

Exergy-based performance analysis for biojet fuel pathways in Brazil

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Abstract:

Increasing efforts in developing sustainable and economically viable technologies to produce transportation fuels have been made in the last decades. Particularly, the aviation industry has conceived that biojet fuels are vital to decrease 50% of the greenhouse gas emissions by 2050 and to achieve carbon-neutral growth by 2020. Thus, the goal of this study is to rank self-sufficient biorefineries for biojet fuel production in Brazil bases on an exergy-based performance analysis aiming to identify the processes irreversibilities. The production capacity assumed for this analysis covers 10% of the projected fuel demand by 2020 in São Paulo (*Guarulhos*) and Rio de Janeiro (*Galeão*) airports and considers that the biojet fuel produced is suitable for blending with fossil jet up to 50%. In this context, the base capacity analysed was 210 kton jet/year considering sugarcane (SC) and SC straw as feedstocks, largely available in Brazil. Hence, 24 scenarios were compared for lignocellulosic and lignin valorization processes. These technological pathways covers eight pre-treatment processes such as *dilute acid (DA)*, *dilute acid + alkaline treatment (DA-A)*, *steam explosion (SE)*, *steam explosion + alkaline treatment (SE-A)*, *organosolv (O)*, *wet oxidation (WO)*, *liquid hot water (LHW)* and *liquid hot water + alkaline treatment (LHW-A)*, followed by enzymatic hydrolysis. Furthermore, three thermochemical processes for the direct conversion of bagasse and lignin upgrade to renewable jet fuel or electricity were considered (*Fast pyrolysis*, *Gasification Fischer-Tropsch and Cogeneration*). The exergy assessment evidenced that combined pre-treatment processes with the alkaline treatment (DA-A, SE-A, LHW-A) have a better global exergetic performance than the lignocellulosic pre-treatments carried out standalone (DA, SE, O, WO, and LHW). In addition, the use of fast-pyrolysis as a technology for the lignin residues presented the higher performance for all the scenarios. It is shown that the CO₂ equivalent index and the renewability exergy index are appropriate metrics to determinate the environmental impact/renewability performance of the technological pathways. Lastly, the environmental analysis shows that all scenarios lead to a 30% reduction of specific CO₂ equivalent emissions in exergy base in comparison to the petroleum-based jet fuel impacts.

Keywords:

Exergy assessment, Environmental impact analysis, Biojet fuel production, Biorefinery design, Integrated biorefinery, Sugarcane and sugarcane straw.

1. Introduction

Biomass-derived jet fuel has turned into a strategic part in the aeronautics business to reduce ecological effects. Specialists from key segments, for example, the oil-refining and aircraft industry, government, biofuel businesses, agricultural groups, and academia are jointly working to develop sustainable and commercially viable processes to obtain biojet fuels (biokerosene) with lowest production costs possible to allow low greenhouse gas (GHG) emissions [1]. For instance, IATA recognizes the need to address the global challenge of climate change and adopted a set of targets to mitigate CO₂ emissions as industry priorities from air transport (*i. Achieve an average improvement in fuel efficiency of 1.5% per year from 2009 to 2020; ii. Carbon-neutral growth from 2020, iii. A reduction in net aviation CO₂ emissions of 50% by 2050, relative to 2005 levels*) [2]. Furthermore, for commercial utilization these fuels must comply with the ASTM International standards to be considered a drop-in substitute for the petroleum-based aviation fuel [1].

In this context, biomass conversion systems should be developed using advanced conversion routes to compete with fossil fuels, *i.e.* Alcohol-to-jet (ATJ), Hydroprocessed esters and fatty acids (HEFA), Fischer-Tropsch synthesis (FT), Aqueous phase reforming (APR), Direct sugar to hydrocarbon (DSHC), and Hydrotreated depolymerized cellulosic jet (HDCJ). These promising configurations for production of the biojet fuel are classified based on the raw materials and the conversion process routes. In addition, in order to assess technological pathways, techno-economic and environmental analysis are performed to support the decision-ranked. Hence, techno-economic analysis and environmental performance have already been reported considering the biojet fuel production supply chains of these production pathways [3–5].

However, even though many studies have reported these kinds of analysis, a multi-criteria approach founded on complementary methods (*i.e.* exergy analysis, environmental assessment-GHG emissions, and renewability exergy criteria) to rank biojet fuel pathways has not yet found in the literature. Consequently, in this work, a multi-criteria analysis to assess 24 technologies for producing biojet fuels using key performance indicators, such as *exergy efficiency, carbon dioxide equivalents (CO_{2e}) emission in exergetic base and, renewability exergy index* are considered into a Brazilian sugarcane biorefinery. Moreover, comparison metrics used for each technology pathways including the Average unitary exergy cost (AUEC) and the Irreversibility to exergy ratio (I/Bp) were investigated.

The multi-criteria analysis was development through technical performance indicators looking for sustainable bio-based production chains, exemplified with the renewable jet fuel demand planning to supply 10% (210 kton_{biojet}) of the 2020 interest of two major air terminals in São Paulo (Guarulhos) and Rio de Janeiro (Galeão), Brazil [5–7]. The specifics of each technological element of the biojet fuel pathway are selected based on the literature review and on previous studies for techno-economic and environmental assessment of biojet fuel production technologies [6,8,9].

Figure 1 shows the selected pathways for biojet fuel and electricity production from lignocellulosic resources and sugar-bearing crops [10].

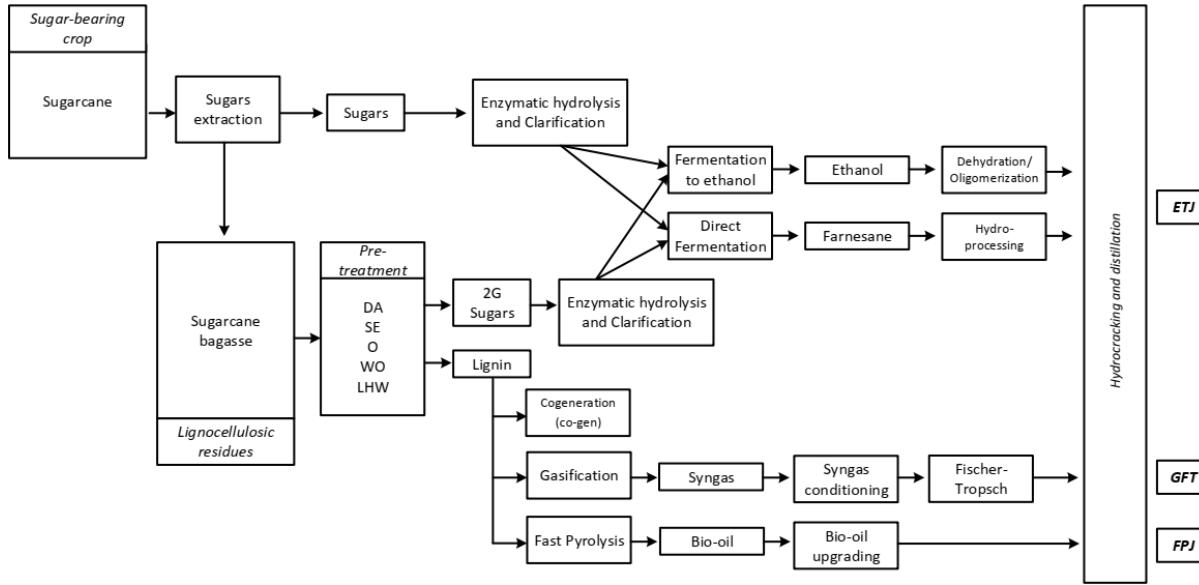


Figure 1. Selected Pathways for biojet fuel production (adapted from [10]).

