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

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## ABSTRACT

Current limits on the sulfur content and Greenhouse Gas (GHG) emissions of marine fuels are 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 (e.g., *Eucalyptus Residues, Pine Residues, Corn Stover, Rice Straw, Wheat Straw, Sugarcane Bagasse, and Sorghum Bagasse*) and three thermochemical pathways (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, the λ renewability performance, the Average unitary exergy cost (AUEC), and the irreversibilities. 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 and AUEC 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) due to 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 called 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 on board 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, equivalent to 271,414 thousand tonnes [3]. This sector consumes more than 330 million tonnes of fuel a year and accounts for more than 900 million tonnes of the global CO2 (2-3%), SOx (4-9%), and NOx emissions (10-15%) [4]. In this context, the marine industry faces 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 reality has expanded interest in alternative fuel options, such as liquid natural gas and advanced 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, when blended with HFO, biofuels offer potential synergistic advantages by reducing sulfur content, improving overall lubricity, and lower ash and emission profiles, notably for particular matters and SOx. As renewable fuels, they also offer the potential to reduce life-cycle CO2 for marine operations [5].

The viability of a lignocellulosic marine biofuel relies 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 centered on blending with traditional marine diesel [6] and marine engine testing [7] or overall comparisons taking into account the entire supply chain from field to ship [4]. 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 configuration).

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 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 to deliver its fair share of the global decarbonisation challenge. Hence, having a feedstock availability and consistent processing technologies to produce competitive biofuels at a large scale are key factors to promote most of the abatement of emissions required to achieve the IMO strategies. In fact, marine shipping industry is a relatively low-energy mode of long-distance transportation that should continue improving its energy efficiency and cost-competitiveness to consolidate the operation into a competitive market with options such as aviation and road transport.

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 the lignocellulosic marine biofuel framework using the exergy principles as indicators was carried out, which could be relevant and support the decision-making process regarding further research on low-carbon footprint, low-sulfur marine biofuels in a competitive market promoting the use of renewables in the shipping sector.

## MATERIALS AND METHODS

## Feedstocks and Process options

First, raw materials were chosen based on projected availability. Next for the selected feedstock and biofuel production technology, process models were developed. The models were designed with a parallel data structure to ensure that each feedstock/technology scenario (21 pairs) used a standardized set of parameters and permitted an exergy-based comparison.

Brazil was selected as a reference because of its competitiveness in agribusiness and its experience in biofuels production, these facts and particularities situated the country in a key position in the biofuel market. Brazil is one of the fastest-growing economies in Latin America and renewable energy sources are strategic into the Brazilian energy matrix. For instance, the electrical matrix of predominantly renewable origin, with emphasis on the hydropower plants that accounts for 64.9% of the domestic energy supply in 2019. Renewable sources account for 83.0% of the domestic supply of electricity, which is the result of the sum of the amounts referring to domestic production plus imports (Wind, Biomass, and Solar resources) in Brazil, which are basically of renewable origin [12]. Hence, this paper is focused on biomass from the agricultural origin, given the Brazilian land resources and its agricultural and forestry residues to explore the potential feedstock for renewable marine fuels.

The most promising potential raw materials for the initial development of marine fuels in Brazil are plants that contain sugars and starches but materials such as plant oils, lignocellulose, and industrial waste residues can be considered for the longer-term feedstocks. This is an important factor since the choice of feedstock takes into account its biomass production cost (usually represent 70%) or more of the overall biofuel price [13]. Thus, Table 1 presents the current status and prospects feedstock given in tropical climate for the maritime industry are studied looking for business opportunities in this sector.

Three thermochemical biofuel pathways that are near-term candidates for large-scale commercial production were analyzed (*e.g.,* Hydrothermal Liquefaction-HTL, Fast Pyrolysis-FP, and Gasification with Fischer-Tropsch synthesis GFT). Both HTL and FP are in early commercialization, with 25-80 million liters of biofuel annually produced from wood feedstock by demonstration plants [14–16]. HTL technology via Hydrodeoxygenation of biofuels has been demonstrated on a pilot scale but has not yet been commercialized. In contrast, GFT has been operating commercially since 1930 using coal and natural gas, and the Sasol plants represent the world's most significant cases of commercialized FT synthesis. The two plants have a total output of approximately 150,000 barrels per day (bpd) and contain 80 Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifiers [17].

