Exergy efficiency of marine biofuel production from residual lignocellulosic biomass using thermochemical conversion technologies

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ABSTRACT

Current restrictions on the sulfur content and greenhouse gas emissions of marine fuels represent a challenge for the maritime shipping industry and an opportunity for alternative fuels in the transition to a low-carbon economy. This work presents an integrated assessment model to compare the exergy efficiency of marine biofuel blendstock supply chains, considering seven agroforestry residues feedstocks and thermochemical technologies (e.g., *Hydrothermal liquefaction, HTL, Fast pyrolysis, FP, and Gasification with Fischer-Tropsch synthesis, GFT*). The biorefineries were modeled for a scale of 500 tonnes per day of biofuel production, with electricity and heat cogeneration. The results were used to rank the marine systems through a trade-off linking the exergy efficiency and the irreversibilities of the pathways. In particular, HTL and GFT systems have the highest biofuel yields. Thus, when wheat straw was used as an input in these configurations, they presented the highest exergetic efficiency and, consequently, the lowest destructed exergy rate of the feedstock-technology combinations.

KEYWORDS

Exergy analysis, Marine fuel, Lignocellulosic feedstock, Thermochemical conversion technologies

INTRODUCTION

According to the International Maritime Organization (IMO), a restriction of the maximum sulfur content (from 3.5 wt% to 0.5 wt%, percent weight) in marine fuel will be achieved from 2020 to 2025. The IMO also estimated a 40% carbon intensity reduction of shipping, relative to 2008 levels, by 2030 and 70% by 2050. Furthermore, IMO regulations on energy efficiency support the demand for greener and cleaner shipping focus on emits less air pollution (reducing greenhouse gas emissions, GHG) as a result of increasingly becoming energy-efficient systems [1]. Hence, it is expected to consolidate a sustainable way to transport commodities and goods.

Almost all large ships use residual fuels (heavy fuel oil - HFO) as their primary fuel. Distillate fuels such as marine diesel oil (MDO) and marine gasoil (MGO) are used by small ships and in some auxiliary engines onboard ships. A small number of ships are using LNG as their primary fuel [2]. For instance, the global demand for marine fuel is mainly met by fuel oil (76%), while gasoil only represents 24% of the market in 2017, which was equivalent to 271,414 thousand tonnes [3]. In this context, the marine industry is facing several challenges related to emission regulations and energy efficiency targets.

Therefore, a new area of research is identifying an alternative to marine residual fuels. This fact has increased interest in alternative fuel options, such as liquid natural gas and biofuels. For example, the potential for blends, especially bio-oil and bio-crude, are promising scenarios, where requirements for cetane number, oxygen, aromaticity, and other properties are much less rigorous than conventional marine fuels. Thus, biofuels offer potential synergistic benefits when blended with HFO by reducing sulfur content, improving overall lubricity, and lower ash and emission profiles, especially for particular matters and SOx. As renewable fuels, they also offer the potential to reduce life-cycle CO₂ for marine operations [4].

The viability of a lignocellulosic marine biofuel depends on the characteristics and availability of the biomass feedstock, as well as the performance of the raw material in the specific biofuel conversion process. Research on drop-in marine biofuels has primarily focused on blending with traditional marine diesel [5] and marine engine testing [6] or overall comparisons taking into account the entire supply chain from field to ship [7]. In particular, a comparison of many lignocellulosic marine biofuel options for use as drop-in blendstock with marine HFO [8]. The referred study conducted a systematic screening of the possible economic and environmental performance of 33 supply chains producing lignocellulosic biofuels. In recent years, several authors have studied the potential of improving the efficiency of a ship and marine fuel system (by recovering the waste heat from the diesel engines or maximizing the power output of the system).

More specifically, Koroglu and Sogut [9] carried out a conventional and advanced exergy analysis that is applied to a marine steam power plant. The results showed that the highest exergy destruction is within the boiler due to chemical reactions. Yao et al. [10] assessed marine high-powered, medium-speed diesel engines using both energy balance and exergy analysis. The authors found that about 25% of the total energy is lost through exhaust heat and 36% during the combustion process. In the case of cruise ships, Baldi et al. [11] attempted to optimize the load allocation among the different engines of the same case study, including considerations related to the efficiency of the heat generation on board.

However, the complexity of the maritime shipping sector offers an opportunity from an energy systems perspective to identify potential areas for improvement, as well as to categorize the minimization of irreversibilities sources. It has become crucial to estimate an optimized design of the most promising system.

In this work, the potential of biofuels and marine blends was assessed from the exergetic point of view. The analysis covers seven agroforestry residues used as raw material and their conversion through three thermochemical biofuel production routes, namely hydrothermal liquefaction with hydrodeoxygenation (HTL), fast pyrolysis with hydrodeoxygenation (FPH), and gasification with Fischer-Tropsch synthesis (GFT). Thus, a technical performance assessment of lignocellulosic marine biofuel systems using the exergy concept as an indicator was carried out, which could be relevant and support the decision-making process regarding further research on low-carbon, low-sulfur marine biofuels.