2. Description of processes and technologies for biojet fuel pathways

24 biorefinery pathways are analyzed based on *i)* use of first-generation 1G sugars (*i.e.* full use for biojet fuel production; and *ii)* use of sugarcane bagasse (*i.e.* pretreatment for second-generation 2G sugars recovery or direct conversion into biojet fuel).

For bagasse pre-treatment are evaluated, eight technologies, dilute acid (DA), dilute acid + alkaline treatment (DA-A), steam explosion (SE), steam explosion + alkaline treatment (SE-A), organosolv (O), wet oxidation (WO), liquid hot water (LHW) and liquid hot water + alkaline treatment (LHW-A)) [5]. After pre-treatment, the resulting streams go through the detoxification and enzymatic hydrolysis steps prior to fermentation as presented in Figure 1.

In case of the lignin fraction, three possibilities are taken into account: Cogeneration (co-gen), Biojet fuel production via fast pyrolysis (FPJ), Biojet fuel production via gasification Fischer-Tropsch (GFT). Moreover, auxiliary sections are considered for each biorefinery scenario (*i.e.* wastewater treatment, WWT and H₂ steam methane reforming, H₂ SMR).

2.1. Production technologies and processing conditions

A sugarcane field with a productivity of 12000 ton sugarcane day⁻¹ (maximum SC milling capacity) was selected as it denotes the state-of-the-art processing capacity of a sugarcane mill (typical operation period is 200 days a year on average) in the São Paulo State, Brazil.

The biorefinery is mainly divided into four different areas: *SC milling, bagasse pre-treatment, fermentation and upgrade (fermentation and intermediate products upgrade to biojet / Thermochemical upgrade of lignin and bagasse to biojet), and auxiliary sections.*

2.1.1. Sugarcane milling

First, sugarcane is grown in the fields, mechanically harvested, transported to the mills, and then fractioned into juice and bagasse. The sugarcane juice stream follows the 1G fermentation pathway, while bagasse follows the 2G pathway, *i.e.* pre-treatment and fractionation into hemicellulose, cellulose and lignin streams.

Tables A.1 presents the operation parameters of milling process. The detailed composition of stalks and bagasse after milling, field productivity and harvesting season for both feedstocks is summarized in [5].

2.1.2. Bagasse pre-treatment technologies

Initially, the pre-treatment methods selected were diluted acid (DA), steam explosion (SE) and liquid hot water (LHW), which produce two streams after your operation: *Hemicellulose hydrolysate and Cellulolignin*. The former undergoes to detoxification while the latter stream is washed and re-filtered, at that point, both are sent to enzymatic hydrolysis, after pH adjustment to 5 [11]. The principle contrasts between these pre-treatments are focused on the solids loading and the kind of catalyst used (H_2SO_4 , SO_2).

Next, Organosolv (O) and Wet oxidation (WO) pre-treatment process selected. In the Organosolv process combined with acid catalysis, the lignin solubilisation is guaranteed by the use of acetone in the pre-treatment [12]. In addition, wet oxidation with Na_2CO_3 allows the solubilisation of lignin [5]. Both O and WO incorporate lignin precipitation by means of lignobost.

When alkaline (A) pre-treatment is adopted, *Cellulolignin* is split into cellulose and black liquor. The latter comprises solubilized lignin that is later precipitated via *lignobost* method [5]. Lignobost hydrolysate stream is then detoxified, alongside hemicellulose hydrolysate. The specifications used in the pre-treatment stage are found in [13]. The reactions considered in the simulation of the enzymatic hydrolysis process for the 2G ethanol production are shown in [14].

2.1.3. Fermentation and intermediate products upgrade to biojet

The Ethanol-to-Jet technology (ETJ) was the fermentative pathway here adopted. Thus, C5 (Pentoses) and C6 (Hexoses) sugars are converted into ethanol, which is recovered through distillation. Afterwards, ethanol is dehydrated to ethylene, then condensed to butylene and later oligomerized. Hydrogenation and distillation permit the recovery of biojet fuel and fuels [5].

Ethanol upgrade to jet occurs through a dehydration step and then the alkene formed (either ethylene or butylene) is oligomerized into a range of olefins that are hydrogenated (*unsaturated double bonds are saturated with hydrogen to generate paraffins*). The final process stage is product separation by distillation [15]. Tables A.2 presents the parameters considered in ethanol upgrade to jet process.

2.1.4. Thermochemical upgrade of lignin and bagasse to biojet

Fast Pyrolysis (FPJ) and Gasification Fischer-Tropsch (GFT) are here selected as the thermochemical technologies for lignin and bagasse conversion, with subsequent upgrading into renewable jet fuel (RJF). Since GFT and FPJ are mature technologies and are ASTM approved for 50% blending with fossil jet fuel [16].

Fast Pyrolysis Jet process has three main sections: fast pyrolysis, hydrotreating, and hydrocracking. Initially, dried biomass is thermochemically decomposed in the pyrolysis reactor with gaseous phase recycling, where bio-oil is recovered after quenching [5]. Then, Bio-oil is hydrotreated and de-oxygenated, and later several biofuels are obtained via distillation process. Lastly, the heavy-oil fraction is hydrocracked and distilled to improve the biojet fuel yield [17].

Gasification Fischer-Tropsch process comprises the following steps: Biomass conditioning, gasification (*syngas with H_2/CO ratio above 2.1*), syngas cleaning, H_2 Steam methane Reforming (SMR) section (*to reduce CH_4 in the outlet to 1.5%*), and water gas shift (WGS) to adjust the ratio to level of 2.2 [6]. Thus, the produced syngas subsequently undergoes the Fischer–Tropsch reaction to convert syngas into new hydrocarbons (in general a paraffinic kerosene-like mix) and water. Tables A.3 and A.4 presents the equipment specifications in GFT and lignin FPJ processes, respectively.

2.1.5. Auxiliary sections

Auxiliary sections are provide or exchange different utilities and services to the biorefinery such as wastewater and clean water (WW), flue gas and H_2 cleaned stream (with hydrogen steam methane reforming - H_2 SMR), solid waste streams or lignin and electricity and steam (cogeneration).

The SMR process supplies the hydrogen required for the FP route while in the case of the GFT technology, hydrogen requirements are covered by the syngas stream obtained in the biomass gasification.