Each feedstock-technology set was modeled using biofuel yields from experimental literature, and the processes were adjusted to produce fuel compatible with marine engines. Exergy efficiencies and irreversibility rates were then assessed 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; for example, FP plants projected in Finland [18] and the Netherlands [16], and UPM's HTL plant in Finland [19].

Additionally, the impact of the biofuel conversion technology was considered for each thermochemical pathway. The biofuels were assumed to be destined for marine fuel blendstock, and therefore the processes were adjusted to generate 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 [20] and GFT [7] biofuels.

## 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). In general, these types of thermochemical conversion processes offer advantages in terms of the biomass recalcitrance for biofuel production when compared with biological routes. Fig. 1 shows the system's boundary adopted in the assessment of the thermochemical pathways.

## Hydrothermal liquefaction (HTL)

HTL technology converts biomass into crude-like bio-oil using moderate temperature and high pressure [4]. In the HTL model, the prepared biomass material was saturated with water heated to 300°C, pressurized to subcritical conditions, and reacted for 10-60 minutes, decomposing into oil, aqueous, char, and gas fractions (Fig. 2) [21]. Table 2 gives the details related to the reactor conditions and yields selected. 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. Next, the unreacted organics in the recycled aqueous feed were supposed to decompose partially into oil and char [22]. Besides, it was adopted a conservative conversion rate of 5-10% related to biofuel-from-aqueous, proportional to fresh-feed yields.

In the HTL model, solid biomass liquefaction in water was considered without the addition of pre-processing or solvents. Therefore, the reactor output was separated from the char and conducted to the cogeneration plant (COGEN). Off-gases were addressed to the hydrogen (H2) production plant with additional feedstock demand satisfied by natural gas, whereas excess off-gases were passing through to the COGEN plant. HTL biocrude derived from lignocellulosic materials is theoretically an acceptable direct substitute for heavy fuel oil [29,30] and directly usable blended with fossil fuel sources in marine engines [7]. Hydrotreatment is expected to increase the HTL biofuel quality by decreasing its sulfur, nitrogen, and oxygen fractions, and increasing its energy content to a comparable amount of biocrude FPH and GFT [8].

## Gasification with Fischer-Tropsch synthesis (GFT)

In the GFT system (Fig. 3), the raw material is gasified/converted into synthesis gas (syngas) rich in hydrogen (H2) and carbon monoxide (CO), cleaned catalytically (remove sod and tar), condensed into a high purity liquid hydrocarbon such as synthetic diesel, biokerosene, and marine biofuel [31]. In this model, the prepared biomass was pressurized with CO2 and gasified in a steam-oxygen environment at 700-830°C, at ratios of 4:1 dry biomass to O2 and 3:2 O2 to steam mass. Table 3 presents the gas yields used in the simulation.

The synthesis gas was cleaned to eliminate solids, tar, ammonia, CO2, and sulfur by a water quench, filters, and monoethanolamine (MEA) based acid gas removal. The removed CO2 was recycled for lock-hopper pressurization. A syngas methane content of 1.5% was assumed using steam methane reforming (SMR) and, if required, a water gas shift (WGS) improved the H2:CO ratio to at least 2.15:1. Besides, the cleaned syngas was modeled to be condensed in an F-T reactor at 200°C, over a Co-Al catalyst [33] with a conversion rate of 78% [26]. The conversion of H2 and CO to hydrocarbons considered the Anderson-Schulz-Flory distribution for cobalt catalysts [33]. Thus, the higher heating value (HHV) of the biofuels were calculated from their hydrocarbon distribution in all cases and obtained roughly 45 MJ/kg.

## Fast pyrolysis with hydrotreatment (FPH)

The fast pyrolysis process occurred in a fluidized bed reactor adopting the parameters and yields presented in Tab. 4. It should be noted that the pulverized biomass was rapidly heated at 500°C in an anaerobic environment. Besides, the combustion of the pyrolysis char was met primarily by the reactor heat demand. Later, gas output was partially recycled for fluidization gas (FG) with the remains used to produce the H2 for hydrotreatment (Fig. 4). It was also assumed that the organic content of the FG flow does not influence the pyrolysis yields [26].

