

Biojet fuel production from oleaginous crop residues: thermoeconomic, life cycle and flight performance analysis

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ABSTRACT

This study assesses an integrated biorefinery model's efficiency for biojet fuel production as Jet A1 blending component through the Alcohol-to-Jet (ATJ) and Hydroprocessed Esters and Fatty Acids (HEFA) thermochemical routes, employing lignocellulosic biomass from oleaginous crops. The ATJ process involved cellulosic ethanol production through steam explosion hydrolysis, simultaneous saccharification and co-fermentation. The anhydrous ethanol was sequentially dehydrated, oligomerized, and hydrotreated. On the other hand, the HEFA process upgraded vegetable oil from residues and fatty acid distillates. The vegetable oil was thermally hydrolyzed, decarboxylated and hydrotreated. The models were simulated in AspenPlus® v.11, achieving a specific biojet fuel production of 48 wt% for the ATJ and 87 wt% for the HEFA. In both cases, a biojet fuel mixture primarily composed of C₉ to C₁₂ isoalkanes was produced. The minimum selling price ranged between 1.01 €/kg to 1.43 €/kg. The studied routes were evaluated through exergetic and thermoeconomic analyses for optimizing. The life cycle assessment was carried out in SimaPro® v.9.0. The estimated net GHG emissions were 75 gCO_{2eq}/MJ for the ATJ and 18 gCO_{2eq}/MJ for the HEFA; nevertheless, significant improvements were achieved from by-product displacement credits. In both cases, the GHG emissions are under those from petroleum-derived Jet A1 production. Finally, the physico-chemical properties fulfilled the ASTM D7566 specifications, and the calculated payload vs range showed a better performance for an intermediate-range flight.

1. Introduction

Air transport is a cornerstone in current globalization, supporting the movement of more than 4.5 billion passengers and nearly 55 Mt of goods equivalent to €5.58 trillion in 2019, before the SARS-CoV-2 [1]. At a European level, 700 large commercial airports home to over 4000 civil aircraft, managing a quarter of the passengers worldwide. On average, 27,400 daily flights pass over its airspace, accounting for around 28% of global air traffic [2]. Nonetheless, the economic outlook for the next 20 years anticipates the number of air passengers to double. Simultaneously, aviation fuel (Jet A1) consumption will rise accordingly, leading to increased greenhouse gas (GHG) emissions (976 Mt of CO₂ in 2019). In addition, Petroleum-derived Jet A1 affects the atmosphere due to pollutant emissions such as NO_x, CO₂, sulphate, aerosols, and soot, contributing to climate change and depleting the ozone layer [3].

In this regard, the aviation industry has committed to the third phase

of the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA), which aims to cut net emissions in half by 2050 compared to 2005 levels while reducing reliance on conventional aviation fuels [4]. Nevertheless, better performance in modern engines, aerodynamic enhancements, and effective air traffic control is insufficient for offsetting the expected emissions [5]. In contrast, alternative jet fuel derived from renewable sources can significantly reduce the aviation industry's net GHG emissions [6]. Therefore, its production is imperative for a carbon-neutral expansion and ensuring energy security.

Lignocellulosic biomass is the most abundant renewable energy source globally. It is primarily composed of two biopolymers: aromatic (lignin) and polysaccharides (cellulose and hemicellulose). Its chemical composition ranges between 40 and 50 wt% of cellulose, 25–35 wt% of hemicellulose, 15–25 wt% of lignin, and, to a lesser extent, 3–7 wt% of extractives and inorganics (ash) [7]. Agriculture, forest, and industry sectors offer most of the lignocellulosic biomass; nonetheless, agricultural wastes are ideal because of their relatively low cost and ease of

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Nomenclature

ΔG	Gibbs free energy [kJ·mol ⁻¹]
ΔH	Enthalpy [kJ·mol ⁻¹]
ΔS	Entropy [J·mol ⁻¹ K ⁻¹]
ΔG^0	free Gibbs energy of formation [kJ mol ⁻¹]
R_S	reference state at [T ₀ , p ₀]
T_0	temperature of the AER [25 °C]
p_0	pressure of the AER [0.1 MPa]
h	specific enthalpy [kJ kg ⁻¹]
h_0	specific enthalpy at T ₀ , p ₀ [kJ kg ⁻¹]
s	specific entropy [kJ kg ⁻¹ K ⁻¹]
s_0	specific entropy at T ₀ , p ₀ [kJ kg ⁻¹ K ⁻¹]
X_{chem}	specific chemical exergy [kJ mol ⁻¹]
X_R	exergy of the resources [MW]
X_P	exergy of the products [MW]
X_I	exergy of the losses [MW]
X_d	exergy destruction [MW]
d_r	relative exergy destruction
X_d/X_R	exergy destruction ratio
E_{ff}	exergetic efficiency
X_q	heat flow exergy [kW]
X^*	exergetic cost [kW]
$\dot{Q}$	heat flow [kW]
$X_{(n \times 1)}$	exergy vector [kW]
$X_d (n \times 1)$	diagnostic vector
$\Omega_{(n \times 1)}$	allocated exergetic cost vector [kW]
$\Phi_{(n \times 1)}$	allocated thermoeconomic cost vector [€ s ⁻¹]
$\Pi_{(n \times 1)}$	thermoeconomic cost vector [€ s ⁻¹]
Π_R	thermoeconomic cost of the resources [€ s ⁻¹]
Π_P	thermoeconomic cost of the products [€ s ⁻¹]
C_R	unit exergoeconomic cost of the resources [€ MWh ⁻¹]
C_P	unit exergoeconomic cost of the products [€ MWh ⁻¹]
$C_R X_P$	Thermoeconomic cost of the products when exergy destruction, losses, and fixed cost are 0