3. Methodology

The methodology for the multi-criteria approach include mass, energy and exergy balances of each configuration based on theoretical and empirical correlations to determine the thermodynamic properties models of each biorefinery system. Then, exergy efficiencies, irreversibility rates and the exergy use/exported per unit of products, as well as the environmental metric (*i.e* specific CO₂ equivalent emissions in exergetic base) related with the conversion processes were considered as indicators, allowing a systematic comparison founded on an exergy-based performance analysis of the sugarcane biorefinery pathways.

3.1. Process simulation

The process simulations use the biofuel database and overall thermodynamic method as reported for the NREL Aspen model for steam explosion of corn stover [18]. Hence, NRTL is the chosen method. For flash vessels the NRTL-RK (with equation of state Redlich Kwong) is chosen. For reactors, NRTL-HC, method is selected, which was also done in the NREL simulation. Then, in acetic acid recovery section NRTL-HOC method is selected which is specifically indicated for carboxylic acids simulations, as suggested by [5]. Related to the reference conditions, 298.15 K 1 atm were used as ambient conditions.

3.2. Exergy assessment

The exergy method, which combines the First and Second Law of Thermodynamics, was used to assess the efficiency of the sugarcane-based biorefineries for biojet fuel production. Exergy is defined as thermodynamic propensity that represents the maximum work that could be obtained by means of reversible processes from a system that interacts with the components of the environment until the equilibrium state (mechanical, thermal and, chemical) is attained [19]. Consequently, exergy analysis provides an effective metric for evaluating the quality and quantity of a resource, as it denotes the maximum of this resource that can be converted into work, given the prevailing environmental conditions [20].

3.2.1. Exergy balance

The sugarcane biorefinery scenarios are based on the calculation of the steady-state mass, energy, and exergy balances, according to Equations (1-3), respectively for each one of the control volume.

$$\sum_{inlet} \dot{m}_i = \sum_{outlet} \dot{m}_e \quad (1)$$

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

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

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). In this work, the chemical (b_{CH}) and physical (b_{PH}) exergies are measured due to the physico-chemical processes involved. Thus, b_{PH} was determinate according to equation (4).

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

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_0 (in K) is the Temperature at the reference state, H_0 (in kW) denotes the Enthalpy flow rate at P_o, T_o and S_0 (in kW/K) is the Entropy rate/flow rate at P_o, T_o.

For the majority of natural resources including lignocellulosic resources other chemical-based raw materials, the chemical exergy is the most important contribution to its exergy value [21].

Conceptually, b_{CH} quantifies the value of a chemical substance, or compound, as measured against a selected reference environment [22]. Equation (5) defines the chemical exergy:

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

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. Hence, the influence of Y was evaluated for each compound permitting to observe that it offers values close to one. Consequently, Y was adopted equal to one, an ideal solution, in mixtures for b_{CH} calculations [13]. The term b_i^{ch} represented the standard chemical exergy. The chemical exergies for various compounds are found in the [19] and [23].

Lastly, the ***exergy efficiency*** for the biorefinery pathways is determinate by the ratio between the exergy of the products and the exergy of the resources, as indicated in Eq. (6).

$$\eta_B = \frac{\sum \dot{B}_{products}}{\sum \dot{B}_{resources}} \quad (6)$$

3.3. Performance analysis of the sugarcane biorefineries

The interconnection between exergy and environmental analysis, renewable share and exergy efficiency are suggested to determinate the global performance of the sugarcane biorefinery scenarios.

3.3.1. Renewability exergy index (λ)

In this study, the exergo-environmental discussion regarding the renewability for the sugarcane biorefineries was conducted through the *renewability exergy index* (λ) [24]. The use of reversible processes concept, the one that having occurred can be reversed to the initial system and surroundings states, in the analysis of the renewability of energy conversion processes can contribute to develop such analysis in a rational basis by using thermodynamic parameters [25].

On the basis of these aspects, the renewability exergy index considers the exergy associated to the useful products ($B_{products}$ or *by-products*) of a given energy conversion process, the destroyed exergy ($B_{destroyed}$), and the exergy associated with chemical inputs (B_{fossil}), the exergy required to dispose wastes, and the exergy related to emissions, residues and untreated wastes, as presented in equation (7):

$$\lambda = \frac{\sum B_{products/byproducts}}{B_{fossil} + B_{destroyed} + B_{deactivation} + B_{disposal} + \sum B_{emissions/residues}} \quad (7)$$

Depending on the value of the λ index, it indicates: *i*). $0 \leq \lambda < 1$ for processes that are environmentally unfavourable; *ii*). $\lambda = 1$, for internally and externally reversible processes with non-renewable inputs; *iii*). $\lambda > 1$ for processes environmentally favourable; and *iv*). $\lambda \rightarrow \infty$, for reversible processes with renewable inputs and with no wastes generated.

When the renewability exergy index is higher than 1, the $B_{products}$ could be used to "restore" the environment to the conditions prior to the occurrence of the process and still obtain a positive flow of exergy to another use. It is emphasized that λ has a strong relationship with the control volume (CV) analyzed, due to the number of energy conversion processes being involved. Thus, when the adopted CV is expanded, the value of λ is decreased as a function of the irreversibility and the contribution of non-renewable (fossil) inputs to the process. For this reason, it is important to ensure the compatibility of the CV when different systems are compared to prevent distortions into the analysis.

3.3.2. Average unitary exergy cost (AUEC)

Exergetic cost is a value accounting for the external exergy necessary to render an exergy flow available within a specific productive process [26]. The AUEC is a conservative measure of the cumulative irreversibility and exergy consumption, which occurs in the upstream processes to form a particular exergy stream. Consequently, higher irreversibilities translate into a higher unit exergy costs.

3.3.3. Irreversibility to exergy (I/B_p) ratio

The ratio between irreversibility and exergy of the products ratio (I/B_p) ratio (in kW/kW) represents the exergy destroyed with respect to the sum of the exergy in the products, as given in (8).

$$I/B_p \text{ ratio} = \frac{\text{Irreversibility}}{\sum \dot{B}_{\text{products}}} \quad (8)$$

3.3.4. Specific CO₂ equivalent emissions in exergetic base (CO₂ EE)

The environmental analysis comprises calculations for GHG emissions in a *cradle-to-gate* plus the cogeneration unit boundaries, with respect to the exergy of the products. The mass allocation was applied to determinate specific GHG emissions of the biorefineries configurations to the biojet fuel. Individual environmental impact factor per type of process input (*e.g.* feedstocks, and utilities) are included in Table A.5. This approach is commonly applied in the bioenergy sector [27–29]. The impact assessment method selected was '*cane sugar production with ethanol by-product*' (Brazilian case-Activity) [30]. The Global Warming Potential (GWP) 100 years is selected as environmental performance indicator, in combination with the exergy of the products for each biorefinery configuration. Hence, it is denominated *specific CO₂ equivalent emissions in exergetic base* (CO₂ EE), as given in (9).

$$CO_{2 \text{ EE}} = \frac{\text{Global CO}_2 \text{ equivalent emissions}}{B_{\text{products}}} \quad (9)$$

4. Results

From the mass and energy balances and the thermodynamic models adopted in the biorefineries scenarios, the processes were completely defined. Thus, this information was used to evaluate the configurations performance according to technical, environmental and economical exergy-based criteria, previously established. The main key performance indicators for each renewable jet fuel pathway are summarized in Table A.6.