The pyrolysis oil obtained is characterized by high oxygen content. Thus, a hydrotreatment process was used to decrease it via catalytic reacting the oil with H2, increasing the stability and energy content of the final marine biofuel. Hence, the pyrolysis oil was deoxygenated in a hydrotreater with a 50% H2 conversion rate. Nearly half of the mass was recovered as biofuel, 40% lost to aqueous separation, and 10% gone to off-gases [43]. For all feedstocks, the final biofuel was assumed to have an energy content of 35 MJ/kg [44], when raw material specific data were unavailable.

The hydrogen unreacted (85%) was recuperated by pressure swing absorption (PSA) and recycled. H2 was produced via steam methane reforming (SMR) and a water gas shift (WGS), adopting a 100% conversion efficiency for a 1.5:1 steam:hydrocarbon ratio, with an 85% recovery of hydrogen via PSA [8]. When off-gases did not cover the H2 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 [45]. Exergy is defined as the thermodynamic property that represents the maximum work that could be achieved using reversible processes from a system that interacts with the components of the environment until the equilibrium state is reached [46].

*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 represents the exergy of the process inputs (), the exergy of the process output (), and the Irreversibility (exergy losses).

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |

In this work, the chemical (bCH) and physical (bPH) exergies are measured due to the physic-chemical processes associated to the biofuel marine configurations. Thus, bPH was defined by 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, *To* (in K) is the temperature at the reference state, *Ho* (in kW) depicts the enthalpy flow rate at Po, To and *So* (in kW/K) is the entropy rate/flow rate at Po,To.

|  |  |
| --- | --- |
|  | (4) |

Conceptually, bCH quantifies the chemical substance value, as measured against a particular reference environment [47]. Equation (5) was adopted to define the chemical exergy of the components. Where *nmix* is the total quantity of moles of all constituents in a mixture, *xi* is the mole fraction of component *i*.

|  |  |
| --- | --- |
|  | (5) |

Besides, *Ὑi* represented the activity coefficient and the term denoted the standard chemical exergy. The chemical exergies for various compounds are given in Szargut et al. [46] and Kotas [48]. More specifically, the bCH considered in the exergy assessment are found in Tab. 5.

In general, the chemical exergy for fuel stream is given in Equation (6).

|  |  |
| --- | --- |
|  | (6) |

Where ɸ represents a correlation related to the bch calculations of the ‘*nonconventional*’ components as specified in Eq. (7). This expression is used in terms of mass ratios for dry organic materials contained in solid fossil fuels consisting of carbon *c*, hydrogen *h*, oxygen *o*, and nitrogen *n* with a mass ratio of oxygen to carbon less than 0.667. The accuracy of this expression is estimated to be better than ± 1% [48].

|  |  |
| --- | --- |
|  | (7) |

The lower heating value (LHV) can be calculated using the expression given in Eq. 8. LHV is more often used and corresponds to the heat (KJ or kWh) produced by the complete oxidation of a fuel, without water in the flue gas condensation.

|  |  |
| --- | --- |
|  | (8) |

where LHV is in MJ/kg, xC is the mass fraction of carbon, xH is the mass fraction of hydrogen, xO is the mass fraction of oxygen, xS is the mass fraction of sulphur and xmoisture is the mass fraction of moisture related to the biomass feedstock [49].

## Performance Assessment

Exergy efficiency, Irreversibility rate, Average unitary exergy cost (AUEC), and Renewability exergy index (λ) were used as key performance indicators (KPI) in the analysis of the thermochemical conversion systems.

*Exergy efficiency:* This indicator determinate by the ratio between the exergy of the outputs (Bproducts) and the exergy of the inputs (Bresources), as indicated in Eq. (9).

|  |  |
| --- | --- |
|  | (9) |

*Irreversibility rate:* The irreversibility was obtained by applying the exergy balance expression introduced in Eq. (3).

*Average unitary exergy cost (AUEC):* The AUEC is a measure of the exergy destruction, which occurs during the upstream processes to form a given exergy stream. The unit exergy cost *c* (kJ/kJ) of the marine biofuel and the electricity production is calculated as the inverse of the exergy efficiency of the marine biofuel process and cogeneration unit, respectively.

|  |  |
| --- | --- |
|  | (10) |

*Renewability exergy index (λ):* λ values indicate if the net exergy of the products could be used to restore the environment to its conditions prior to the process and yet have a net output of exergy.

|  |  |
| --- | --- |
|  | (11) |

λ term is founded on the concept of reversible processes to develop the renewability analysis in a rational basis by thermodynamic parameters. For more details and applications refer to [51,53].