MATERIALS AND METHODS

Feedstock and Process options

The modeled supply chains include agroforestry residues feedstocks produced in Brazil (Table 1). Besides, three thermochemical biofuel pathways that are near-term candidates for large-scale commercial production were analyzed (*e.g.*, hydrothermal liquefaction with hydrodeoxygenation-HTL, fast pyrolysis with hydrodeoxygenation-FPH, and gasification with Fischer-Tropsch synthesis GFT). Both hydrothermal liquefaction and fast pyrolysis are in early commercialization, with existing demonstration plants producing 25-80 million liters of biofuel annually from wood feedstocks [12–14]. Hydrodeoxygenation of biofuels has been demonstrated on a pilot scale but has not yet been commercialized. In contrast, GFT has been operating commercially for coal and natural gas since 1930, and the Sasol plants represent the most significant example of commercialized FT synthesis in the world. The two plants contain 80 Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifiers, and total output from both of the plants is approximately 150,000 barrels per day (bpd), reaching 160,000 bpd in 2006 [15].

Table 1. Agroforestry residues feedstocks composition

Feedstock		Eucalyptus	Pine	Corn	Rice	Wheat	Sugarcane	Sorghum
Туре	Units	Residues	Residues	Stover	Straw	Straw	Bagasse	Bagasse
Biomass dry ¹	kg	100	100	100	100	100	100	100
Moisture	% ww ²	42.00	50.00	15.00	15.00	15.00	53.80	54.00
Ash	$%dw^3$	1.50	0.50	6.00	18.00	7.00	3.50	7.00
			Dry Matt	er Compositi	ion			
Lignin	%dw	27.00	27.70	15.00	13.00	18.00	20.50	8.50
Cellulose	%dw	43.00	42.00	37.00	37.00	37.00	35.00	36.00
Hemicellulose	%dw	18.00	26.50	29.00	24.00	37.00	35.50	25.50
Other	%dw	10.50	3.30	13.00	8.00	1.00	5.50	23.00
			Eleme	ntal Analysis				
С	%daf¹	50.50	52.20	49.50	48.50	49.00	49.60	47.10
Н	%daf	6.10	6.20	6.00	6.00	6.00	6.00	7.00
N	%daf	0.30	0.17	0.75	1.00	0.70	0.40	1.50
S	%daf	0.04	0.08	0.10	0.14	0.15	0.10	0.20
O	%daf	43.10	41.40	43.70	44.40	44.20	43.90	44.20
HHV	MJ/kg	20	20.7	19	18.8	19.4	19.3	19.2

¹daf = dry ash free weight. ²ww = wet weight. ³dw = dry weight.

First, feedstock options were selected based on projected availability. Next, the process models were created for the selected feedstock and biofuel production technology. Thus, the model was designed with a parallel data structure to ensure that each feedstock/technology scenario (21 pairs) used a standardized set of parameters and allowed for an exergy-based comparison of parameters and results.

Each feedstock-technology combination was simulated using biofuel yields from experimental literature, and the processes were adapted to produce fuel compatible with marine engines. Exergy efficiencies and irreversibility rates were then estimated for a biorefinery case study operating in Brazil, modeled to process 500 dry tonnes of biomass per day, which represents a consistent scale with biorefineries currently planned or in operation, such as fast pyrolysis plants in Finland [16] and the Netherlands [14], and UPM's HTL plant in Finland [17].

Additionally, each biofuel pathway considered a thermochemical process focus on the influence of the conversion technology itself. The biofuels were assumed to be destined for marine fuel blendstock, and therefore the processes were adapted to output an undistilled biocrude. Theoretically, the biocrudes could be blended directly into marine fuels, in proportions of up to 30%, as shown by previous tests for HTL [18] and GFT [6] biofuels. For clarity of comparison, the results are presented for pure biofuels, rather than for bio-fossil blends.

Process Simulation

This section offers a brief description of the selected conversion technologies, namely, hydrothermal liquefaction with hydrodeoxygenation (HTL), fast pyrolysis with hydrodeoxygenation (FPH), and gasification with Fischer-Tropsch synthesis (GFT). Fig. 1 shows the system's boundary adopted in the assessment of the thermochemical pathways.

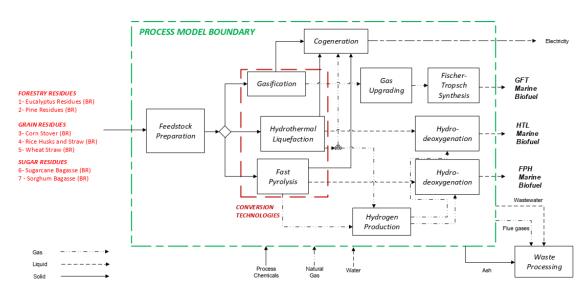


Figure 1. Processes Boundary

Hydrothermal liquefaction (HTL)

In the HTL model given in Figure 2, the prepared biomass material was saturated with water heated to 300°C, pressurized to subcritical conditions, and reacted for 10-60 min, decomposing into oil, aqueous, char, and gas fractions [19]. Table 2 details the reactor conditions and yields used in this study.

Furthermore, it was assumed that 80% of the aqueous fraction to be recycled back into the hot water injection process in order to replace freshwater. The unreacted organics in the recycled aqueous feed were supposed to decompose partially into oil and char [20]. Besides, it was adopted a conservative conversion rate of 5-10% related to biofuel-from-aqueous, proportional to freshfeed yields.