4.1. Exergy assessment

In this section, the results of the exergy performance for the 24 biorefinery scenarios is presented in Figure 2. It is noted in the evaluated bagasse pre-treatment methods, that the wet oxidation (WO) process reported the higher exergy efficiency. Following by the organosolv (O-AA) technology Included the acetic acid recovery.

In general, it was obtained a better performance combined the pre-treatment processes with the alkaline treatment (DA-A, SE-A, LHW-A), than the lignocellulosic pre-treatments carried out standalone (DA, SE, O, WO, and LHW).

On the other hand, Figure 2 represented the alternative uses for the lignin destination (FPJ, GFT and CO-GEN). Predominantly, it is emphasized that the global exergy efficiency stated better performance for the scenarios that use Fast-pyrolysis (FPJ) as technology.

In this figure, the colour convention is focused on the technologies for the final use of the lignin residues. Thus, the blue bar represents the fast pyrolysis process (FPJ), the red bars are related to the Gasification followed by Fischer–Tropsch process (GFT), and grey bars indicated the cogeneration system.

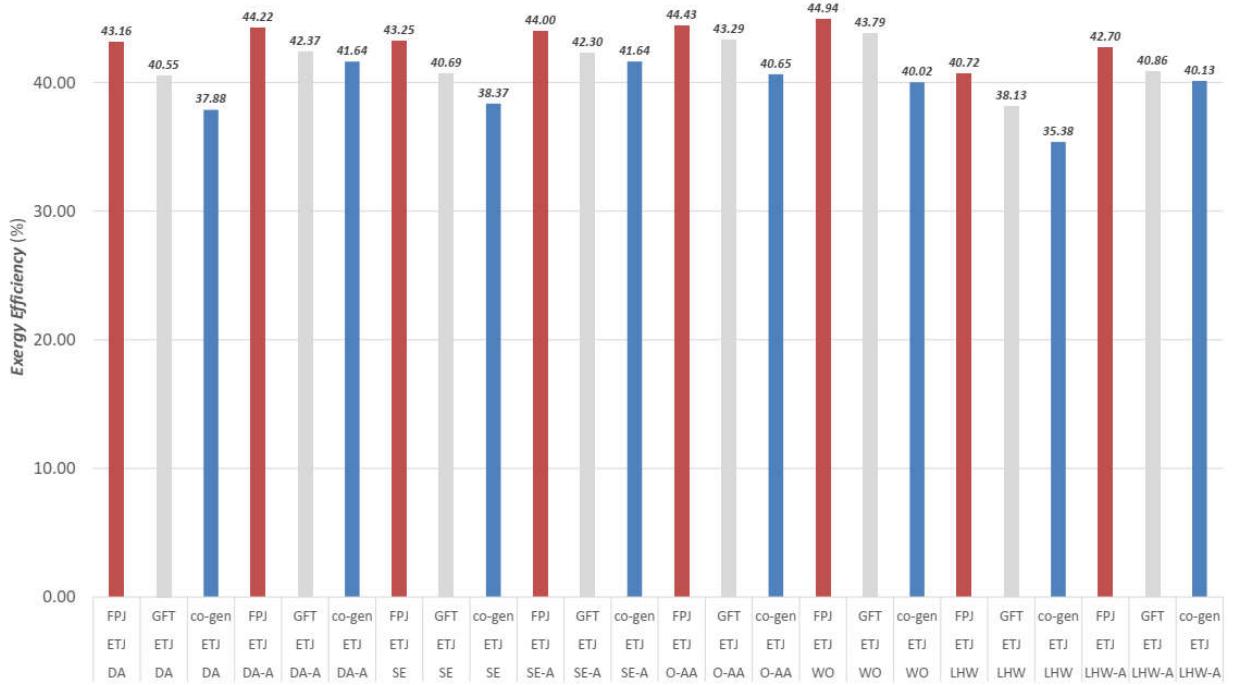


Figure 2. Exergetic efficiency of the biorefineries configurations.

4.2. Performance analysis for biojet fuel pathways

4.2.1. Renewability exergy index

This index considered the exergy of the products (biojet fuel and electricity) that could be obtained through the residues processing. The results of the renewability exergy index are shown in Figure 3.

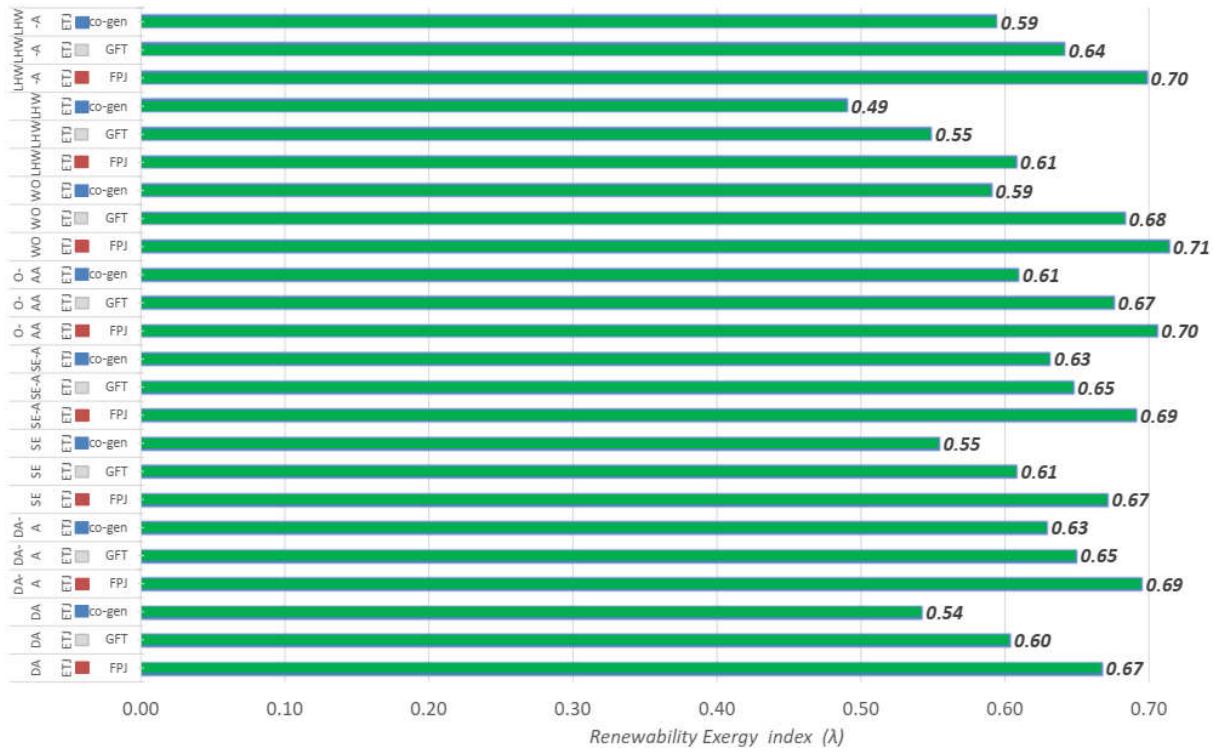


Figure 3. Renewability exergy index of the technological biorefinery.