## 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 of feedstock/technology. Thus, Fig. 5 shows the systems performance concerning the Hydrothermal Liquefaction route, the main findings related to Fast Pyrolysis technology and the principal results associated with the Gasification Fischer-Tropsch configuration to illustrate the primary outcomes of the exergetic analysis.

In brief, the lower irreversibility rate was found on the wheat straw/HTL (25 MW), wheat straw/GFT (24 MW), and corn stover/FP (21 MW) feedstock/technology pairs. Consequently, these pathways presented the highest exergetic efficiency among the considered systems. In contrast, the sorghum bagasse/FP has the lowest estimated exergetic efficiency of all scenarios (21 pairs feedstock/technology, Fig. 5, due to the low H2 syngas composition and attributable to losses during the syngas upgrading process.

In light of these results, HTL and FPH pathways have a biofuel yields of 9.5 GJ/tdb. Particularly, marine biofuels produced via HTL and FPH routes from forestry and grain residues have comparable biofuel yields per year. In contrast, GFT yields are lower approximately 6.5 GJ/tdb, attributable to losses during the syngas upgrading step (*e.g.,* Sorghum GFT achieved the lowest yield of 5 GJ/tdb), due to the low H2 syngas composition.

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

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

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 addition, the exergy inputs, exergy output flows, and distribution of exergy destruction in the different units of the biorefinery configurations by processes are given in the Grassmann diagrams (Fig. 6). Later, the technical performance trade-off by technology and feedstock in terms of the average unitary exergy cost (AUEC) and the renewability exergy index (λ) is illustrated in Fig. 7. λ renewability performance was ranked as environmentally favorable for most configurations in this study. λ index trend was to increase according to the use of by-products into the supply chain (levels of integration) and also to avoid the external consumption of natural gas in the utility plant.

Furthermore, all the thermochemical pathways have a λ lower than 1 when using corn as a feedstock, indicating that these processes may not be considered renewable from the second law of thermodynamics point of view due to natural gas consumption as supplementary fuel. The same pattern was presented when adopted the FP system for wheat and sugarcane materials.

Figure 7 compares the technological configurations to verify the relation between λ renewability performance and the AUEC of these marine biofuel systems. In general, process performance results show higher exergy efficiencies and λ indexes for Gasification Fischer-Tropsch systems using Rice straw, Wheat straw, Sugarcane bagasse, and Sorghum bagasse as feedstock. In contrast, the AUEC parameter for these processes presents a reduction as a consequence of the irreversibility minimization.

At this point, it is important to mention that a key factor regarding the availability of feedstock for marine biofuel production is the capacity of the feedstock to comply with sustainability requirements. In this case, low-carbon marine fuels were assessed through the λ indexes focus on the industrial processes stage and emissions associated with land-use change or aspects related to impact on food prices and food security in the case of the AUEC term are not included in the scope of the study.

## CONCLUSION

This study used an integrated model to estimate the technical performance of marine biofuel supply chains through a trade-off linking the exergy efficiency and the thermodynamic losses. A comparison of lignocellulosic marine biofuels based on thermochemical production pathways and agroforestry raw materials was carried out. These results highlight the synergies between process efficiency and exergy-based indexes, indicating low-emissions alternative fuels for the maritime sector that could be implemented in national decarbonization strategies.

In general, a significant quantity of sustainable biomass could be produced in Brazil, which could represent advantages in the production of low-emissions alternative fuels for the maritime transportation sector taking into account the market potential for biofuels, particularly biofuel blends at the current volumes demanded by the shipping industry and new regulatory fuels requirements.

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 due to the low-hydrogen syngas composition and attributable to irreversibilities during the synthesis gas upgrading step.

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 that focus on the production of biofuels (from sustainable feedstocks) and marine blends/renewable bunker fuels.

