gal, the low sulfur HFO price becomes \$2.61/gal. The low sulfur HFO prices would be the maximum threshold that shipowners are willing to pay for the biofuels for a one-to-one replacement; namely, the maximum acceptable biofuel prices would be the same as the low sulfur fuel oil prices. However, as the biofuel blending ratio increases, the biofuel price is allowed to increase, and still meet the maximum price limit. For example, the MFSP for GBTL is \$2.37/gal, and if the HFO (3.5% S) is \$2.00/gal or \$2.11/gal for the 0.5% S fuel, up to about 50% of the GBTL biofuel blendstock can be blended with the high sulfur fossil HFO and still meet the \$2.11/gal limit. Figure 7 also reveals the significant market penetration potential for marine biofuels. With annual total marine fuel consumption of 330 million metric tons, even a five percent biofuel blending will translate to nearly four billion gallons of biofuel market. Here we assume biofuels contain virtually no sulfur and can be near linearly blended with the sulfur components.

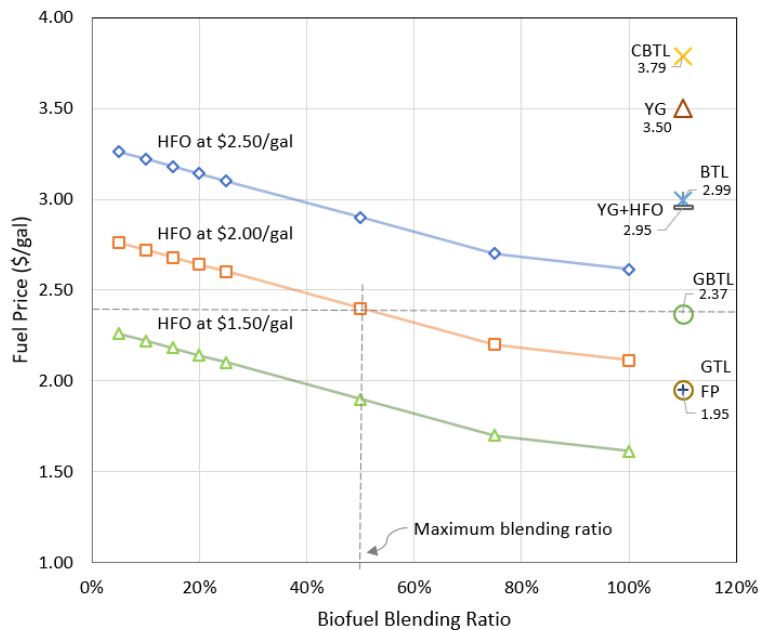


Figure 7. Estimated maximum allowable biofuel price for blending with conventional heavy oil (3.50% m/m S content) to achieve the 0.50% m/m sulfur target. Biofuel price estimates are based on a \$30/metric ton premium of 0.50% over 3.50% m/m.

3.6 Life Cycle GHG and CAP Emissions

Figure 8 presents life-cycle GHG emissions of 19 cases, which include feedstock production and transportation (feedstock), fuel production and fuel transportation (conversion), and fuel use (combustion); for biomass-derived fuels, biogenic carbon uptake emissions are considered as emission credits. The sum of these stages becomes WTH GHG emissions. The functional unit is MJ of marine fuel produced and utilized, and the values in Figure 8 present relative differences compared to the baseline HFO (2.7% sulfur). All diesel results are based on emission factors of MSD with NO_x regulations for Tier 3, while results can be generated using emission factors of other engine types.

First, WTH GHG emissions of the baseline HFO (2.7% sulfur) and MGO (1.0% sulfur) are estimated at 95.5 and 88.9 gCO_{2e}/MJ, respectively, and combustion emissions take around 85% of total WTH GHG emissions. Low sulfur petroleum-derived marine fuels have slightly higher WTH GHG emissions due to additional hydrogen inputs. HFO (1.0% sulfur) and MGO (1.0% sulfur) have WTH GHG emissions of 97.3 and 89.7 gCO_{2e}/MJ, respectively, which are 1.9% and 0.9% higher compared to those of HFO (2.7% sulfur) and MGO (1.0% sulfur).