In this figure, the green bars denoted the renewability exergy index (λ) of the biojet fuel pathway. In addition, the previous colour convention was maintained for the final use of the lignin. Hence, the blue squares indicated the FPJ process, the red squares are associated to the GFT process, and grey squares designated the cogeneration system. Furthermore, the Ethanol-to-Jet (ETJ) process is pointed on the Y-axis.

It is observed that the λ index for the evaluated sugarcane biorefineries was environmentally unfavourable for all the 24 scenarios, indicating that the exergy of the products could not be used to restore the environment to the prior conditions to the occurrence of the process. This is mainly due to the total irreversibility found in the biojet fuel production and electricity generation processes.

Similarly, Figure 3 indicated that λ index presented better performance for the biorefinery scenarios that use Fast-pyrolysis as a method for the lignin destination, stating the relationship between the technological pathways renewability and the exergetic performance.

4.2.2. Average unitary exergy cost

The exergetic cost is the measure of the cumulative irreversibility and exergy consumption, which occurs in the biojet fuel. Thus, the AUEC of the 24 configurations was calculated for each biorefinery in Figure 4. It should be noted that the lower exergy cost of the systems was obtained in the FPJ technology as alternative to the lignin destination. In this figure, the orange bars denoted the average unitary exergy cost (in kJ/kJ) of the biojet fuel pathway. Furthermore, the previous colour convention was maintained for the final use of the lignin on the Y-axis.

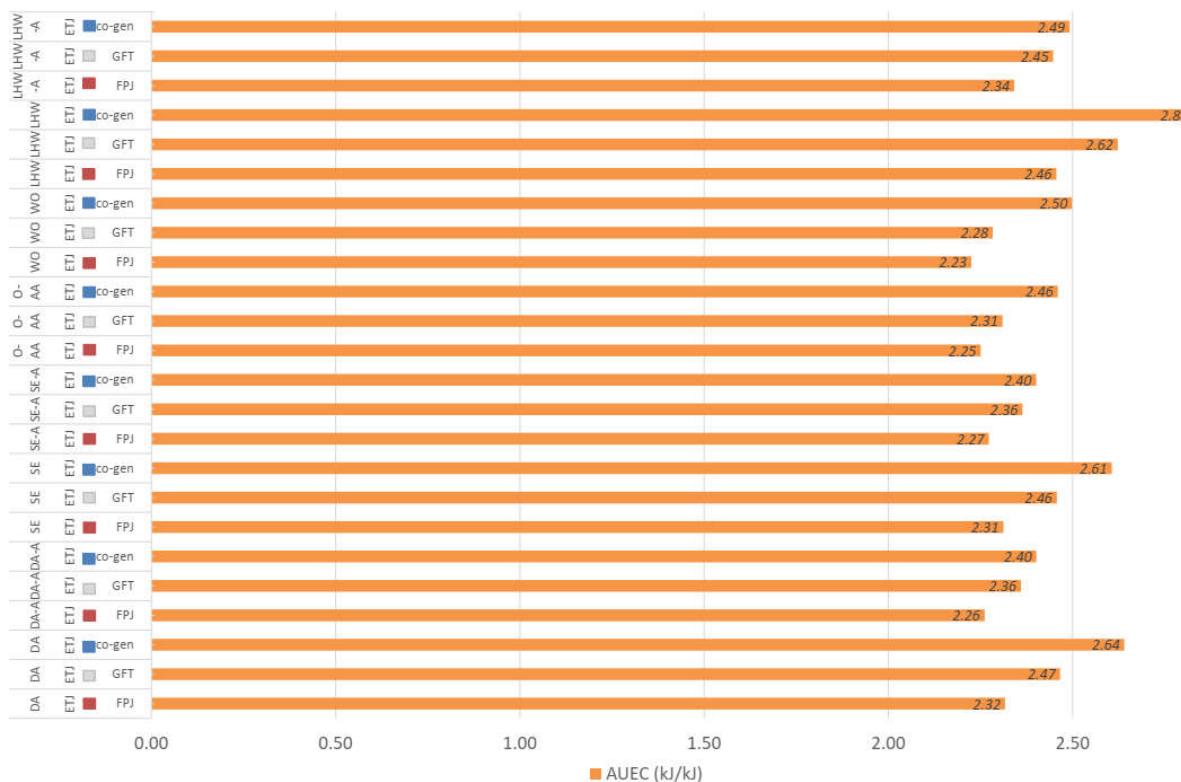


Figure 4. Performance indicator-Average unitary exergy cost.

4.2.3. Irreversibility to exergy ratio

In addition, the I/B_p ratio presented a complementary indicator to assess the sugarcane pathways, which represents the irreversibility with respect to the total exergy of the products. It was identified that the higher ratio of the systems occurs when the cogeneration (co-gen) technology is used as an alternative to the lignin destination as given in Figure 5.

Consequently, higher irreversibility to exergy ratio translates into a lower exergy efficiency (*Fig. 2*) and higher unit exergy costs (*Fig. 4*), stating the relationship between the global exergy performance and (I/Bp) ratio.