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## NOMENCLATURE

Barrels per day (bpd)

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)

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Table 1. Agroforestry residues feedstocks composition

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** |  | **Eucalyptus Residues** | **Pine**  **Residues** | **Corn**  **Stover** | **Rice**  **Straw** | **Wheat**  **Straw** | **Sugarcane Bagasse** | **Sorghum** **Bagasse** |
|  | *Units* |  |  |  |  |  |  |  |
| 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 Matter Composition** | | | | | | | | |
| 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 |
| **Elemental Analysis** | | | | | | | | |
| C | %daf1 | 50.50 | 52.20 | 49.50 | 48.50 | 49.00 | 49.60 | 47.10 |
| H | %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 |

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

Which correlation for HHV and LHV?

Sumatorias = 100%

Table 2. Reactor conditions, yields, and heating values adopted in the HTL system

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Raw material** | **Reactor inlet** | **Reactor**  **yields** | | | | **Product**  **HHV** | |  | **Recyclate conversion** | | **Ref.** |
|  |  | *% of dry biomass* | | | | *(MJ/kg)* | |  | *% of recycled organics* | |  |
|  | H2O-feed ratio | Oil | Aqueous | Char | Gas | Oil | Char | Gas | Oil | Char |  |
| Eucalyptus | (6:1) | 23% | 16% | 27% | 19% | 27 | 26 | 4 | 5% | 15% | [23] |
| Pine | (6:1) | 35% | 35% | 6% | 18% | 25 | 29 | 4 | 8% | 23% | [24] |
| Corn | (8:1) | 23% | 38% | 9% | 14% | 30 | 26 | 2 | 5% | 15% | [25] |
| Rice | (6:1) | 24% | 11% | 31% | 20% | 26 | 18 | 4 | 5% | 16% | [26] |
| Wheat | (6:1) | 29% | 34% | 24% | 5% | 27 | 26 | 4 | 7% | 19% | [27] |
| Sugarcane | (6:1) | 25% | 39% | 22% | 4% | 25 | 24 | 4 | 6% | 16% | [27] |
| Sorghum | (5:1) | 42% | 19% | 23% | 17% | 30 | 30 | 4 | 10% | 28% | [28] |

Sumatorias = 100%

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

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** | **Reactor temp** | **Yields** | | | **Syngas Composition** | | | | | **HHV** | **Ref.** |
|  | *(oC)* | *% inlet feed* | | |  |  |  |  |  | *(MJ/kg)* |  |
|  |  | *Syngas* | Char | Liquid | H2(%) | CO(%) | CO2(%) | CH4  (%) | C2-C4  (%) | *Syngas* |  |
| Eucalyptus | 700 | 72% | 2% | 27% | 9% | 33% | 58% | 0% | 0% | 15.9 | [32] |
| Pine | 700 | 72% | 1% | 27% | 9% | 33% | 58% | 0% | 0% | 17.4 | [32] |
| Corn | 780 | 79% | 7% | 14% | 2% | 32% | 57% | 4% | 5% | 11.7 | [33] |
| Rice | 830 | 70% | 16% | 14% | 2% | 44% | 38% | 15% | 1% | 15.7 | [26] |
| Wheat | 830 | 54% | 20% | 26% | 2% | 33% | 42% | 11% | 11% | 15 | [34] |
| Sugarcane | 800 | 93% | 2% | 3% | 1% | 30% | 60% | 4% | 5% | 9.6 | [35] |
| Sorghum | 700 | 76% | 9% | 14% | 1% | 30% | 63% | 6% | 0% | 8.3 | [36] |

*C2-C4 refers to light hydrocarbons in the range of C2Hn and C4Hn*

Sumatorias = 100%

H2(%) mole fraction or weight percent?

Table 4. Fast pyrolysis parameters

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

Sumatorias = 100%

Table 5. Chemical exergies for several components

|  |  |  |
| --- | --- | --- |
| **Compound** | **MJ/kg** | **Ref.** |
| Light naphtha (*green naphtha*) | 44.5 | [50] |
| Jet fuel | 45.3 | [50] |
| Diesel | 44.2 | [50] |
| Heavy fuel oil (HFO) | 41.4 | [50] |
| 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 | [50] |
| Natural gas | 48.87 | [51] |
| Wood chips | 18.3 | [50] |
| Soy biodiesel | 40.1 | [52] |

\*Based on PCI (MJ/kg)