Fuel combustion emissions are dependent on carbon contents, which do not show significant variations (except for pyrolysis oil with very low heating value [Table 5]); the main differences in WTH emissions are from other factors such as emissions during fuel production, biogenic carbon contents, and CH₄ leakages. For NG uses, Figure 8c shows corresponding pathways (LNG and FTD using NG) involve significantly higher CH₄ emissions compared to other pathways. Due to CH₄'s high GWP, CH₄ emissions magnify the overall WTH GHG emissions. In particular, LNG involves significantly high CH₄ emissions throughout its supply chain. While WTH CO₂ emissions of the LNG pathway is estimated at 65.4 g/MJ, which is 28.0% lower than HFO (2.7% sulfur), WTH GHG emissions are 94.0 gCO_{2e}/MJ, similar to those of HFO (2.7% sulfur) due to contribution of CH₄ emissions (Figure 8d); only 0.916 g CH₄/MJ contributes 29.2% of its WTH GHG emissions. In particular, CH₄ slip during downstream combustion significantly influences LNG's WTH GHG emissions.⁴⁰

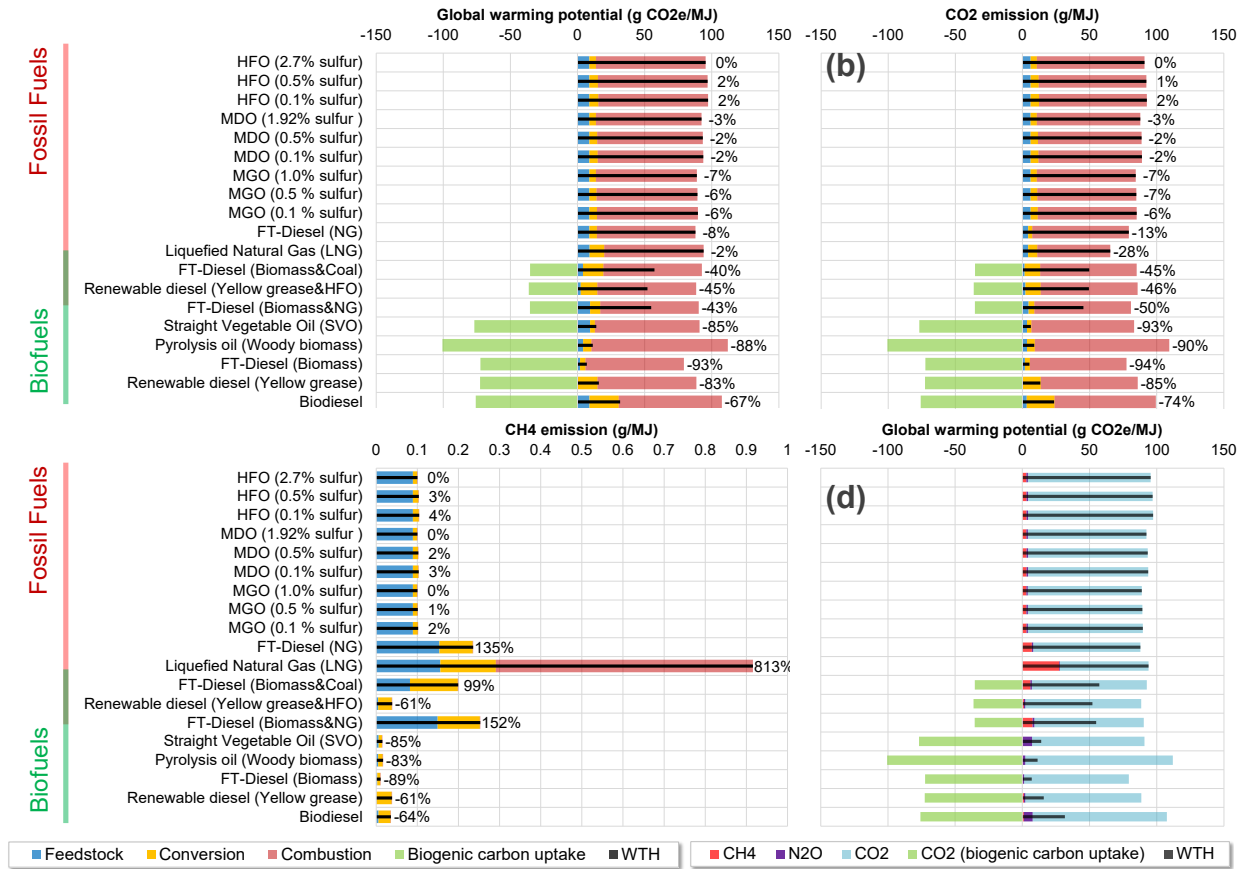


Figure 8. WTH GHG emissions of marine fuel pathways. The numbers present emissions relative to baseline (HFO 2.7% sulfur) emissions. MSD engines. MSD engines under the IMO emission regulation tier of three are assumed to be used.