$C_R X_I$	thermoeconomic cost of the exergy losses [€ s ⁻¹]
$C_R X_d$	thermoeconomic cost of the exergy destruction [€ s ⁻¹]
$(C_P - C_R) X_P$	absolute overcost [€ s ⁻¹]
$(C_P - C_R)/C_R$	relative overcost
f	exergoeconomic factor
Z	Equipment fixed cost flow [€ s ⁻¹]
ASTM	American Society for Testing and Materials
ATJ	Alcohol-to-Jet
CAPEX	capital expenditure
CO _{2eq}	equivalent CO ₂ emissions
EFB	empty fruit bunches
EU ETS	European Union emissions trading system
FAD	Fatty acid distillates
FCI	Fixed capital investment
FFA	Free fatty acids
FFB	Fresh fruit bunches
FP	flash point
GHG	greenhouse gases
HEFA	Hydroprocessed ester and fatty acids
IC	Installed costs
LCA	Life cycle assessment
LHSV	Liquid hourly space velocity
LHV	Lower heating value
MBSP	Minimum biojet fuel selling price
Pv.R	Payload vs range
RED II	EU Renewable Energy Directive II
SI	supplementary information
SPK	synthesized paraffinic kerosene
SSCF	Simultaneous saccharification and co-fermentation
SP	smoke point
T	temperature
T_f	freezing point
TEA	Techno-economic analysis
TCI	Total capital investment
ρ	density
ν	viscosity

transportation/storage [8]. With this in mind, oleaginous crops account for about 18% of the global cultivated area, producing 210 Mt of vegetable oil in 2020. Also, the annual per capita consumption is projected to reach 20 kg by 2026 [9,10]. The production of main vegetable oils includes coconut (3%), cottonseed (4%), olive (2%), palm (32%), palm kernel (4%), peanut (4%), rapeseed (14%), soybean (29%), and sunflower oil (8%). Throughout the extracting process of vegetable oil from the fresh fruit bunches (FFB), lignocellulosic biomass is obtained, such as empty fruit bunches (EFB) (23 wt%), oilseed kernel (7 wt%), mesocarp fibre (15 wt%), shell (7 wt%) and decanter cake (6 wt%). At the same time, the plantation area produces plant fronds (24%) and trunk residues (15%) during FFB harvesting [11]. Moreover, lignocellulosic biomass from oleaginous crops contains a higher sugar fraction, releasing more glucose and xylose during Biomass-to-Liquid conversion, achieving higher efficiencies [12].

Globally, primary biofuels used in gasoline blending of land transport are cellulose-derived oxygenates. However, their suitability as jet fuel blending components is constrained due to their lower volumetric energy density, increased volatility, corrosivity, and incompatibility with existing infrastructure [13]. Hence, synthesized paraffinic kerosene (SPK) from renewable sources is required. In addition, the SPK or biojet fuel contains no sulphur or nitrogen, avoiding the formation of SO₂ and H₂SO₄ during combustion [14]. In this sense, biojet fuel produced through the certified routes by the American Society for Testing and Materials (ASTM) comprises linear, branched, and cyclic hydrocarbons compatible with Jet A1 as 'drop-in' fuels, *i.e.* blending components at a

determined ratio. Biojet fuel can not replace Jet A1 completely; for this to happen, the synthesis of a certain fraction (about 20 wt%) of aromatics in the C₉-C₁₃ range would be needed [15].

Nonetheless, biojet fuel must suit aircraft engines' design and fuel distribution systems. Physico-chemical homogeneity between both fuels is crucial for combusting behaviour due to specific conditions regarding viscosity, non-freezing or cloudiness phenomena at low temperature, freezing point, etc. Also, to meet storage and transport safety requirements [16]. Approved technologies involve the conversion of (i) Hydrogen, carbon monoxide, and dioxide carbon mixture (syngas) in a Fischer-Tropsch (FT) reactor into a wide range of hydrocarbons via power-to-liquid (PtL) process [17]; (ii) Hydroprocessed esters and fatty acids (HEFA) by reacting triglycerides from fats and oils with hydrogen; (iii) Synthesized *iso*-paraffin produced through hydroprocessed fermented sugars (SIP-HFS) employing farnesene as feedstock; (iv) Synthesized kerosene with increased aromatics content (FT-SPK/A) by alkylation of light aromatic compounds from renewable sources [17]; (v) Alcohol-to-jet synthetic paraffinic kerosene (ATJ) from lignocellulosic-derived alcohols; (vi) and recently, Catalytic hydro-thermolysis jet (CHJ) and co-processing jet from triglycerides and vegetable, waste, or algal oils [18-20].

A detailed scheme describing the ASTM routes is contained in the supplementary information (SI1). The ATJ and HEFA pathways were selected for the biorefinery design. The ATJ upgrades the cellulose-derived alcohol into biojet fuel, whereas the HEFA pathway processes vegetable oil, as shown in Fig. 1.