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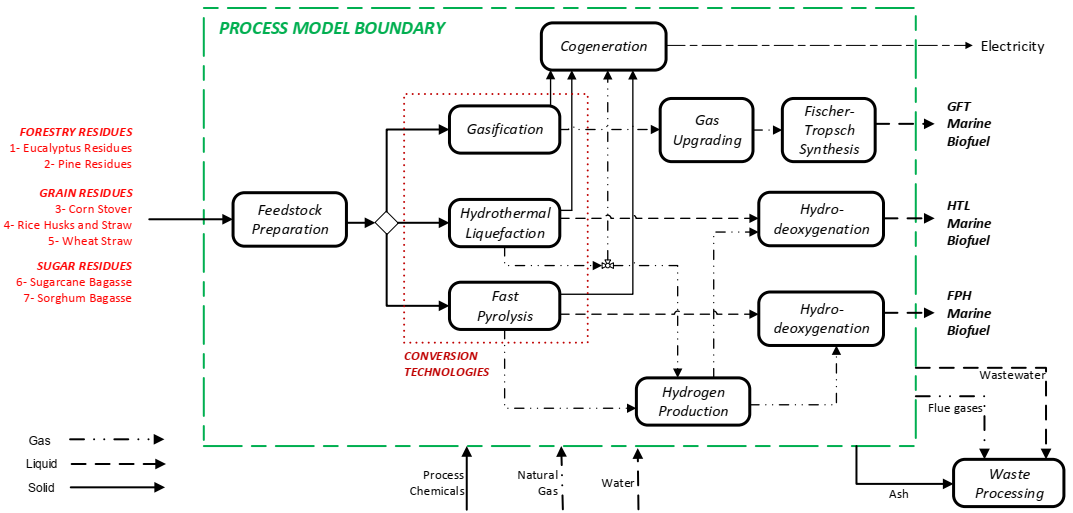


Figure 1. Processes boundary of thermochemical systems for marine biofuels production