Fuels from biomass have significantly lower WTH GHG emissions, mainly due to their biogenic carbon credits. Depending on the share of biogenic carbon, emission reduction rates vary. For example, marine fuel production using both fossil and biomass feedstocks (50% and 50% by weight), WTH GHG emission reductions in GHG emissions compared to HFO (2.7% sulfur) are estimated at 40–45%. Biofuels produced from 100% biomass have much higher reductions in GHG emissions (67–93%).

Figure 9 presents major WTH CAP emissions (SO_x , NO_x , $\text{PM}^{2.5}$, and CO), which shows that the combustion stage is dominant for CAP emissions. SO_x emissions are dependent on sulfur contents in marine fuels; thus, desulfurization reduces life-cycle SO_x emissions significantly (Figure 9a) while slightly increases WTH GHG emissions (Figure 8a). The baseline HFO (2.7% sulfur) has WTH SO_x emissions of 1.35 g/MJ, and low sulfur HFOs with 0.5% and 0.1% have WTH SO_x emissions of 0.26 and 0.06 g/MJ, respectively, which are 81% and 95% lower than the baseline HFO, respectively. MGO (1.0% sulfur) has SO_x emissions of 0.47 g/MJ, and this can be reduced to 0.24 and 0.06 g/MJ through desulfurization to 0.5% and 0.1%, respectively. Biomass-derived fuels are mostly free of sulfur leading to significant reductions in SO_x emissions (97–100%) except for renewable diesel from yellow grease with HFO inputs (1.51% sulfur) because of sulfur from HFO. PM emissions mainly consist of base PM and PM derived from sulfur. For NO_x and CO

emissions, all fuels are within a relatively narrow boundary, except for LNG. LNG shows 25% lower NOx emissions and 28% higher CO emissions. Note that the results may vary depending on the types of engines and emission regulation tiers.