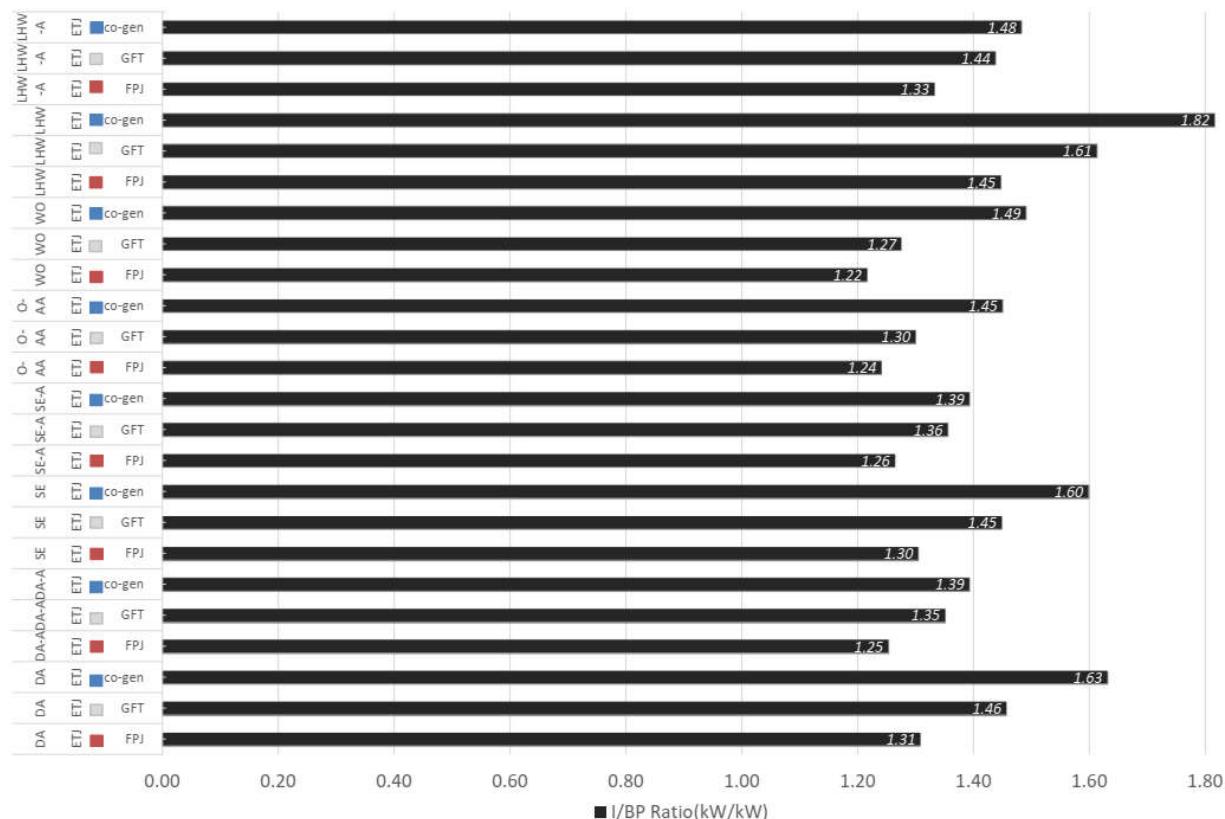


Figure 5. Performance indicators-Irreversibility to exergy ratio.

The black bars indicated the irreversibility to exergy ratio (in kW/kW) of the biojet fuel pathway. Furthermore, the previous colour convention was maintained for the final use of the lignin on the Y-axis.

4.2.4. Environmental performance: Specific CO₂eq emissions in exergetic base

Figure 6 depicts the specific CO₂ equivalent emissions in exergy base for the sugarcane biorefinery pathways. It must be underlined that all cases should lead to, at least, 30% decrease of environmental impacts when compared to the fossil jet fuel emissions, which is 85 kg CO₂ GJ⁻¹ [31].

The colour convention presented in Figure 6 is focused on the technologies for the lignin final use. Thus, the blue bar represents the fast pyrolysis process (FPJ), the red bars are related to the Gasification followed by Fischer–Tropsch process (GFT), and grey bars indicated the cogeneration system.

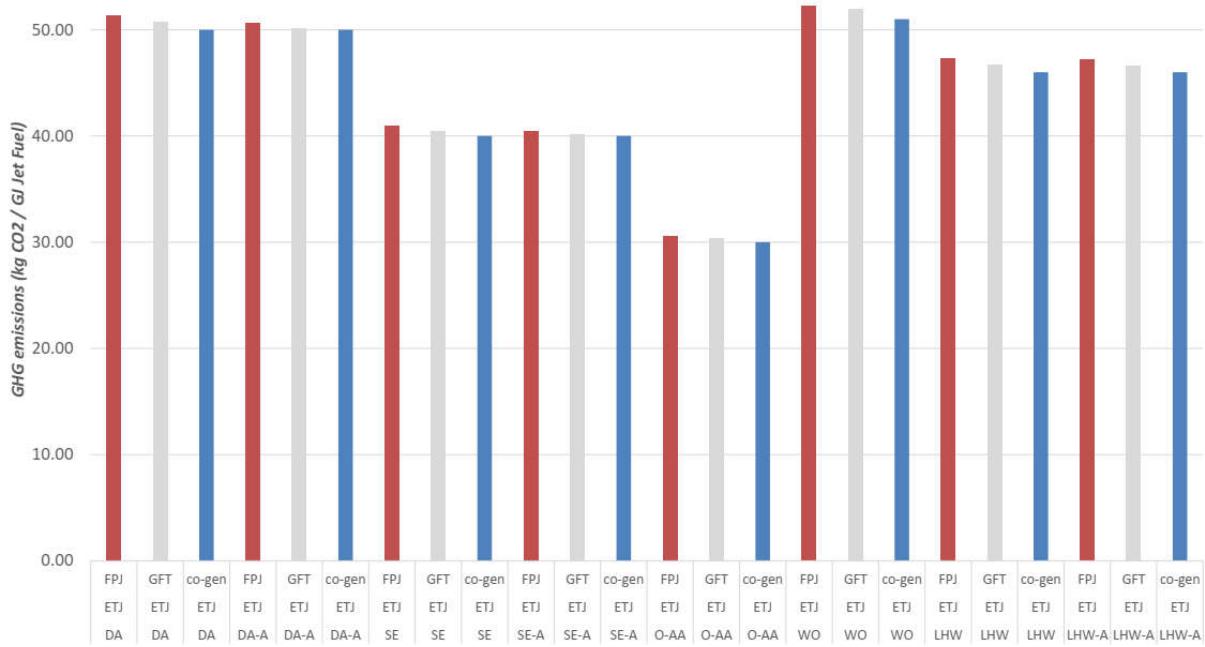


Figure 6. Environmental performance for the biorefinery scenarios.

Pathways adopting dilute acid (DA), dilute acid + alkaline treatment (DA-A), and wet oxidation (WO) as bagasse pre-treatment technologies were ranked as the systems with higher emissions within the 24 biorefineries. On the other hand, steam explosion (SE), steam explosion + alkaline treatment (SE-A), organosolv (O) were steadily below the emission targets because of higher biojet fuel yield.

Thus, through the application of the CO₂ equivalent indicator in exergetic base and renewability exergy index, the exergy concept was used as an environmental metric to quantify the processes irreversibilities and to determine the presence of traces left in the surroundings.

4.3. Comparisons of the production pathways for renewable jet fuel

In terms of the biojet fuel production when compared with the scenarios evaluated by Klein et al. [32], involving configurations based on the integration of 1G and 1G-2G technologies were reported for the exergy performance of the Fischer-Tropsch (FT) scenario 25 % and 60 % for the Alcohol-to-jet (ATJ), respectively. In order to synthesize the main results explored by [32] the parameters considered in the assessment of these biomass conversion technologies are shown in Table 1.

Table 1. Parameters of renewable jet fuel pathways.