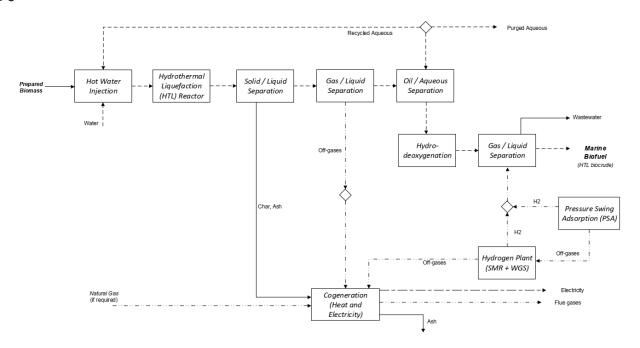


Figure 2. HTL model

Table 2. Hydrothermal liquefaction reactor conditions, yields, and heating values of reaction products for all biomass feedstocks

Feedstock	Reactor inlet	Reactor Yields				Product HHV			Recyclate conversion		Ref.
			% of dry biomass			(M.		% of recycled organics			
	H ₂ O-feed ratio	Oil	Aqueous	Char	Gas	Oil	Char	Gas	Oil	Char	
Eucalyptus	(6:1)	23%	16%	27%	19%	27	26	4	5%	15%	[21]
Pine	(6:1)	35%	35%	6%	18%	25	29	4	8%	23%	[22]
Corn	(8:1)	23%	38%	9%	14%	30	26	2	5%	15%	[23]
Rice	(6:1)	24%	11%	31%	20%	26	18	4	5%	16%	[24]
Wheat	(6:1)	29%	34%	24%	5%	27	26	4	7%	19%	[25]
Sugarcane	(6:1)	25%	39%	22%	4%	25	24	4	6%	16%	[25]
Sorghum	(5:1)	42%	19%	23%	17%	30	30	4	10%	28%	[26]

Only liquefaction of solid biomass in water was considered without the addition of pre-processing or solvents in the HTL model. Therefore, the reactor output was separated from the char and conducted to the cogeneration plant (COGEN). Off-gases were addressed to the hydrogen production plant with additional feedstock demand satisfied by natural gas, whereas any excess off-gases were passing through to the COGEN plant. HTL biocrude obtained from lignocellulosic materials is potentially an acceptable direct replacement for heavy fuel oil [27,28] and directly useable blended with fossil fuels in marine engines [6].

However, hydrotreatment was expected to increase the quality of the HTL biofuel by reducing its sulfur, nitrogen, and oxygen fractions, and increasing is energy content to a comparable level of the FPH and GFT biocrudes.

Gasification with Fischer-Tropsch synthesis (GFT)

In the GFT system (Fig. 3), biomass is converted to a syngas, cleaned catalytically condensed into a high purity biofuel [29]. In this model, the prepared feedstock was pressurized with CO_2 and gasified in a steam-oxygen environment at 700-830°C, at ratios of 4:1 dry biomass to O_2 and 3:2 O_2 to steam mass. The gas yields used are presented in Table 3.

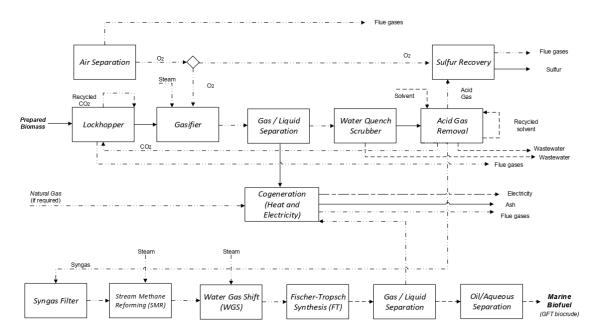


Figure 3. GFT model

Table 3. Gasifier conditions, yields, and heating values of reaction products

Feedstock	Reactor temp		Yields			Syngas Composition					Ref.
	(°C)		% inlet feed							(MJ/kg)	
		Syngas	Char	Liquid	H ₂ (%)	CO(%)	CO ₂ (%)	CH ₄ (%)	C ₂ -C ₄ (%)	Syngas	
Eucalyptus	700	72%	2%	27%	9%	33%	58%	0%	0%	15.9	[30]
Pine	700	72%	1%	27%	9%	33%	58%	0%	0%	17.4	[30]
Corn	780	79%	7%	14%	2%	32%	57%	4%	5%	11.7	[31]
Rice	830	70%	16%	14%	2%	44%	38%	15%	1%	15.7	[24]
Wheat	830	54%	20%	26%	2%	33%	42%	11%	11%	15	[32]
Sugarcane	800	93%	2%	3%	1%	30%	60%	4%	5%	9.6	[33]
Sorghum	700	76%	9%	14%	1%	30%	63%	6%	0%	8.3	[34]

 C_2 - C_4 refers to light hydrocarbons in the range of C_2H_n and C_4H_n

The syngas was cleaned to remove solids, tar, ammonia, CO₂, and sulfur via a water quench, filters, and monoethanolamine (MEA) based acid gas removal. The removed CO₂ was recycled for lockhopper pressurization. A syngas methane content of 1.5% was ensured using steam methane reforming (SMR) and, if necessary, a water gas shift (WGS) improved the H₂:CO ratio to at least 2.15:1. Thus, the cleaned syngas was modeled to be condensed in a Fischer-Tropsch reactor at 200°C, over a Co-Al catalyst [31] with a conversion rate of 78% [24]. The conversion of H₂ and CO to hydrocarbons considered the Anderson-Schulz-Flory distribution for cobalt catalysts [31]. The biofuels' HHVs were calculated from their hydrocarbon distribution in all cases and obtained approximately 45 MJ/kg.