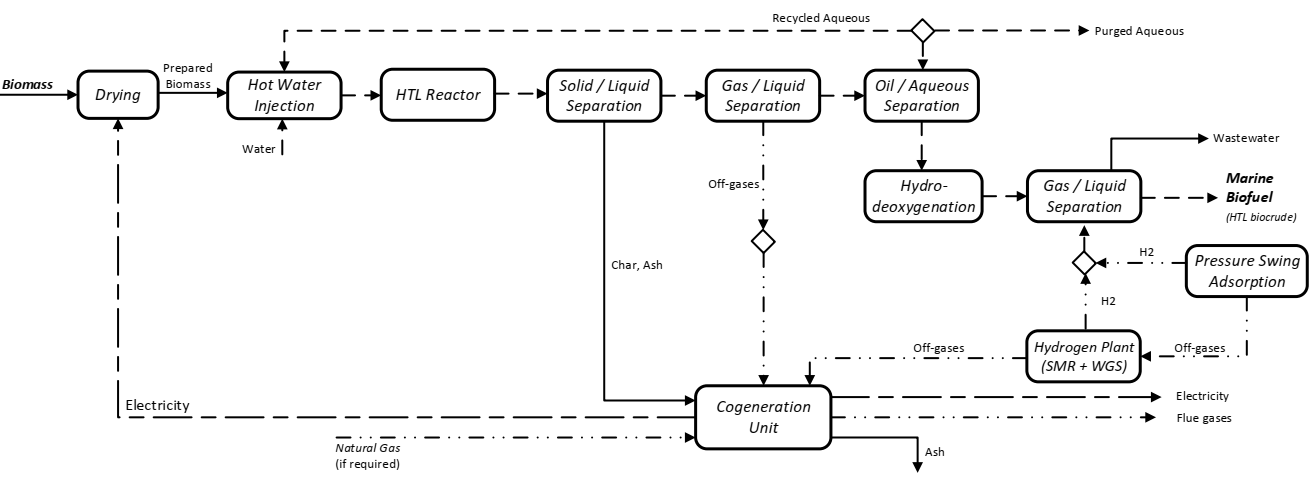


Figure 2. Hydrothermal liquefaction model

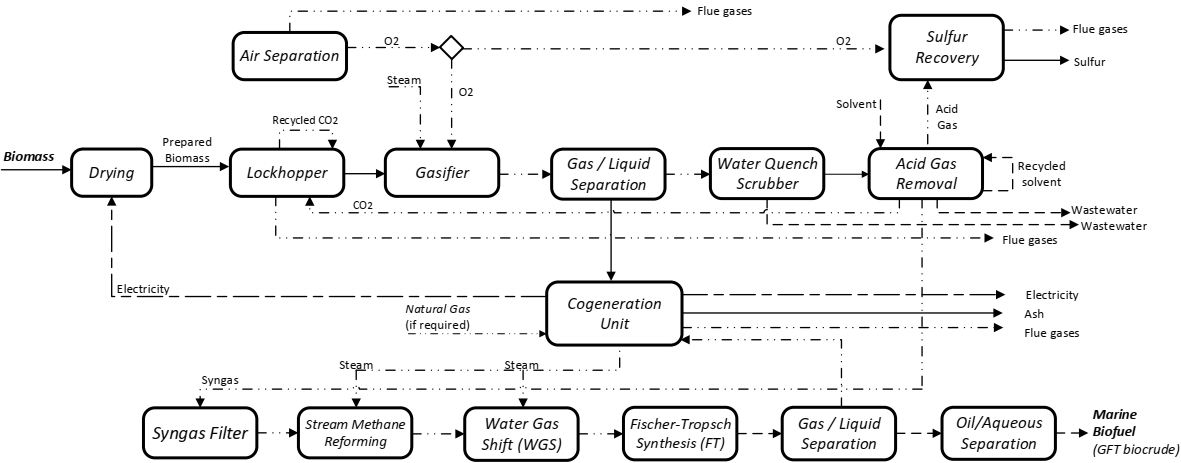


Figure 3. Gasification with Fischer-Tropsch model

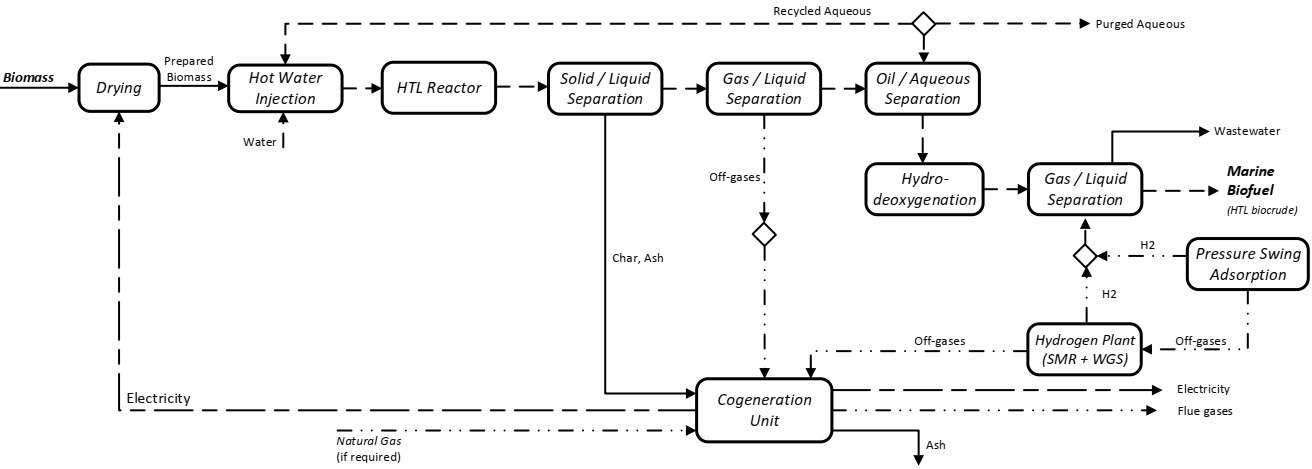


Figure 4. Fast pyrolysis model

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| --- |
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|  |

Figure 5. Systems technical performance of the configurations based on the exergetic efficiency and destroyed exergy rate

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|  |  |  |
|  |  |  |
| *a). Hydrothermal Liquefaction* | *b). Fast Pyrolysis* | *c). Gasification Fischer-Tropsch* |

Figure 6. Grassmann diagrams of the processes boundary adopted in the thermochemical pathways assessment

|  |
| --- |
|  |
| *a). Hydrothermal Liquefaction* |
|  |
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|  |
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Figure 7. Trade-off between the technologies and feedstocks pairs