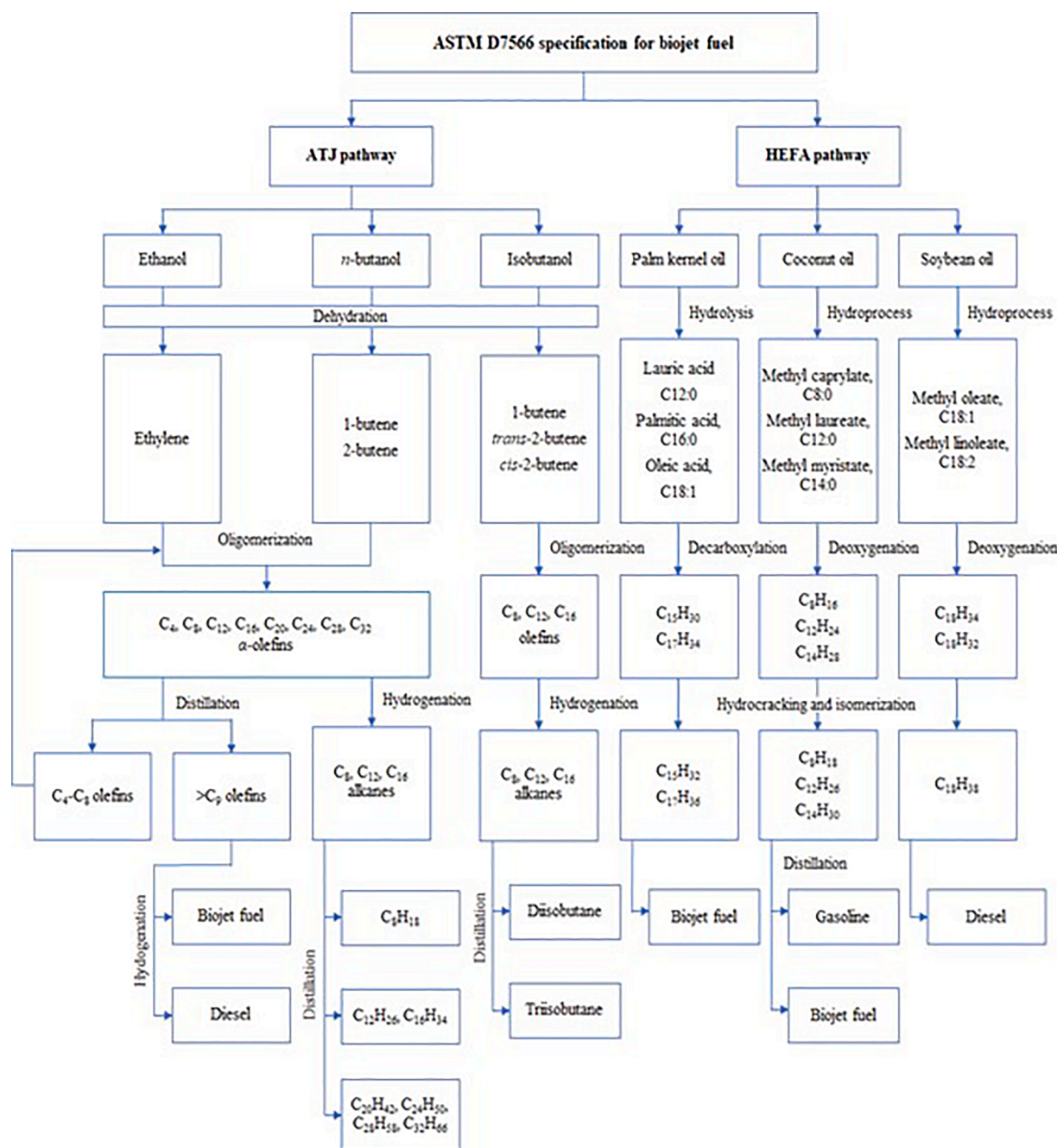


Fig. 1. Biojet fuel production through the ATJ and HEFA pathways from different feedstocks.

Currently, several companies are producing biojet fuel. For instance, Byogy Renewables Inc. technology can effectively process ethanol, propanol or butanol via catalytic synthesis to obtain biojet fuel [21,22]. Among cellulosic alcohols, ethanol is a versatile platform molecule to form long-chain hydrocarbons [20]. Ethanol processing is a well-understood industrial-scale technology, environmentally sustainable and cost-effective, with production capacity reaching near-theoretical thermodynamic yields [23,24]. Besides, it is the most prevalent liquid fuel produced from biomass presently. One way to meet the growing demand for middle and heavier distillate fuels (jet fuel and diesel) is to derive these from ethanol [25]. The ethanol is dehydrated during the ATJ route to produce ethylene, which is subsequently oligomerized over a solid acid catalyst in a single or double processing phase to obtain linear α -olefins. An alternative approach involves a single-stage oligomerization; however, up to 40% of undesirable selectivity to C_1 – C_4 light

hydrocarbons have been reported [26,27]. Efficient conversion of ethylene to heavier hydrocarbons (C_{8+}) has been observed through a two-step oligomerization process, minimizing the formation of aromatics and naphtha-like compounds by shorter chain product recycling [28]. Products distribution is determined by the water content in the feed, reaction conditions, and the catalysts' surface acidity regulated by zeolites additives and Si/Al ratio [29].

On the other hand, the HEFA route employs thermal hydrolysis, decarboxylation, hydrocracking, and isomerization to treat triglycerides from vegetable oil [30,31]. It is currently the most well-known and fully commercialized on an extensive industrial-scale process [5,30]. Many companies opt to implement biorefineries using the HEFA technology because much lower capital is required than lignocellulose-based technologies [32]. For example, Neste® operates two refineries in Finland and two others in the Netherlands and Singapore, target to increase

waste and residues share from the current 83% to 100% of renewable raw material inputs by 2025 [33]. Plant kernel is a valuable residue from vegetable oil processing due to its oil content ranging between 5 and 12 wt%, depending on the type and cultivation conditions [34]. Furthermore, fatty acid distillates (FAD) recovered from the stripping and deodorisation stages (5–10 wt%) during vegetable oil alkali refining contain unsaturated and saturated free fatty acids (C12 to C30) for increasing decarboxylation reactor yield [35]. Both feedstocks have received significant interest owing to their potential to produce biojet fuel with a higher cetane number and lower aromatic content.

Biojet fuels techno-economic and environmental assessments are widely available in the literature. For example, Atsonios *et al.* determined that biochemical alcohol fermentation with subsequent upgrading is more economically feasible than the production via mixed-alcohol synthesis [13]. In comparison, Tanzil *et al.* found that HEFA is the most competitive biojet fuel technology on the market today. Its costs are relatively low and have a high fuel yield than lignocellulosic biomass-based technology, notwithstanding triglycerides are several times the price of those inputs [36]. While the studied feedstocks are entirely characterized, detailed information on their composition and availability exists, there is a general lack of understanding of their effect on hydrocarbon yield, particularly biojet fuel blend yield and overall process thermoeconomics. Therefore, new detailed information is required to approach a substantial improvement in developing a sustainable Jet A1 surrogate, combining thermodynamics and physico-chemical properties with the produced biojet fuels' combustion behaviour.