Fast pyrolysis with hydrotreatment (FPH)

In this system, the fast pyrolysis occurred in a fluidized bed reactor, assuming the conditions and yields presented in Tab. 4. It should be noted that the pulverized biomass was rapidly heated in an anaerobic environment to 500°C. Besides, the reactor heat demand was met primarily by the combustion of the pyrolysis char. Later, part of the gas output was recycled for fluidization gas, with the remainder used to produce the hydrogen for hydrotreatment (Fig. 4). It was also assumed that the organic content of the fluidization gas does not influence the pyrolysis yields [24].

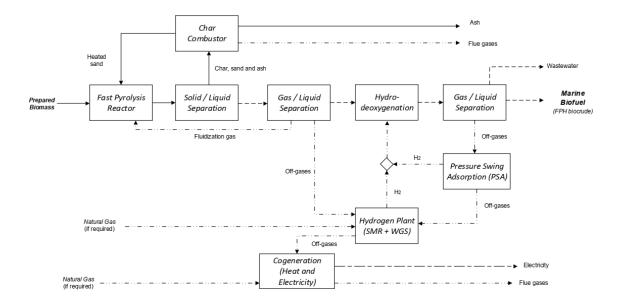


Figure 4. FPH model

Reactor **Feedstock** Reactor yields **Product HHV** Ref. temp. (^{o}C) % ash-free biomass (MJ/kg)Pyrolysis Oil Oil Char Gas Char Gas (% H₂O) Eucalyptus 22% 31 [37] 500 59% (26%) 13% 17 10 27 [22] Pine 520 64% (24%) 17% 18% 17 10 Corn 22 [38] 500 65% (9%) 17% 21% 22 6 [39] Rice 491 75% (25%) 18% 17% 19 22 9 Wheat 500 54% (46%) 15 28 5 [40] 32% 14% [41] Sugarcane 495 70% (26%) 17% 13% 18 25 11 [42] Sorghum 510 69% (15%) 13% 17% 16 23 6

Table 4. Fast pyrolysis parameters

The resulting pyrolysis oil had a high oxygen content. Thus, a hydrotreatment process was used to reduce it via catalytic reacting the oil with hydrogen, increasing the stability and energy content of the final biofuel. Hence, the pyrolysis oil was deoxygenated in a hydrotreater with a 50% hydrogen conversion rate. Approximately half of the mass was recovered as biofuel, 40% lost to aqueous separation, and 10% lost to off-gases [35]. For all raw materials, the final biofuel was assumed to have an energy content of 35 MJ/kg [36], as feedstock specific data were unavailable. The unreacted hydrogen (85%) was recuperated by pressure swing absorption (PSA) and recycled.

Hydrogen was produced via steam methane reforming (SMR) and a water gas shift (WGS), assuming a 100% conversion efficiency for a 1.5:1 steam:hydrocarbon ratio, with an 85% recovery of hydrogen via PSA. When off-gases did not satisfy hydrogen demand, natural gas was used as supplementary fuel. Lastly, any excess off-gases were addressed for the COGEN plant.

Exergy Analysis

Exergy analysis can play an essential role in identifying opportunities for improving efficiency at scales ranging from individual processes to the economy. It can also help by determining the feasibility of emerging technologies and identifying limits to efficiency improvement through the First and Second Law of Thermodynamics [43]. Exergy is defined as the thermodynamic propriety that represents the maximum work that could be obtained using reversible processes from a system that interacts with the components of the environment until the equilibrium state is attained [44].

Exergy balance. The thermochemical conversion scenarios are based on the calculation of the steady-state mass, energy, and exergy balances for each one of the control volume, according to Equations (1-3). Where $\sum_{inlet} \dot{m}_i b_i$ represents the exergy of the process inputs (\dot{B}_{inputs}) , $\sum_{outlet} \dot{m}_e b_e$ the exergy of the process output $(\dot{B}_{products})$, and (\dot{I}) the Irreversibility (exergy losses).

$$\sum_{inlet} \dot{m}_i = \sum_{outlet} \dot{m}_e \tag{1}$$

$$\sum_{inlet} \dot{m}_i h_i + \dot{Q}_{CV} = \sum_{outlet} \dot{m}_e h_e + \dot{W}_{CV} \tag{2}$$

$$\sum_{inlet} \dot{m}_i = \sum_{outlet} \dot{m}_e$$

$$\sum_{inlet} \dot{m}_i h_i + \dot{Q}_{CV} = \sum_{outlet} \dot{m}_e h_e + \dot{W}_{CV}$$

$$\sum_{inlet} \dot{m}_i b_i + \dot{Q}_{CV_i} \left(1 - \frac{To}{T} \right) = \sum_{outlet} \dot{m}_e b_e + \dot{W}_{CV_e} + \dot{I}$$
(3)

In this work, the chemical (b_{CH}) and physical (b_{PH}) exergies are measured due to the physicchemical processes involved. Thus, b_{PH} was defined according to equation (4). Where H (in kW) is the enthalpy flow rate at P, T, S (in kW/K) represents the entropy rate/flow rate at P, T, T_o (in K) is the temperature at the reference state, H_o (in kW) denotes the enthalpy flow rate at P_o , T_o and S_o (in kW/K) is the entropy rate/flow rate at P_o , T_o .

$$B_{PH} = H - H_0 - T_0(S - S_0) (4)$$

Conceptually, b_{CH} quantifies the value of a chemical substance, or compound, as measured against a selected reference environment [45]. Equation (5) was adopted to define the chemical exergy of the components. Where n_{mix} is the total amount of moles of all constituents in a mixture, x_i is the mole fraction of component i in the mixture.

$$B_{CH} = n_{mix} \left[\sum_{i} x_i b_i^{ch} + R_u T_0 \sum_{i} x_i ln Y_i x_i \right]$$
 (5)

Besides, Y_i represented the activity coefficient and the term b_i^{ch} denoted the standard chemical exergy. The chemical exergies for various compounds are found in the Szargut et al. [44] and Kotas [46]. More specifically, the b_{CH} considered in the exergy assessment are given in Tab. 5.