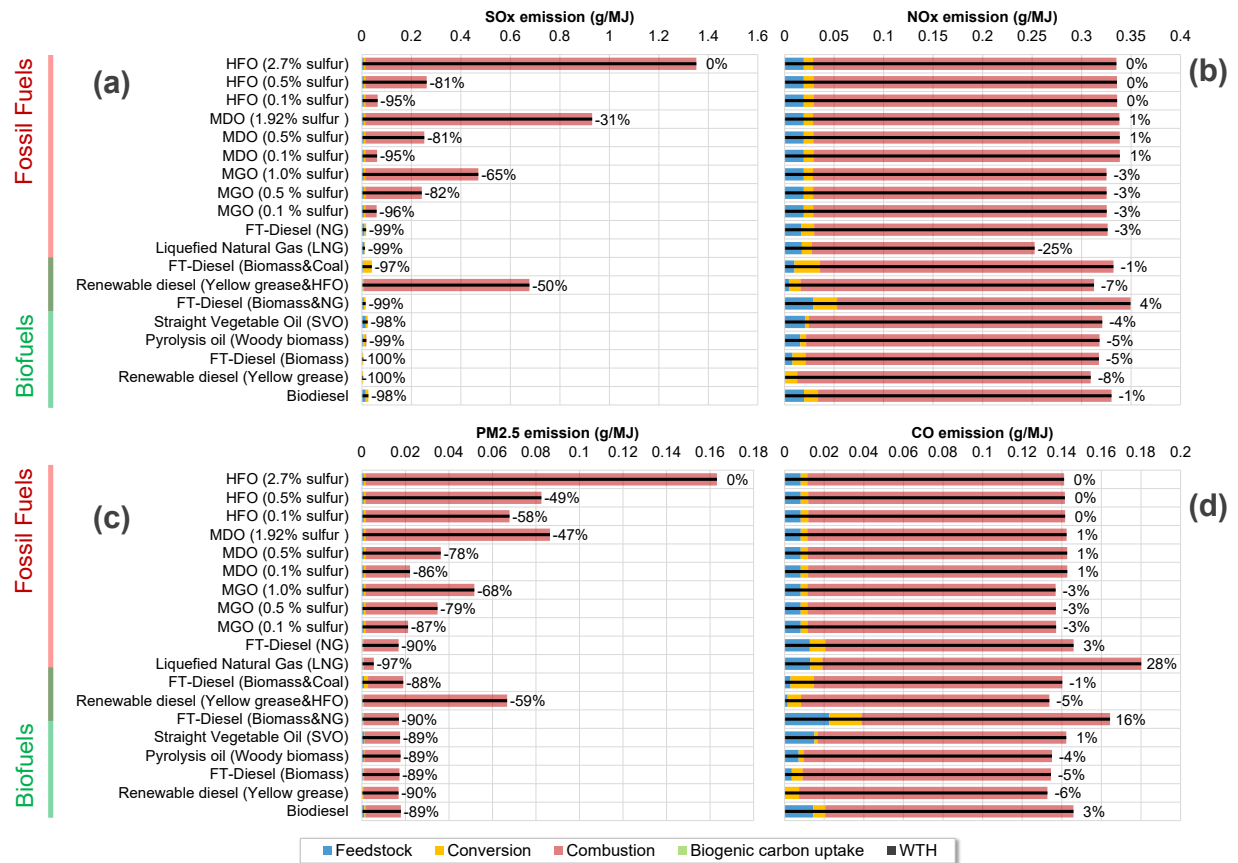


Figure 9. WTH CAP emissions. The numbers present emissions relative to baseline (HFO 2.7% sulfur) emissions. MSD engines under the IMO emission regulation tier of three are assumed to be used.

WTH GHG emissions of trips vary by the types of marine vessels and corresponding trip characteristics as well as fuel types (Figure 10). Here, domestic and international trips of three types of marine vessels in the Pacific using two different fuels (FT-marine diesel [biomass] and HFO [0.5% sulfur]) are presented as an example. More detailed analyses are available using GREET by setting trip parameters and fuel types for each trip segment. Due to its low carbon intensity (g CO₂/MJ), FT-diesel (biomass) generates much lower GHG emissions for the same trip conditions as expected. However, trip characteristics result in significant differences in WTH GHG emission results, mainly due to the differences in fuel consumption (operation hours). When it comes to million MT-km results, tanker VLCC emissions become smaller, mainly due to its high payload and longer distance compared to others.