RJF route Scenario	FT		ATJ		
	RJF feedstock	FT1 Sugarcane SC	FT2 SC + Eucalyp.	ATJ1 1G EtOH	ATJ2 1G2G EtOH
Exergy Efficiency (%)	25.15	22.33	59.54	59.88	
B _{inputs} [MW]	732.75	1993.14	318.50	416.62	
B _{outputs} [MW]	184.26	445.09	189.62	249.48	
Irreversibilities [MW]	548.50	1548.05	128.88	167.14	
I/Bp ratio(kW/kW)	2.98	3.48	0.68	0.67	
AUEC (kJ/kJ)	3.98	4.48	1.68	1.67	

The irreversibility reported was obtain by applying the exergy balance expression introduced in Eq. (3), and the exergy efficiency performance was calculated by using Eq. (8). Furthermore, the relation between the Irreversibility (I) and the exergy of the products (B_p) for these configurations was determined (I/B_p ratio) by Eq. (7). The specific exergy values of the inputs considered were: Sugarcane 5130 kJ/kg, Straw 16725 kJ/kg, and Bagasse 9667 kJ/kg. Concerning the exergy of the products, it was adopted for sugar 17479 kJ/kg and for ethanol 27042 kJ/kg, respectively.

5. Conclusions

A multi-criteria decision support analysis to rank 24 promising biojet fuel pathways in Brazil based on the application of key performance indicators, allowed to quantify the irreversibility of these technological scenarios and to determine the environmental impact.

Regarding the exergy-based performance analysis, it was found that the renewability exergy index presented a better performance for all the scenarios that use fast-pyrolysis as a technology for the lignin destination. Spite of sugarcane biorefineries were ranked as environmentally unfavourable, which indicated that the exergy of the products could not be used to restore the environment to the prior conditions to the occurrence of the process. The exergy assessment proved that combined pre-treatment processes with the alkaline treatment (DA-A, SE-A, LHW-A) has a higher global exergetic performance than the lignocellulosic pre-treatments carried out standalone (DA, SE, O, WO, and LHW).

Complementary indicators allow calculating the average unitary exergy cost and the irreversibility to exergy ratio of the technological pathways. These metrics stating the relationship between the global exergy performance and exergy destruction rate, respectively.

Lastly, the environmental performance using the CO₂ equivalent index and the renewability exergy index as impact/renewability metrics shows that all scenarios lead to a 30% reduction of specific CO₂ equivalent emissions in exergy base in comparison to the petroleum-based jet fuel impacts.

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Nomenclature

B	Exergy flow rate (kW)
b	Specific exergy (kJ/kg)
bch	Standard chemical exergy (kJ/kg)
CO ₂ EE	Specific CO ₂ equivalent emissions (<i>exergetic base</i>)
CV	Control volume
h	Specific enthalpy (kJ/kg)
\dot{m}	mass flow rate, (kg/s)
P	Pressure (kPa, bar)
Q'	Heat rate (kW)
s	Specific entropy (kJ/kg K)
t	temperature, (°C, K)
W'	Power, (kW)
x	Mole or mass fraction

Abbreviations

- Aqueous phase reforming (APR)
- Alcohol-to-jet (ATJ)
- Direct sugar to hydrocarbon (DSHC)
- Ethanol-to-Jet (ETJ)
- Fischer-Tropsch (FT)
- Hydrotreated depolymerized cellulosic jet (HDCJ)
- Hydroprocessed esters and fatty acids (HEFA)
- Hydrogen steam methane reforming (H₂SMR)
- Gasification Fischer-Tropsch (GFT)
- Greenhouse gas emissions (GHG)
- Wastewater treatment (WWT)

Greek symbols

- η efficiency
- λ Renewability exergy index

Appendices

Table A.1. Operation parameters of milling process.

<i>Unit</i>	<i>Condition</i>	<i>Value</i>
<i>Cleaning and crushing</i>	Water make-up (m ³ /TC)	0.05
	Fibers separation efficiency (%)	100
	Bagasse moisture (%)	53.82
	Imbibition water (ton/TC)	0.280
	Imbibition water recycling (%)	100
<i>Liming settling and filtration</i>	Sugars (sucrose, glucose) recovered (%)	95
	H ₃ PO ₄ (kg /ton SC)	0.2
	CaO (kg/TC)	1
	Flocculant polymer (g/TC)	2.5
	Fraction of soluble solids retained in filter	65%
	Fraction of insoluble solids precipitated (%)	99.70%
	Washing water (kg /kg sugars)	8.19
<i>Juice concentration</i>	Pressure in 5 _{th} effect (bar)	0.16
	Temperature in 1 _{st} effect (°C)	115
	Juice solids content to sell (%)	65
Juice solids content to fermentation (%)	Defined in fermentation with constrains: -final solids content ≤ 65% -EtOH conc. end of fermentation ≤10%	

The technical parameters of this section are based on [5].

Table A.2. Operation parameters considered in ethanol upgrade to jet process.

<i>Unit</i>	<i>Condition</i>	<i>Value</i>
<i>Pump</i>	ΔP (bar)	4
<i>Dehydration reactor</i>	P (bar) / T ($^{\circ}$ C)	4 / 375
	Catalyst used	Heterogeneous, 0.5%La–2%P H-ZSM-5
	Reactor specifications	Multi-tubular fixed bed in a furnace
<i>Decanter</i>	Fraction of components in the gas outlet	
	Water	1.16%
	ethylene	100%
<i>Compressor</i>	ΔP (bar)	30
<i>Oligomerization reactor – butylene synthesis</i>	P (bar) / T ($^{\circ}$ C)	30 / 200
<i>Oligomerization reactor – butylene oligomerization</i>	P (bar) / T ($^{\circ}$ C)	89 / 200
<i>Oligomerization general</i>	Catalyst	Ziegler Natta-type
	Reactor type	Fixed bed
<i>Compressor of H₂</i>	ΔP (bar)	30
<i>Hydrogenation reactor and decanter</i>	P (bar) / T ($^{\circ}$ C)	30 / 250
	Catalyst	palladium and platinum over GAC
	WHSV (h-1) w/w	3
	Life-time (years)	5
	H ₂ requirement (kg / kg olefins)	0.05
	H ₂ excess	50% of amount reacted
	Live steam required (kg/kg paraffin)	0.258
<i>Steam distillation</i>	Fraction of compounds in LPG stream	
	LPG	97%
	Naphtha	32%
	Water	2.38%
	Fraction of compounds in naphtha stream	
	LPG	3%
	Naphtha	62%
	Water	0.01%

Adapted from [5].

Table A.3. Operation parameters considered in lignin fast pyrolysis.

Unit	Condition	Value
Lignin dryer	Max. lignin moisture	8%
	T final (°C) of FPJ-3	307
	Air make-up (kg air/kg water evaporated)	2.605
Lignin grinder	Diameter of lignin particles (mm)	≈2
Fast pyrolysis fluidized auger bed	P (bar) / T (°C) / Residence time (s)	1.5 / 500 / 2
	Sand/biomass (kg/kg)	14.5
	Fluidization gas/lignin (kg/wet kg lignin)	3
Cyclone	Solid/Gas separation efficiency	100%
Quenching column	Chilled water/inlet stream (kg/kg)	1.445
	Fraction of components in the bio-oil stream	
	Phenolics (organic liquid fraction of bio-oil)	100%
	Light ends	49.34%
	Water	45.06%
	Non-condensable compounds	0%
Sand heater/Char combustor	T of-gas and sand (°C)	608
	O ₂ excess (kg O ₂ / kg O ₂ consumed in char combustion)	1.2

The technical parameters of this section are based on [5].