Table 5. Chemical exergies for several components

Compound	MJ/kg	Ref.
Light naphtha (green naphtha)	44.5	[47]
Jet fuel	45.3	[47]
Diesel	44.2	[47]
Heavy fuel oil (HFO)	41.4	[47]
Marine gas oil (MGO)*	43	[8]
HTL biocrude*	35	[8]
FP+HT biocrude*	35.6	[8]
GFT biocrude*	43.1	[8]
Greenwood*	9.5	[8]
Wax*	40	[8]
Liquid natural gas (GNL)	52.4	[47]
Natural gas	48.87	[48]
Wood chips	18.3	[47]
Soy biodiesel	40.1	[49]

*Based on PCI (MJ/kg)

Performance Assessment

Exergy efficiency and irreversibility rate were used as a key performance indicator (KPI) in the analysis of the thermochemical conversion systems.

<u>Exergy efficiency</u>. This indicator determinate by the ratio between the exergy of the products and the exergy of the resources, as indicated in Eq. (6).

$$\eta_B = \frac{\sum \dot{\mathbf{B}}_{products}}{\sum \dot{\mathbf{B}}_{resources}} \tag{6}$$

<u>Irreversibility rate.</u> The irreversibility was obtained by applying the exergy balance expression introduced in Eq. (3).

RESULTS AND DISCUSSION

To synthesize the impact of the marine biofuel yields in terms of the selected KIPs for assessing the thermochemical systems, the exergetic efficiency and destroyed exergy rate were determined for each pair feedstock/technology. Thus, Fig. 5 shows the results concerning the Hydrothermal Liquefaction system. Then, the main findings related to Fast Pyrolysis technology are shown in Fig. 6. Lastly, the principal results associated with the Gasification Fischer-Tropsch system are presented in Fig. 7.

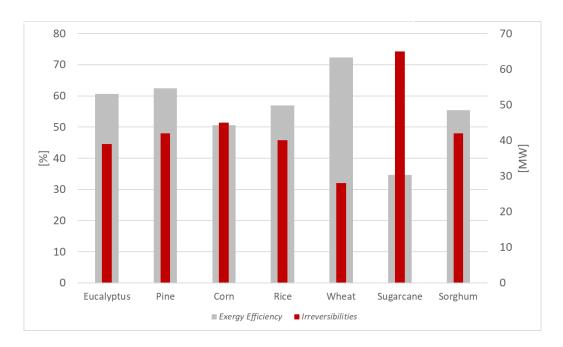


Figure 5. Hydrothermal liquefaction performance

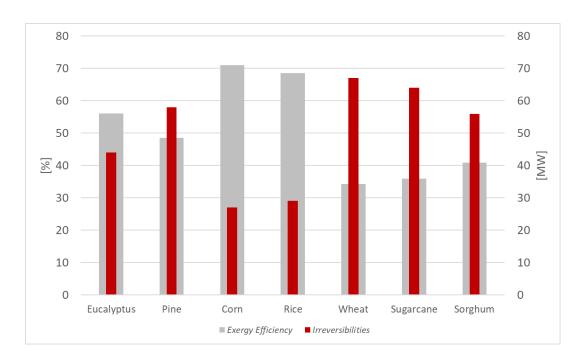


Figure 6. Fast Pyrolysis performance

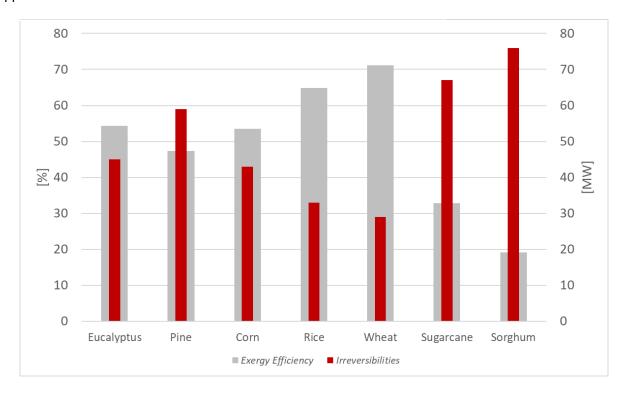


Figure 7. Gasification Fischer-Tropsch system

To illustrate the primary outcomes of the exergetic analysis, Tables 5 and 6 represent the exergy efficiencies and irreversibilities for all configurations and biomass feedstocks, respectively.