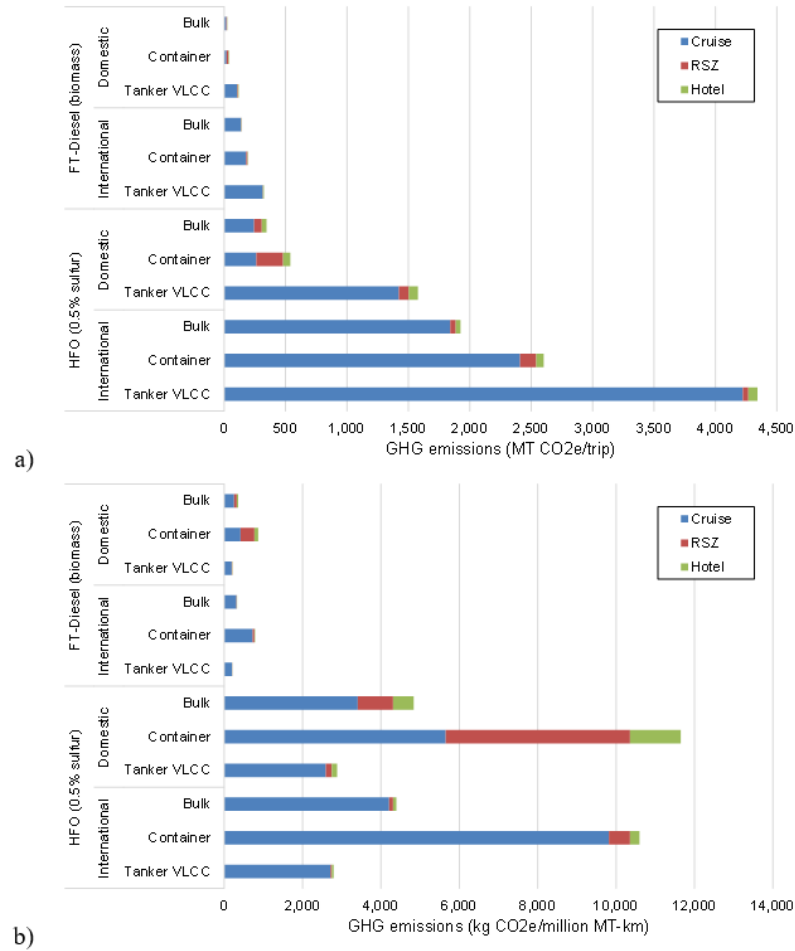


Figure 10. WTH GHG emissions (per trip and million MT-km), for example trip conditions using FT-marine diesel (biomass) and HFO (0.5% sulfur). Three marine vessel types for domestic and international trips in the Pacific are presented.

Variations in WTH CAP emissions depending on vessel types and trip characteristics are presented in Figure 11.



Figure 11. WTH GHG and CAP emissions, for example, trip conditions using FT-marine diesel. These are for three marine vessel types (bulk, tanker, and container) for two trip conditions in the Pacific (domestic and international). The numbers presented right-hand side of each chart represent total emissions during the trip.

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Author Contributions

ECDT, LT, and PAM conducted TEA of Pathways 1, 2, and 3, respectively. TRH and UL performed LCA. ECDT and TRH designed the TEA and LCA study, respectively, and wrote the manuscript with input from all co-authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- (1) Wan, Z.; el Makhoulfi, A.; Chen, Y.; Tang, J. Decarbonizing the International Shipping Industry: Solutions and Policy Recommendations. *Mar. Pollut. Bull.* **2018**, *126*, 428–435. <https://doi.org/10.1016/j.marpolbul.2017.11.064>.
- (2) UNCTAD. *Review of Maritime Transport 2018*; United Nations Conference on Trade and Development, 2018.
- (3) Tanzer, S. E.; Posada, J.; Geraedts, S.; Ramírez, A. Lignocellulosic Marine Biofuel: Technoeconomic and Environmental Assessment for Production in Brazil and Sweden. *J. Clean. Prod.* **2019**, *239*, 117845. <https://doi.org/10.1016/j.jclepro.2019.117845>.
- (4) Mohd Noor, C. W.; Noor, M. M.; Mamat, R. Biodiesel as Alternative Fuel for Marine Diesel Engine Applications: A Review. *Renew. Sustain. Energy Rev.* **2018**, *94*, 127–142. <https://doi.org/10.1016/j.rser.2018.05.031>.
- (5) Kass, M. D.; Abdullah, Z.; Bidy, M. J.; Drennan, C.; Haq, Z.; Hawkins, T.; Jones, S.; Holliday, J.; Longman, D. E.; Menter, S.; et al. *Understanding the Opportunities of Biofuels for Marine Shipping*; ORNL/TM--2018/1080, 1490575; 2018; p ORNL/TM--2018/1080, 1490575. <https://doi.org/10.2172/1490575>.
- (6) Squirrell, D. A Multi-Fuel Future: The Impact of the IMO Sulphur Cap, 2017.
- (7) Pearce, F. How 16 ships create as much pollution as all the cars in the world | Daily Mail Online <https://www.dailymail.co.uk/sciencetech/article-1229857/How-16-ships-create-pollution-cars-world.html> (accessed Apr 23, 2019).
- (8) Sofiev, M.; Winebrake, J. J.; Johansson, L.; Carr, E. W.; Prank, M.; Soares, J.; Vira, J.; Kouznetsov, R.; Jalkanen, J.-P.; Corbett, J. J. Cleaner Fuels for Ships Provide Public Health