The research examines a biorefinery simulation to produce biojet fuel via the ATJ and HEFA processes from oleaginous crop waste. It describes lignocellulosic ethanol production as an intermediate molecule in the ATJ route and kernel oil and FAD as feedstocks for the HEFA route. The process feasibility and efficiency were evaluated through comprehensive thermodynamic and techno-economic analyses and complemented with a life cycle assessment (LCA). Furthermore, both biojet fuels' combustion properties were estimated and compared to the ASTM physico-chemical specifications. Finally, a payload vs range calculation was conducted to evaluate biojet fuels' performance when replacing Jet A1 during a flight.

2. Methods

2.1. Process design and basic assumptions

The ATJ and HEFA routes were modelled and simulated in the chemical engineering software AspenPlus® v.11 (Aspen Technology Inc., USA) based on experimentally obtained data and approved methodologies. The NRTL (non-random two liquid) property method was selected for the vapour-liquid equilibrium calculations and thermodynamic and transport properties estimation. The simulation models were used to evaluate optimal operating conditions and perform precise mass and energy balances. The biorefineries were designed to produce 132,000 t of biojet fuel per year from lignocellulosic biomass, kernel oil, and FAD. Furthermore, based on the conversion rate and carbon selectivity in each stage, unreacted reagents were recirculated employing the AspenPlus Design Specs® tool.

The waste extraction after FFB harvesting included sterilization, stripping, digestion and pressing stages. Then the crude vegetable oil is separated, and the EFB, palm bone (kernel), mesocarp fibre, and shells are recovered from the press cake. Finally, the kernel oil is extracted from the palm bone after a second pressing. In comparison, the FAD are obtained from residues of crude vegetable oil refining [37]. The ATJ process transformed that lignocellulosic biomass, whereas the HEFA process converted those vegetable oil-based materials. Lignocellulosic biomass was previously cleaned, minced, crushed, and milled on preparation units. The feed rate of ash-free lignocellulose was fixed to 77 t/h with a moisture content of 50 wt% and an ash fraction of 3.70 wt% [38]. Oleaginous crops lignocellulosic composition corresponds to generic

lignocellulose based on its experimentally characterized solid waste [39], as listed in Table 1.

The lignocellulosic biomass was obtained assuming a plantation with an equilateral triangular spacing with a hexagonal pattern to accommodate up to 143 oil plants and yield 19 t_{FFB}/ha [40]. Hemicellulose, for most hardwoods and agricultural residues, is composed mainly of xylans (β-1,4-linked xylose) with side branches of (methylated) glucuronic acid (α-glucuronic), acetate, and arabinose (α-arabinofuranose) [41].

On the other hand, the HEFA process's feed rate was fixed to 4.68 t/h of kernel oil and 1.46 t/h of FAD. The feed rate was calculated considering 5.4 t/ha of produced vegetable oil, generating 15% and 5% kernel oil and FAD, respectively [10]. On average, palm oil production is nearly ten times more than sunflower, rapeseed, and soybean; thus, palm kernel oil composition was the reference. Furthermore, palm kernel oil is a promising feedstock for biojet fuel production given its dominant lauric acid (C₁₂H₂₄O₂) content, achieving an upper 90% conversion yield for Jet A1 range hydrocarbons and selectivity to C₁₀-C₁₂ alkanes of approximately 58% [42]. At the same time, the FAD contain 93 wt% of free fatty acids (FFA), mainly composed of 45.6% palmitic acid (C₁₆H₃₂O₂), 33.3% oleic acid (C₁₈H₃₄O₂), 7.7% linoleic acid (C₁₈H₃₂O₂), 3.8% stearic acid (C₁₈H₃₆O₂), and 1.0% myristic acid (C₁₄H₂₈O₂). The remaining components involve triglycerides, glycerides, and unsaponifiable matters (vitamin E) [43]. The block diagram of both processes is shown in Fig. 2.

2.2. ATJ process

2.2.1. Lignocellulosic biomass pretreatment

The inter- and intramolecular hydrogen bonds between cellulose molecules result in microfibrils with crystalline and highly organized regions further intertwined with hemicellulose and lignin polymers, developing a robust and complex architecture resilient to degradation [41,44]. Lignocellulosic biomass pretreatment involved breaking the crystalline structure of cellulose, depolymerising it and solubilising the lignin and hemicellulose. As a result, the production rate increases because a higher amount of polymeric sugars is released. Furthermore, the contact area between cellulolytic enzymes and cellulose increases, enhancing fermentation yield [45]. The employed physico-chemical procedure consisted of a diluted acid-catalyzed (H₂SO₄) steam explosion at 0.6 MPa and 190 °C with maximum cellulose to glucose conversion up to 92%, hemicellulose depolymerization of 90%, and lignin solubilization of < 2% [46,47]. The assumed reaction time was 0.25 h to volatilize low molar mass components [48]. In addition, the recovered solution from pretreatment was neutralized and detoxified with calcium hydroxide with a molarity of 0.12 M.

2.2.2. Cellulosic ethanol production

Following pretreatment, extracted oligomeric sugars (mainly gluco-oligomers and xylo-oligomers) must be broken down into monomeric sugars. The conversion of gluco-oligomer (C6) to glucose and fructose and xylo-oligomer (C5) to xylose is achieved via enzymatic hydrolysis (saccharification). Due to the enzyme's activity, efficiencies approach the theoretical maximum (89%), which is in excellent agreement with processes using lignocellulosic biomass pretreated with dilute acid,

Table 1
Chemical composition of the dry lignocellulose.