Table A.4. Operation parameters adopted in syngas Fischer-Tropsch

<i>Unit</i>	<i>Condition</i>	<i>Value</i>
Syngas polishing	P (bar)/ T (°C)	25 /150
	Guard bed packing	1/3 molecular sieves and 2/3 activated carbon and ZnO
	Packing/lignin flowrate (kg/kg dry lignin/day)	0.853
	Max. H ₂ S concentration (kg/kg clean syngas)	5.0x10 ⁻⁸
	Max.NH ₃ concentration (kg/kg clean syngas)	1.0x10 ⁻⁵
H ₂ SMR	P (bar) / T (°C)	25 / 870
	catalyst	Ni and aluminum
	Catalyst/ H ₂ synthesized flowrate (kg/kg H ₂ /day)	0.058
	HP steam/ CH ₄ inlet (mol/mol)	6
	CH ₄ concentration in the outlet (%)	1.5
Water gas shift	T outlet (°C) of cooling water	300
	Catalyst	Copper -zinc
PSA	Catalyst/ lignin flowrate (kg/kg/day)	0.00297
	H ₂ recovery efficiency (%) / Purity (%)	85% / 100%
	Packing	2/3 with activated carbon and 1/3 with molecular sieve
FT reactor	H ₂ /carbon compounds in PSA outlet (mass %)	0.0136
	P (bar) / T (°C)	25 / 200
	Catalyst	Cobalt on Al ₂ O ₃
Separator / Decanter	Catalyst/ lignin flowrate (kg/kg/day)	0.0926
	Water/gas/organic phase separation efficiency	100%
Hydroprocessing	H ₂ requirement (kg H ₂ /kg waxes)	0.06, minimum

Adapted from [5].

Table A.5. GHG emissions per compound or utility.

<i>Compound</i>	<i>Input/output</i>	<i>GHG (kg CO₂/x)</i>	<i>Units (x)</i>	<i>Comments</i>
Sugarcane	input	0.034	kg sugarcane	Including transportation, without trash burning, with sugar yield of our process
SC trash	input	0.01	kg sugarcane trash	Using our yield of sugars, of sugarcane trash/sugarcane
H ₃ PO ₄ (15%)	input	1.423	kg H ₃ PO ₄	Commercial phosphoric acid used has a concentration of 85% by mass.
CaO (100%)	input	0.15	kg CaO	Lime
H ₂ SO ₄	input	0.124	kg H ₂ SO ₄	Sulfuric acid
NH ₄ OH	input	2.089	kg NH ₄ OH	ammonia, liquid, at regional storehouse/kg/RER
Enzyme	input	4.09	kg Enzyme	kg of enzyme
NaOH	input	1.096	kg NaOH	Analyzing 1 kg 'Sodium hydroxide, 50% in H ₂ O, production mix, at plant/RER U'
SO ₂	input	0.44	kg SO ₂	Sulphur dioxide, liquid, SO ₂
Acetone	difference between input and output	2.19	kg Acetone	Liquid
Acetic acid	input	1.403	kg CH ₃ COOH	Acetic acid via methanol carbonylation
Na ₂ CO ₃	input	0.59	kg Na ₂ CO ₃	Sodium carbonate (caustic soda), 50%, Na ₂ CO ₃
Juice transportation	output ISBL	0.7	ton.km	Transportation for 20 km, with a road transporter - CO ₂ emissions from freight
Cake from mills	output	0	kg	Assumed that it will be used in co-generation
Catechol	input	3.163	kg	kg CO ₂ /kg tert-butyl catechol produced from lignin has a CO ₂ reduction in 2% compared to the biochemical process
Waste to landfill	output end life	0.329	kg	Disposal, average incineration residue, 0% water, to residual material landfill
Electricity	input	0.486	kwh	Electricity, production mix RER/kWh/RER
Water	output-input	0	kg	Water is produced in WWT process
Chilled water	input	0.002	kg	Estimated from electricity of a cooling pump with 80% efficiency to cool down 1kg water, ΔT=15-5°C
Natural gas	input	1.422	kg	Emissions in production from fossil fuels, considering extraction, transportation and processing.
Natural gas	output	2.284	kg	Combustion of CH ₄ emissions
LPG	input	2.871 / 0.139	kg	Combustion emissions / extraction and processing of LPG
Gasoline	input	2.789 / 0.503	kg	Emissions in utilization / emissions in production from fossil fuels
Diesel	input	2.966 / 0.568	kg	Emissions in utilization / emissions in production from fossil fuels
Jet fuel transportation	output	4.5 / 17.1	ton.km	Sao Paulo, by train - 150 km / Rio de Janeiro, by train - 570 km

The technical parameters of this section are based on [5].

Table A.6. Key performance indicators for each configuration.

PRE-TREATMENTS TECHNOLOGIES	DA	DA	DA	DA-A	DA-A	DA-A	SE	SE	SE	SE-A	SE-A	SE-A	O-AA	O-AA	O-AA	WO	WO	WO	LHW	LHW	LHW	LHW-A	LHW-A	LHW-A
<i>Lignin destination</i>	FPJ	GFT	cogen	FPJ	ETJ	ETJ																		
Exergy Efficiency (%)	43.16	40.55	37.88	44.22	42.37	41.64	43.25	40.69	38.37	44.00	42.30	41.64	44.43	43.29	40.65	44.94	43.79	40.02	40.72	38.13	35.38	42.70	40.86	40.13
<i>Irreversibilities [MW]</i>	119	125	130	117	121	122	119	124	129	117	121	122	116	119	124	115	118	126	124	130	136	120	124	125
<i>I/BP Ratio (kW/kW)</i>	1.31	1.46	1.63	1.25	1.35	1.39	1.30	1.45	1.60	1.26	1.36	1.39	1.24	1.30	1.45	1.22	1.27	1.49	1.45	1.61	1.82	1.33	1.44	1.48
<i>AUEC (kJ/kJ)</i>	2.32	2.47	2.64	2.26	2.36	2.40	2.31	2.46	2.61	2.27	2.36	2.40	2.25	2.31	2.46	2.23	2.28	2.50	2.46	2.62	2.83	2.34	2.45	2.49
<i>GHG emissions (kg CO₂/GJ Jet Fuel)</i>	51.35	50.73	50.00	50.64	40.15	51.00	40.99	40.50	40.00	40.47	40.14	40.00	30.56	30.40	30.00	52.23	51.97	51.00	47.33	46.73	46.00	47.19	46.65	46.00

TECHNOLOGIES

ETJ	Ethanol fermentation
FPJ	Fast pyrolysis
GFT	Gasification Fischer-Tropsch
COGEN	Cogeneration

PRE-TREATMENTS

DA	Dilute-acid
DA-A	Dilute acid + alkaline treatment
SE	SO ₂ -steam explosion
SE-A	Steam explosion + alkaline treatment
O	Organosolv
WO	Alkaline wet oxidation
LHW	Liquid hot water
LHW-A	Liquid hot water + alkaline treatment

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