- Benefits with Climate Tradeoffs. *Nat. Commun.* **2018**, *9* (1), 406. <https://doi.org/10.1038/s41467-017-02774-9>.
- (9) Olmer, N.; Comer, B.; Roy, B.; Mao, X.; Rutherford, D. Greenhouse Gas Emissions from Global Shipping, 2013-2015. International Council on Clean Transportation 2017.
 - (10) Birch, C.; Grati, H.; Barrow, K.; Sayal, S.; Pravettoni, E.; Jew, S. Refining and Shipping Industries Will Scramble to Meet the 2020 IMO Bunker Fuel Rules. IHS Markit August 4, 2017.
 - (11) Chu Van, T.; Ramirez, J.; Rainey, T.; Ristovski, Z.; Brown, R. J. Global Impacts of Recent IMO Regulations on Marine Fuel Oil Refining Processes and Ship Emissions. *Transp. Res. Part Transp. Environ.* **2019**, *70*, 123–134. <https://doi.org/10.1016/j.trd.2019.04.001>.
 - (12) Tan, E. C.; Tao, L. *Economic Analysis of Renewable Fuels for Marine Propulsion*; NREL/TP-5100-74678, 1566063; 2019; p NREL/TP-5100-74678, 1566063. <https://doi.org/10.2172/1566063>.
 - (13) Zhang, Y.; Sahir, A. H.; Tan, E. C. D.; Talmadge, M. S.; Davis, R.; Bidy, M. J.; Tao, L. Economic and Environmental Potentials for Natural Gas to Enhance Biomass-to-Liquid Fuels Technologies. *Green Chem.* **2018**. <https://doi.org/10.1039/C8GC01257A>.
 - (14) Dutta, A.; Hensley, J.; Bain, R.; Magrini, K.; Tan, E. C. D.; Apanel, G.; Barton, D.; Groenendijk, P.; Ferrari, D.; Jablonski, W.; et al. Technoeconomic Analysis for the Production of Mixed Alcohols via Indirect Gasification of Biomass Based on Demonstration Experiments. *Ind. Eng. Chem. Res.* **2014**, *53* (30), 12149–12159. <https://doi.org/10.1021/ie402045q>.
 - (15) Dutta, A.; Bain, R. L.; Bidy, M. J. Techno-Economics of the Production of Mixed Alcohols from Lignocellulosic Biomass via High-Temperature Gasification. *Environ. Prog. Sustain. Energy* **2010**, *29* (2), 163–174. <https://doi.org/10.1002/ep.10445>.
 - (16) AspenTech. *Aspen Plus IGCC Model*; Aspen Technology, Inc.: Bedford, MA, 2016.
 - (17) Tao, L.; Milbrandt, A.; Zhang, Y.; Wang, W.-C. Techno-Economic and Resource Analysis of Hydroprocessed Renewable Jet Fuel. *Biotechnol. Biofuels* **2017**, *10* (1), 261. <https://doi.org/10.1186/s13068-017-0945-3>.
 - (18) Marker, T. L.; Ellis, G. D.; Gosling, C. D. Integrated Process for Oil Extraction and Production of Diesel Fuel from Biorenewable Feedstocks. US8003834B2, August 23, 2011.
 - (19) Abhari, R.; Tomlinson, L.; Havlik, P.; Jannasch, N. Process for Co-Producing Jet Fuel and LPG from Renewable Sources. US7846323B2, December 7, 2010.
 - (20) Jones, S. B.; Meyer, P. A.; Snowden-Swan, L. J.; Padmaperuma, A. B.; Tan, E.; Dutta, A.; Jacobson, J.; Cafferty, K. *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-Oil Pathway*; PNNL--23053, NREL/TP--5100-61178, 1115839; 2013; p PNNL--23053, NREL/TP--5100-61178, 1115839. <https://doi.org/10.2172/1115839>.
 - (21) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. *Energy Fuels* **2010**, *24* (2), 1380–1388. <https://doi.org/10.1021/ef901107f>.
 - (22) Tan, E. C. D. An Integrated Sustainability Evaluation of High-octane Gasoline Production from Lignocellulosic Biomass. *Biofuels Bioprod. Biorefining* **2019**, bbb.2045. <https://doi.org/10.1002/bbb.2045>.
 - (23) Tan, E. C. D.; Snowden-Swan, L. J.; Talmadge, M.; Dutta, A.; Jones, S.; Ramasamy, K. K.; Gray, M.; Dagle, R.; Padmaperuma, A.; Gerber, M.; et al. Comparative Techno-Economic Analysis and Process Design for Indirect Liquefaction Pathways to Distillate-Range Fuels