Table 5. Exergy efficiency for all configurations and biomass feedstocks

Exergy Efficiency (%)	Eucalyptus Residues	Pine Residues	Corn Stover	Rice Straw	Wheat Straw	Sugarcane Bagasse	Sorghum Bagasse
HTL	60.6	62.4	50.6	57.0	72.3	34.6	55.4
FPH	56.1	48.5	71.0	68.6	34.2	35.9	40.9
GFT	54.4	47.3	53.5	64.8	71.1	32.9	19.2

Table 6. Irreversibilities for all configurations and biomass feedstocks

Irreversibilities	Eucalyptus	Pine	Corn	Rice	Wheat	Sugarcane	Sorghum
(MW)	Residues	Residues	Stover	Straw	Straw	Bagasse	Bagasse
HTL	39	42	45	40	28	65	42
FPH	44	58	27	29	67	64	56
GFT	45	59	43	33	29	67	76

In light of these results, HTL and FPH technologies have mean biofuel yields around 9.5 GJ/tdb. Particularly, marine biofuels produced via HTL and FPH from forestry and grain residues have similar biofuel yields per year. In contrast, GFT yields are lower approximately 6.5 GJ/tdb, due to losses during syngas upgrading (*e.g.*, Sorghum GFT achieved the lowest yield of 5 GJ/tdb), attributable to the low-hydrogen syngas composition.

Another aspect to be highlighted is that FPH combinations required supplementary fuel, natural gas, to cover 20% of the internal energy demand, whereas Corn HTL also required additional energy due to the higher equilibrium reactor flow resulting in a system heating demand 40% above the HTL mean.

From the exergy analysis point of view, the assessment shows the potential of the energy resources and the merit of the energy conversion systems and irreversibilities distribution, regardless of the nature of feedstocks and technologies considered. Hence, this practical approach was used to determine the maximum potential for work that can be produced from all the pairs feedstock/technology.

The results based on the Second Law of Thermodynamics shows the quality of the energy resources in terms of substance or exergy flow to accurately compare energy technologies by using a methodology that allows calculating the technical performance, as well as for the associated irreversibilities of each system. Hence, this study demonstrated the potential of second-generation feedstock coupled with a thermochemical process to determine/identify promising systems that focus on the production of biofuels and marine blends.

In brief, the lower irreversibility rate was found on the Wheat Straw/HTL (28 MW), Wheat Straw/GFT (29 MW), and Corn Stover/FPH (27 MW) feedstock/technology pairs (Tab. 6). Consequently, these pathways presented the highest exergetic efficiency among the considered systems. In contrast, the sorghum bagasse/GFT has the lowest estimated exergetic efficiency of the all scenarios (21 pairs feedstock/technology, Tab. 5), attributable to the low-hydrogen syngas composition and due to losses during syngas upgrading.

CONCLUSION

This study used an integrated model to estimate the technical performance of seven marine biofuel supply chains through a trade-off linking the exergy efficiency and the thermodynamic losses. Thus, a comparison of lignocellulosic marine biofuel options based on thermochemical production technologies and agroforestry feedstocks were carried out.

In particular, Hydrothermal liquefaction (HTL) and Gasification with Fischer-Tropsch synthesis (GFT) technologies have the highest biofuel yields. For instance, when used wheat straw as an input in the HTL and the GFT systems, it was presented the highest exergetic efficiency and, consequently, the lowest destructed exergy rate of the configurations.

Concerning the Fast pyrolysis with hydrotreatment (FPH), the highest exergy performance was reached when corn stover was employed as a feedstock. In contrast, the sorghum GFT has the lowest estimated exergetic efficiency attributable to the low-hydrogen syngas composition and due to losses during syngas upgrading.

Overall, the most significant recommendation from the exergy point of view is that the Wheat Straw/HTL, Wheat Straw/GFT, and Corn Stover/FPH pairs (within 21 feedstock/technology scenarios) were identified as the promising systems. Thus, these possible pathways could support the transition (medium-term targets) of the marine transport sector towards higher energy efficiency/low-carbon systems focus on the production of biofuels (from sustainable feedstocks) and marine blends.

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NOMENCLATURE

Barrels per day (bpd)
Dry tones of lignocelly

Dry tones of lignocellulosic biomass (tdb)

Cogeneration plant (COGEN)

Hydrothermal liquefaction with hydrodeoxygenation (HTL)

Fast pyrolysis with hydrodeoxygenation (FPH)

Gasification with Fischer-Tropsch synthesis (GFT)

Monoethanolamine (MEA)

Steam methane reforming (SMR)

Water gas shift (WGS)

REFERENCES

- [1] International Maritime Organization (IMO), Sulphur 2020 cutting sulphur oxide emissions., 2020. http://www.imo.org/en/MediaCentre/HotTopics/Pages/Sulphur-2020.aspx (accessed February 2, 2020).
- [2] Concawe, Marine fuel facts, Concawe, n.d. https://www.concawe.eu/ (accessed March 3, 2020).
- [3] FuelsEurope, STATISTICAL REPORT 2018, FuelsEurope, Belgium, 2018. https://www.fuelseurope.eu/ (accessed October 1, 2020).
- [4] Oak Ridge National Laboratory (ORNL), Understanding the Opportunities of Biofuels for Marine Shipping, Oak Ridge National Laboratory (ORNL), United States, 2018. https://info.ornl.gov/sites/publications/Files/Pub120597.pdf (accessed March 15, 2020).
- [5] J. Fu, S.Q. Turn, Characteristics and stability of biofuels used as drop-in replacement for NATO marine diesel, Fuel. 236 (2019) 516–524. https://doi.org/10.1016/j.fuel.2018.09.042.
- [6] M.N. Nabi, J.E. Hustad, Investigation of engine performance and emissions of a diesel engine with a blend of marine gas oil and synthetic diesel fuel, Environmental Technology. 33 (2012) 9–15. https://doi.org/10.1080/09593330.2010.483599.
- [7] C. Hsieh, C. Felby, Biofuels for the marine shipping sector. An overview and analysis of sector infrastructure, fuel technologies and regulations., International Energy Agency (IEA), Copenhagen, Denmark, 2017. https://task39.sites.olt.ubc.ca/files/2013/05/Marine-biofuel-report-final-Oct-2017.pdf (accessed May 3, 2020).
- [8] S.E. Tanzer, J. Posada, S. Geraedts, A. Ramírez, Lignocellulosic marine biofuel: Technoeconomic and environmental assessment for production in Brazil and Sweden, Journal of Cleaner Production. 239 (2019) 117845. https://doi.org/10.1016/j.jclepro.2019.117845.
- [9] T. Koroglu, O.S. Sogut, Conventional and advanced exergy analyses of a marine steam power plant, Energy. 163 (2018) 392–403. https://doi.org/10.1016/j.energy.2018.08.119.
- [10] Z.-M. Yao, Z.-Q. Qian, R. Li, E. Hu, Energy efficiency analysis of marine high-powered medium-speed diesel engine base on energy balance and exergy, Energy. 176 (2019) 991–1006. https://doi.org/10.1016/j.energy.2019.04.027.
- [11] F. Baldi, F. Ahlgren, T.-V. Nguyen, M. Thern, K. Andersson, Energy and Exergy Analysis of a Cruise Ship, Energies. 11 (2018) 2508. https://doi.org/10.3390/en11102508.