Component	Content (wt %)
Cellulose	41.24
Lignin	25.50
Xylan	20.00
Arabinan	1.70
Mannan	0.20
Galactan	0.80
Extract	7.50
Ash	3.06

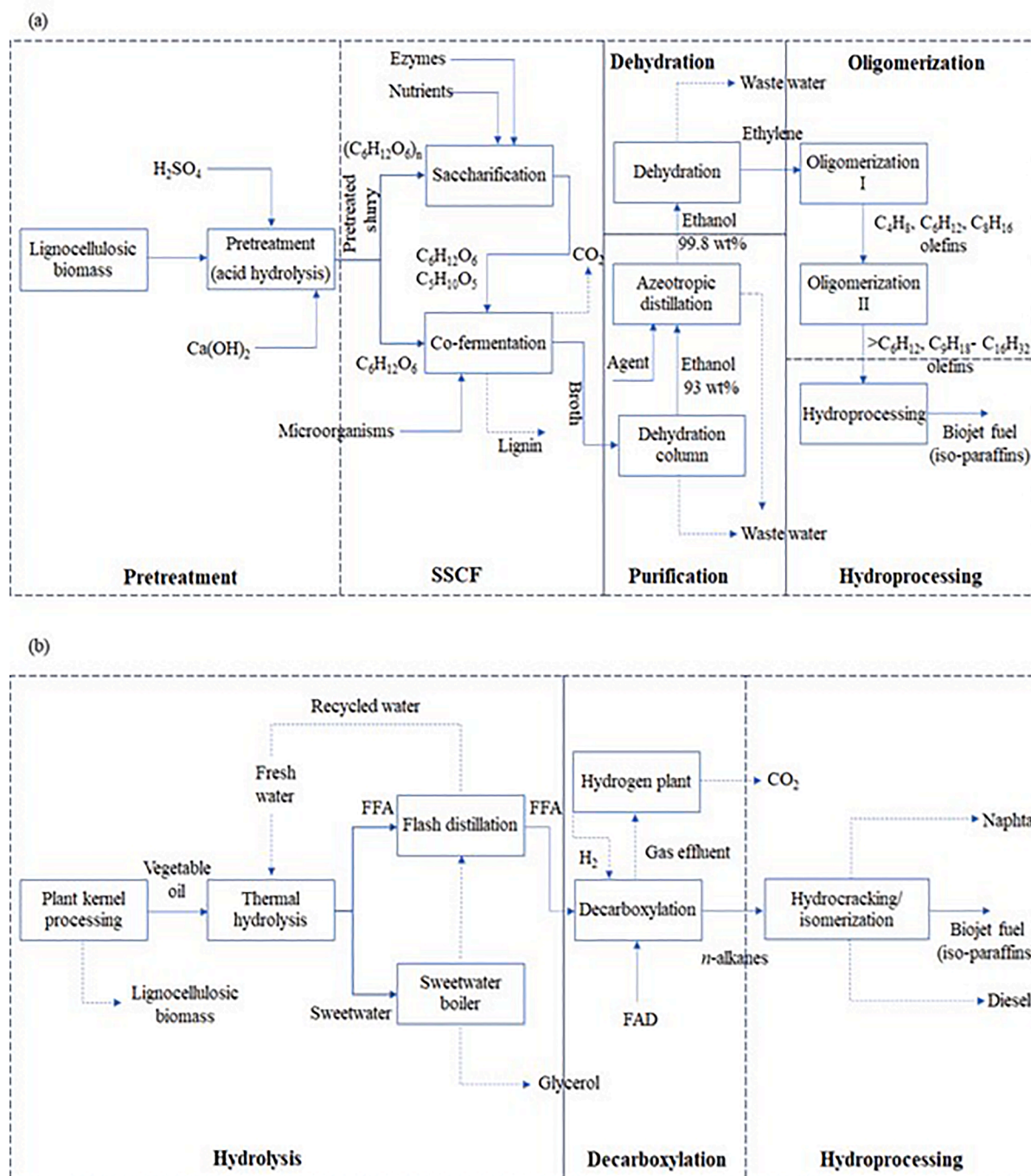


Fig. 2. Simplified block diagram of the lignocellulosic biomass to jet fuel processes: (a) ATJ process and (b) HEFA process.

organosolv solution, liquid hot water, and acid-catalyzed steam explosion technologies [46]. The hydrolyzed slurry is inoculated with glucose-xylose co-fermenting microorganism *Zymomonas mobilis*. The transformation of xylose, glucose and fructose to middle distillate fuel was carried out through anaerobic fermentation, assuming 92% glucose yield and 85% xylose yield [45]. Minor sugars (arabinose, galactose, and mannose) were considered non-fermentable. The reactions were modelled following simultaneous saccharification and co-fermentation (SSCF) configuration to reduce production costs and to improve process efficiency. Operating conditions were 0.1 MPa and 40 °C in RStoic reactors. The assumed residence time for enzymatic hydrolysis and fermentation reactions is 168 h [28]. The outgoing streams from the SSCF involved ethanol, carbon dioxide, water, and minor amounts of

unreacted reagents.

Upon completing the SSCF, the ethanol was separated and purified through a distillation stage due to its lower boiling temperature than the other fermentation broth components. An extractive distillation was modelled to obtain a solution containing near 87 wt% of ethanol. Once this purity is reached, the liquid and vapour have the same composition, and no further separation occurs due to minimum boiling ethanol–water azeotrope [49]. Therefore, an azeotropic distillation column was designed and simulated to obtain 99.8 wt% ethanol. The extractive column employed nine stages with a distillate to feed mole ratio of 0.8 and a reflux ratio of 3.5, removing approximately 90% of the water.

On the other hand, the azeotropic column was designed using the DSWTU AspenPlus® tool. Several entrainers can be used for this specific

process: benzene, cyclohexane, isooctane, heptane, hexane, pentane, acetone, and diethyl ether are all options as the mixture. Of these, benzene and cyclohexane have been used the most often utilized. Nonetheless, the total energy consumption of azeotropic distillation using cyclohexane (13.39×10^6 kJ/h) is considerably higher than benzene (8.99×10^6 kJ/h) [50]. Therefore, benzene was selected as a solvent for azeotropic distillation, as shown in the ternary diagram contained in the supplementary information (SI2). Design specifications for the RadFrac included an azeotropic convergence, nine stages with a distillate rate of 21.32 t/h and an actual reflux ratio of 1.4, implementing an atmospheric pressure total condenser.