- via Biomass-Derived Oxygenated Intermediates Upgrading. *Biofuels Bioprod. Biorefining* **2017**, *11* (1), 41–66. <https://doi.org/10.1002/bbb.1710>.
- (24) GREET. *Argonne National Laboratory Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Computer Model (2016)*; 2016.
- (25) Dupuis, D. P.; Grim, R. G.; Nelson, E.; Tan, E. C. D.; Ruddy, D. A.; Hernandez, S.; Westover, T.; Hensley, J. E.; Carpenter, D. High-Octane Gasoline from Biomass: Experimental, Economic, and Environmental Assessment. *Appl. Energy* **2019**, *241*, 25–33. <https://doi.org/10.1016/j.apenergy.2019.02.064>.
- (26) Tan, E. C. D.; Ruddy, D.; Nash, C.; Dupuis, D.; Dutta, A.; Hartley, D.; Cai, H. *High-Octane Gasoline from Lignocellulosic Biomass via Syngas and Methanol/Dimethyl Ether Intermediates: 2018 State of Technology and Future Research*; Technical Report NREL/TP-5100-7195 7; National Renewable Energy Laboratory: Golden, CO, 2018.
- (27) MYPP. Department of Energy’s Bioenergy Technologies Office Multi-Year Program Plan: March 2016 <https://energy.gov/eere/bioenergy/downloads/bioenergy-technologies-office-multi-year-program-plan-march-2016> (accessed Nov 13, 2017).
- (28) EIA. Average Sales Price of Coal by State and Coal Rank <https://www.eia.gov/coal/annual/pdf/table31.pdf> (accessed Apr 26, 2019).
- (29) Davis, R.; Tao, L.; Tan, E. C. D.; Biddu, M. J.; Beckham, G. T.; Scarlata, C.; Jacobson, J.; Cafferty, K.; Ross, J.; Lukas, J.; et al. *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons*; NREL/TP-5100-60223, 1107470; 2013; p NREL/TP-5100-60223, 1107470. <https://doi.org/10.2172/1107470>.
- (30) EIA. U.S. Residual Fuel Oil Prices by Sales Type https://www.eia.gov/dnav/pet/pet_pri_resid_dcunus_a.htm (accessed Apr 26, 2019).
- (31) Wang, M.; Elgowainy, A.; Benavides, P. T.; Burnham, A.; Cai, H.; Dai, Q.; Hawkins, T. R.; Kelly, J. C.; Kwon, H.; Lee, D.-Y.; et al. *Summary of Expansions and Updates in GREET® 2018*; ANL-18/23, 1483843; 2018; p ANL-18/23, 1483843. <https://doi.org/10.2172/1483843>.
- (32) Adom, F.; Dunn, J. B.; Elgowainy, A.; Han, J.; Wang, M. Life Cycle Analysis of Conventional and Alternative Marine Fuels in GREET. *Energy Syst. Division Argonne Natl. Lab. Argonne IL* **2013**, 58.
- (33) Elgowainy, A.; Han, J.; Cai, H.; Wang, M.; Forman, G. S.; DiVita, V. B. Energy Efficiency and Greenhouse Gas Emission Intensity of Petroleum Products at U.S. Refineries. *Environ. Sci. Technol.* **2014**, *48* (13), 7612–7624. <https://doi.org/10.1021/es5010347>.
- (34) Forman, G. S.; Divita, V. B.; Han, J.; Cai, H.; Elgowainy, A.; Wang, M. U.S. Refinery Efficiency: Impacts Analysis and Implications for Fuel Carbon Policy Implementation. *Environ. Sci. Technol.* **2014**, *48* (13), 7625–7633. <https://doi.org/10.1021/es501035a>.
- (35) Burnham, A.; Han, J.; Clark, C. E.; Wang, M.; Dunn, J. B.; Palou-Rivera, I. Life-Cycle Greenhouse Gas Emissions of Shale Gas, Natural Gas, Coal, and Petroleum. *Environ. Sci. Technol.* **2012**, *46* (2), 619–627. <https://doi.org/10.1021/es201942m>.
- (36) Cai, H.; Burnham, A.; Chen, R.; Wang, M. Wells to Wheels: Environmental Implications of Natural Gas as a Transportation Fuel. *Energy Policy* **2017**, *109*, 565–578. <https://doi.org/10.1016/j.enpol.2017.07.041>.
- (37) IPCC. International Panel on Climate Change (IPCC) Fifth Assessment Report - Impacts, Adaptation and Vulnerability <http://www.ipcc.ch/report/ar5/wg2/> (accessed Apr 16, 2017).
- (38) McKetta Jr, J. J. *Petroleum Processing Handbook*; CRC press, 1992.