- [12] Licella Holdings, Pulp and paper. Creating renewable crude at a comparable price to conventional crude., (2020). https://www.licella.com.au/pulp-paper/ (accessed March 1, 2020).
- [13] Valmet, Bio-oil, (2020). https://www.valmet.com/more-industries/bio/bio-oil/ (accessed October 1, 2020).
- [14] BTG-BTL, Empyro project, (2020). https://www.btg-btl.com/en/company/projects/empyro (accessed March 20, 2020).
- [15] The National Energy Technology Laboratory (NETL), Commercial Use of Fischer-Tropsch Synthesis, (n.d.). https://www.netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/sasol (accessed February 16, 2020).
- [16] Fortum, First industrial-scale integrated bio-oil plant, (2012). https://www.fortum.com/media/2012/03/fortum-invests-eur-20-million-build-worlds-first-industrial-scale-integrated-bio-oil-plant (accessed June 11, 2019).
- [17] ETIP Bioenergy, UPM Biofuels commercial plant in Lappeenranta, Finland, European Technology and Innovation Platform Bioenergy. (2016). http://www.etipbioenergy.eu/images/Factsheet_UPM_final.pdf.
- [18] M.N. Nabi, M.M. Rahman, M.A. Islam, F.M. Hossain, P. Brooks, W.N. Rowlands, J. Tulloch, Z.D. Ristovski, R.J. Brown, Fuel characterisation, engine performance, combustion and exhaust emissions with a new renewable Licella biofuel, Energy Conversion and Management. 96 (2015) 588–598. https://doi.org/10.1016/j.enconman.2015.02.085.
- [19] Y. Zhang, Hydrothermal Liquefaction to Convert Biomass into Crude Oil, in: Biofuels from Agricultural Wastes and Byproducts, John Wiley & Sons, Ltd, 2010: pp. 201–232. https://doi.org/10.1002/9780813822716.ch10.
- [20] Z. Zhu, L. Rosendahl, S.S. Toor, D. Yu, G. Chen, Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation, Applied Energy. 137 (2015) 183–192. https://doi.org/10.1016/j.apenergy.2014.10.005.
- [21] M. Sugano, H. Takagi, K. Hirano, K. Mashimo, Hydrothermal liquefaction of plantation biomass with two kinds of wastewater from paper industry, J Mater Sci. 43 (2008) 2476–2486. https://doi.org/10.1007/s10853-007-2106-8.
- [22] I.J. Tews, D.C. Elliott, Low-Severity Hydroprocessing to Stabilize Bio-oil: TechnoEconomic Assessment, Pacific Northwest National Lab. (PNNL), Richland, WA (United States), 2014. https://doi.org/10.2172/1227072.
- [23] E. Panisko, T. Wietsma, T. Lemmon, K. Albrecht, D. Howe, Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks, Biomass and Bioenergy. 74 (2015) 162–171. https://doi.org/10.1016/j.biombioe.2015.01.011.
- [24] C. da Silva, Techno-Economic and Environmental Analysis of Oil Crop and Forestry Residues Based Integrated Biorefineries in Brazil, PDEng Thesis, Delft University of Technology, 2016.
- [25] Singh et al., Hydrothermal liquefaction of agricultural and forest biomass residue: comparative study, Springerprofessional.De. (2015). https://www.springerprofessional.de/hydrothermal-liquefaction-of-agricultural-and-forest-biomass-res/5335084 (accessed April 15, 2020).
- [26] Z. Bi, J. Zhang, E. Peterson, Z. Zhu, C. Xia, Y. Liang, T. Wiltowski, Biocrude from pretreated sorghum bagasse through catalytic hydrothermal liquefaction, Fuel. 188 (2017) 112–120. https://doi.org/10.1016/j.fuel.2016.10.039.
- [27] S. Anouti, G. Haarlemmer, M. Déniel, A. Roubaud, Analysis of Physicochemical Properties of Bio-Oil from Hydrothermal Liquefaction of Blackcurrant Pomace, (2015). https://doi.org/10.1021/acs.energyfuels.5b02264.