2.2.3. Ethanol to biojet fuel

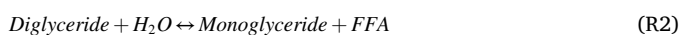
Finally, the anhydrous ethanol is dehydrated to ethylene in a parallel reaction pathway with a residence time within 0.005–2.2 s [51]. The hydroxyl functional group was removed in an isothermal fixed bed reactor (RStoic) operating in the presence of *mesoporous silica* at 0.1 MPa and 350 °C, with ethylene selectivity and ethanol conversion of 99.9% and 100%, respectively [52]. Ethylene is subsequently oligomerized to produce longer chain α -olefins in a two-reactor setup. The first oligomerization occurs in an RStoic reactor at 2.2 MPa and 55 °C, assuming the presence of Ni-based catalyst in *n*-heptane solvent to obtain a stable conversion and highly selective for C₄ (butylene) and minor amounts of C₆ and C₈ olefins [53]. The second oligomerization employed using a crystalline molecular sieve catalyst to react to the feed containing C₄ (70 wt%), C₆ (27 wt%) and C₈ (3 wt%) olefins with an olefinic recycling stream rich in C₉- hydrocarbons in an RYield reactor at 7 MPa and 235 °C. The conversion yield of C₄ olefin ranges from 88 wt% to 99 wt% (see the SI3 section) [54]. Finally, the oligomerized effluent stream was separated in a RadFrac distillation column into a hydrocarbon product stream primarily composed of C₉ + and the mentioned olefinic recycle stream. The distribution of the product stream corresponded to 85/15 vol% jet fuel and diesel, respectively. The olefin recycling rate was 45 wt % (relative to feed) to control the oligomerization reaction's exothermicity. Simultaneously, the recycling composition allows for heavier oligomers formation, generating a distillate product with a higher molecular weight and density [55].

After completing the oligomerization stage, the straight-chain olefinic molecules are hydrogenated and further processed with either cracking or isomerization. The isomerization step improves biojet fuel's freezing point and cold flow characteristics. At the same time, the cracking process converts the molecule into the required carbon chain (C₈–C₁₆) [56]. Hydrogenation is a very exothermic reaction, whereas isomerization requires significant energy to transform linear alkanes. The operating conditions in the RStoic reactors during the hydrogenation and cracking/isomerization were 3.45 MPa at 185 °C and 6 MPa at 280 °C, respectively, assuming a metal catalyst (Pt/Al₂O₃) [57]. Hydroprocessing yields for the cracking and isomerization reactor are detailed in the SI4 section. The stage design included a hydrogen recovery unit for recirculation, ensuring efficient response control.

2.3. HEFA process

2.3.1. Hydrolysis

Hydrolysis of kernel oil was simulated in an RStoic reactor, assuming a 2:1 water–oil ratio to achieve 99.7% of the Colgate-Emery process's theoretical yield [58]. The conversion mechanism is described as three consecutive reversible reaction steps [59].



Produced FFA were separated from the glycerol and water through a flash distillation in a Flash unit at atmospheric pressure and 125 °C. As a

result, the stream containing the FFA mixture also had minor moisture, insoluble, and unsaponifiable (MIU), whereas the glycerol stream included MIU and much of the excess water (sweetwater).

While triglyceride hydrolysis is a well-understood field from the biofuels industry perspective, further optimization could be achieved by the process's thermodynamical understanding [60]. Thus, the reaction was assessed at different states. The equilibrium constants were determined based on the critical properties and acentric factor of triglycerides, FFA and glycerol and estimated through group contribution methods [61,62]. State 1 occurred at 25 °C and 0.1 MPa (T_1 , P_1), and state 2 at 250 °C and 5 MPa (T_2 , P_2) to determine both states' feasibility based on Gibbs free energy (ΔG), as defined in Eq. (1).

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

Where ΔH is the reaction enthalpy, ΔS is the entropy, and T is temperature. Enthalpy (H) of a real fluid is described in Eq. (2).

$$H = H^{ig} + H^d \quad (2)$$

Where H^{ig} corresponds to the ideal gas enthalpy and H^d is the departure enthalpy. Based on Equation 2, reaction enthalpy at state 1 is shown in Eq. (3).

$$\Delta H_1 = \sum H_{\{product\}} - \sum H_{\{reactant\}} \quad (3)$$

This approach can be extended to entropy as well. Reaction enthalpy for state 2 is calculated from Eq. (4).

$$\Delta H_2 = H^d(T_2, P_2) - H^d(T_1, P_1) + \int_{T_1}^{T_2} C_p^0(T) dT \quad (4)$$

Where C_p^0 is ideal gas specific heat (J/mol K) at T temperature. Whereas entropy is defined as shown in Eq. (5).

$$\Delta S_2 = S^d(T_2, P_2) - S^d(T_1, P_1) + \left(\int_{T_1}^{T_2} \frac{C_p^0}{T} dT - R \ln \frac{P_2}{P_1} \right) \quad (5)$$

Equations 4 and 5 explain the enthalpy derivations between an ideal gas and a real fluid. The Peng-Robinson equation of state was employed to model the property changes due to its suitability for multi-component systems at liquid phase densities [63]. Departure enthalpy and entropy are described in Eq. (6) and Eq. (7), respectively.

$$H^d = RT_c \left[T_r(z-1) - 2.078(1+k)\sqrt{\alpha} \ln \left(\frac{z+2.414B}{z-0.414B} \right) \right] \quad (6)$$

$$S^d = R \left[\ln(z-B) - 2.078k \left(\frac{1+k}{\sqrt{T_r}} - k \right) \ln \left(\frac{z+2.414B}{z-0.414B} \right) \right] \quad (7)$$

T_c and T_r are critical and reduced temperatures. R and z correspond to the gas constant and compressibility factor, and α is a modified function to improve the vapour pressure prediction. Detailed information describing the calculation of both equations is contained in the SI5 section. Specific thermodynamic parameters are rarely detailed because of triglycerides and FFA complex geometrical structure; hence, the assessment was simplified to triolein hydrolysis to obtain oleic acid.