- (39) IMO. Third IMO Greenhouse Gas Study 2014. **2014**.
- (40) Thomson, H.; Corbett, J. J.; Winebrake, J. J. Natural Gas as a Marine Fuel. *Energy Policy* **2015**, *87*, 153–167. <https://doi.org/10.1016/j.enpol.2015.08.027>.
- (41) EPA. *Regulatory Impact Analysis: Control of Emissions of Air Pollution from Category 3 Marine Diesel Engines*; US Environmental Protection Agency (EPA) USA, 2009.
- (42) Tan, E. C.; Talmadge, M.; Dutta, A.; Hensley, J.; Snowden-Swan, L. J.; Humbird, D.; Schaidle, J.; Bidy, M. Conceptual Process Design and Economics for the Production of High-Octane Gasoline Blendstock via Indirect Liquefaction of Biomass through Methanol/Dimethyl Ether Intermediates. *Biofuels Bioprod. Biorefining* *10* (1), 17–35. <https://doi.org/10.1002/bbb.1611>.
- (43) IHS Markit. IMO 2020: What Every Shipper Needs to Know. March 2019.
- (44) Molloy, N. *The IMO's 2020 Global Sulfur Cap: What a 2020 Sulfur-Constrained World Means for Shipping Lines, Refiners and Bunker Suppliers*; Shipping Special Report; S&P Global Platts, 2016.