- [28] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Hydrothermal liquefaction of biomass: Developments from batch to continuous process, Bioresource Technology. 178 (2015) 147–156. https://doi.org/10.1016/j.biortech.2014.09.132.
- [29] S.S. Gill, A. Tsolakis, K.D. Dearn, J. Rodríguez-Fernández, Combustion characteristics and emissions of Fischer–Tropsch diesel fuels in IC engines, Progress in Energy and Combustion Science. 37 (2011) 503–523. https://doi.org/10.1016/j.pecs.2010.09.001.
- [30] García et al., Catalytic Steam Gasification of Pine Sawdust. Effect of Catalyst Weight/Biomass Flow Rate and Steam/Biomass Ratios on Gas Production and Composition, (n.d.). https://pubs.acs.org/doi/10.1021/ef980250p (accessed April 15, 2020).
- [31] R.M. Swanson, A. Platon, J.A. Satrio, R.C. Brown, D.D. Hsu, Techno-Economic Analysis of Biofuels Production Based on Gasification, National Renewable Energy Lab. (NREL), Golden, CO (United States), 2010. https://doi.org/10.2172/994017.
- [32] D.L. Carpenter, R.L. Bain, R.E. Davis, A. Dutta, C.J. Feik, K.R. Gaston, W. Jablonski, S.D. Phillips, M.R. Nimlos, Pilot-Scale Gasification of Corn Stover, Switchgrass, Wheat Straw, and Wood: 1. Parametric Study and Comparison with Literature, Ind. Eng. Chem. Res. 49 (2010) 1859–1871. https://doi.org/10.1021/ie900595m.
- [33] J. Figueroa, Y. Ardila, R. Maciel Filho, M. Maciel, Fluidized Bed Reactor For Gasification Of Sugarcane Bagasse: Distribution Of Syngas, Bio-tar And Char, Scopus. (2014). https://doi.org/10.3303/CET1437039.
- [34] K.D. Panopoulos, D. Vamvuka, Experimental evaluation of thermochemical use of two promising biomass fuels, (2009). http://citeseerx.ist.psu.edu/viewdoc/summary?doi=10.1.1.463.2597.
- [35] P.A. Meyer, L.J. Snowden-Swan, K.G. Rappé, S.B. Jones, T.L. Westover, K.G. Cafferty, Field-to-Fuel Performance Testing of Lignocellulosic Feedstocks for Fast Pyrolysis and Upgrading: Techno-economic Analysis and Greenhouse Gas Life Cycle Analysis, Energy and Fuels. (2016). https://doi.org/10.1021/acs.energyfuels.6b01643.
- [36] J. Wildschut, Pyrolysis Oil Upgrading to Transportation Fuels by Catalytic Hydrotreatment, PhD thesis, University of Groningen, 2009. https://www.rug.nl/research/portal/files/2648400/thesis.pdf.
- [37] S. Chang, Z. Zhao, A. Zheng, X. Li, X. Wang, Z. Huang, F. He, H. Li, Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor, Bioresource Technology. 138 (2013) 321–328. https://doi.org/10.1016/j.biortech.2013.03.170.
- [38] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass and Bioenergy. 34 (2010) 67–74. https://doi.org/10.1016/j.biombioe.2009.09.012.
- [39] S.-H. Jung, B.-S. Kang, J.-S. Kim, Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system, Journal of Analytical and Applied Pyrolysis. 82 (2008) 240–247. https://doi.org/10.1016/j.jaap.2008.04.001.
- [40] C.J. Mulligan, L. Strezov, V. Strezov, Thermal Decomposition of Wheat Straw and Mallee Residue Under Pyrolysis Conditions†, Energy and Fuels. (2009). https://doi.org/10.1021/ef9004797.
- [41] T. Hugo, Pyrolysis of Sugarcane Bagasse, Thesis (MScEng, Process Engineering), University of Stellenbosch, 2008.
- [42] J. Piskorz, P. Majerski, D. Radlein, D.S. Scott, A.V. Bridgwater, Fast pyrolysis of sweet sorghum and sweet sorghum bagasse, Journal of Analytical and Applied Pyrolysis. 46 (1998) 15–29. https://doi.org/10.1016/S0165-2370(98)00067-9.
- [43] B. Bakshi, Sustainable Engineering, Cambridge University Press, 2019. https://doi.org/10.1017/9781108333726.

- [44] J. Szargut, D. Morris, F. Steward, Exergy analysis of thermal, chemical, and metallurgical processes., Hemisphere Publishing Corporation, New York, 1988.
- [45] H. Marais, G. van Schoor, K.R. Uren, The merits of exergy-based fault detection in petrochemical processes, Journal of Process Control. (2017). https://doi.org/10.1016/j.jprocont.2017.11.005.
- [46] T.J. Kotas, The Exergy Method of Thermal Plant Design, Butterworths, London-UK, 1985.
- [47] I. Dinçer, C. Zamfirescu, Sustainable Energy Systems and Applications, Springer, 2011. https://www.springer.com/gp/book/9780387958606.
- [48] P. Silva, R. Maciel, J. Posada, Mass and Heat Integration in Ethanol Production Mills for Enhanced Process Efficiency and Exergy-Based Renewability Performance, Processes. 7(10) (2019) 670. https://doi.org/10.3390/pr7100670.
- [49] K. Ptasinski, Efficiency of Biomass Energy: An Exergy Approach to Biofuels, Power, and Biorefineries, John Wiley & Sons, Ltd, 2016. https://doi.org/10.1002/9781119118169.ch2.