2.3.2. Decarboxylation and reforming

Once all the glycerides from kernel oil are converted to FFA, catalytic decarboxylation is required to obtain mainly C₁₁–C₁₇ straight-chain *n*-alkanes by removing the carboxyl group on the FFA while releasing carbon dioxide [58]. The reaction was conducted in an RStoic reactor in the presence of hydrogen to saturate the double bonds on the unsaturated FFA at 2 MPa, and 280 °C with an H₂/feed volume ratio (v/v) of 750 and a liquid hourly space velocity (LHSV) of 2 h⁻¹ on a Pd/C catalyst [64]. The stage achieved a 95% theoretical yield. The gaseous effluent contains CO₂ and hydrogen surplus. It was recovered through a two-step cooling process while maintaining the high-pressure

environment to condensate CO₂ (dry ice) and recycling the hydrogen to the decarboxylation reactor by employing the AspenPlus DesignSpec® tool [31].

After the decarboxylation stage, selective cracking and isomerization of the *n*-alkanes product were performed by adding hydrogen. The reaction took place in an RStoic reactor at 6 MPa, and 280 °C in the presence of a Pt/Al₂O₃ catalyst and LHSV of 1 h⁻¹ and H₂/feed volume ratio 750 [65]. The reaction path net of hydrocracking and the jet fuel paraffinic mixture's isomerization was a cascade reaction from the *n*-alkane to single-branched isomers with multi-branched isomers not occurring to any appreciable extent. The liquid hydrocarbon mass yield from the cracked/isomerized was 92% (see the SI4 section) [66,67].

2.4. Techno-economic analysis

The techno-economic analysis (TEA) compares the investigated biojet fuel processes based on their economic feasibility and relative potential in the marketplace. The TEA was developed by combining technical data, the AspenPlus Economic Evaluator® package, and a complete mass and energy balance from the simulated biorefineries. The economic analysis integrated the operating and capital costs, materials, biojet fuel production cost, processes energy, and direct emissions to calculate the minimum biojet fuel selling price (MBSP) through a cash flow assessment with a net present value (NPV) equal to zero at an acceptable internal rate of return (IRR). The economic assumptions are described in Table 2.

Besides, equipment sizing and purchasing price, operating costs, and capital investment were estimated using the material and energy balance data. Then, equipment costing was assigned employing economic assumptions, exponential scaling, and the Chemical Engineering Plant Cost Index (CEPCI) adjustment [70], as shown in Eq. (8).

$$\text{Newcost} = \text{Basecost} \times (\text{Size})^{\text{exp}} \times \left(\frac{\text{CEPCI}_{\text{innewyear}}}{\text{CEPCI}_{\text{inbaseyear}}} \right) \quad (8)$$

The installation costs included complementary equipment costs, installation labour, engineering costs, and contingencies costs [72,73]. The total capital investment (TCI) and the fixed capital investment (FCI) were calculated after completing the overall purchasing and installation charges, as Table 3 describes.

Production cost involved variable operating costs (feedstock and waste disposal costs, by-product benefits, and recurring expenses) and fixed operating costs (staff payroll, labour burden, tax insurance, and facilities maintenance) [71]. The feedstock logistics and agriculture

Table 2
Economic assumptions.

Description	Assumed value
Base year	2020
Plant financing debt/equity	60%/40% of total capital investment
Construction period ^a	8% 1st year, 60% 2nd year, 32% 3rd year
Start-up time	0.5 years
Plant life	25 years
Income tax rate	35%
CEPCI 1987/2019 ^b	323.8/607.5 USD
Lang factor ^c	4.8
Work capital ^d	5%
Minimum acceptable internal rate ^e	9%
The interest rate for debt financing	9% annually
On-stream factor	97% (8400 operating hours per year)
The term for debt financing	10 years
US dollar exchange rate	1.25 \$·€ ⁻¹

^a The percentage of the cost of the project cost throughout each year of construction.

^b Based on 2019 chemical engineering plant cost index annual average [68].

^c Lang factor for a solid–fluid processing plant [70].

^d Of the fixed cost investment.

^e Consistent with the NREL research [71].

Table 3
TCI and FCI calculation assumptions.

Parameter	Description	Cost
Direct cost	Equipment cost (EC)	Σ EC
Installation	Installed cost (IC)	Lang factor × Σ EC
Additional Direct costs	10% of the total IC	0.1 × Σ IC
Total Direct Cost (TDC)		1.1 × Σ IC
Construction fee	20% of TDC	0.2 × TDC
Project contingency	10% of TDC	0.1 × TDC
Prorated expenses	10% of TDC	0.1 × TDC
Field expenses	10% of TDC	0.1 × TDC
Other	10% of TDC	0.1 × TDC
Total Indirect Cost (TIC)		0.6 × TDC (or 0.66 × Σ IC)
Fixed Capital Investment (FCI)	TDC + TIC	1.76 × Σ IC
Land		Land cost
Working capital	10% of FCI	0.1 × FCI
Total Capital Investment (TCI)		1.936 × Σ IC + land cost

were not considered within the analysis. The variable operating costs are detailed in Table 4.

2.5. Thermoeconomic analysis

Thermoeconomic modelling combines the exergetic and economics to evaluate the efficiency and renewability of biojet fuel processing comprehensively, identifying irreversibilities, discerning their causes and rigorously quantifying them. The systematic assessment involved developing a macro in Visual Basic Application (VBA) to perform the exergy and thermoeconomy algorithm/calculations of the biojet fuel production simulated models [83]. The required thermodynamic data for the application, such as enthalpy, entropy and mass flow from the streams of matter, work and heat, were collected from AspenPlus® models. Fig. 3 shows the logical connections between the performed analyzes starting from the exergy calculations.

2.5.1. Exergy

Exergy (*X*) is the amount of entropy-free energy available to be used when the system is brought into thermodynamic equilibrium with its environment. The assessment started with the exergy calculations of each equipment streams. The specific exergy can be described as the stream's internal exergy by adding the physical and chemical exergies [84], as shown in Eq. (9).

Table 4
Primary variable operating costs involved in the processes.

Parameter	Process		
	ATJ	HEFA	Source
Feedstocks			
Lignocellulose	95 (€/t)	–	[74]
Benzene	855 (€/t)	–	[75]
Sulfuric acid	345.67 (€/t)	–	[71]
Enzymes	577.17 (€/t)	–	[76]
Kernel oil	–	735 (€/t)	^a
FAD	–	271 (€/t)	[77] ^b
Delivered feedstock cost	25 (€/t)		
Water	1.87 (€/m ³)		[78]
Hydrogen	1196.05 (€/t)		[21]
Natural gas	434.63 (€/t)		[78]
Electricity	0.083 (€/kWh)		[21]
By-products			
CO ₂ emission cost	52 (€/t CO ₂)		[21]
Unsaturated green diesel	0.82 (€/L)	–	^c
Dry lignin	270 (€/t)	–	[21]
Glycerol	–	160 (€/t)	[79]

^a Based on the reported selling price of palm kernel oil in 2020 [80].

^b Delivered cost regarding feedstock preprocessing and storage [81].

^c Corresponding to the bunker fuel selling price [82].

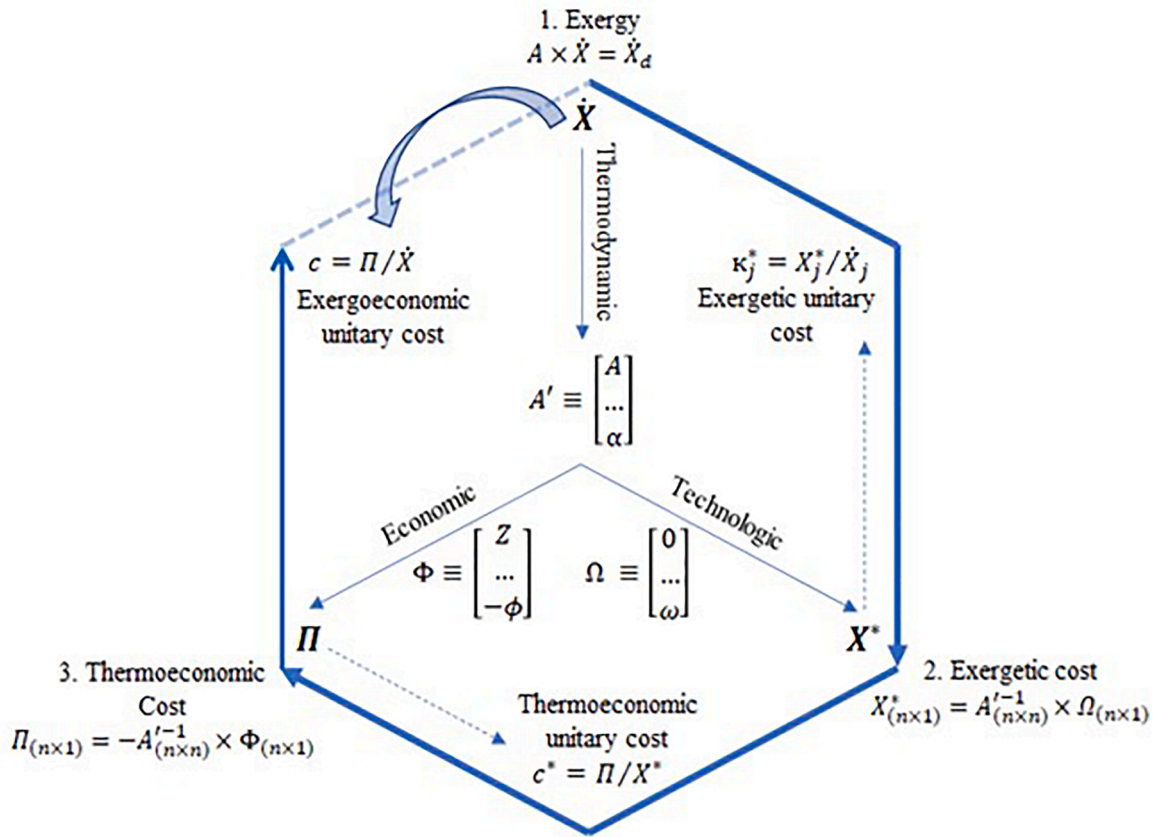


Fig. 3. Thermoeconomic 3D hexagon costs.

$$X = X_{phys} + X_{chem} \quad (9)$$

Kinetic and potential exergies were disregarded in the calculations. Instead, both processes were evaluated as open systems in thermodynamic equilibrium. Internal exergy calculations and heat are described in Table 5.

Physical exergy required information from the simulated models. Aspen Plus® estimated each stream enthalpy and entropy at operating conditions throughout the process. Their respective values at the stable reference state (25 °C, 0.1 MPa) were obtained using a heat exchanger, fed by a stream with the same composition as the evaluated stream [83]. While chemical exergy was calculated considering the stream composition and the pure substance elements exergy listed in SI6.

2.5.2. Process and economic structure

Graph Theory and Linear Algebra provided a mathematical render of the system's structure through an incidence matrix (A) composed of m equipment connected by n streams. Then, the exergy balance execution

was performed by matrix algebra to obtain the exergy destruction on each piece of equipment by multiplying the incidence matrix and the internal exergy (X), as defined in Eq. (10).

$$A_{(m \times n)} \times X_{(n \times 1)} = X_{d(m \times 1)} \quad (10)$$

Irreversibilities leading to exergy destruction include processes associated with a chemical reaction such as reactant and product mixing, the pressure drop across the system, and heat loss to the environment [88]. The economic structure, on the other hand, classified the streams as resources (R), products (P), or losses (I) depending on the equipment characteristics, configuration and utility, to calculate the exergetic costs [89]. The $R/P/I$ classification was fed into three different matrixes (R , P , and I matrix) with a similar structure to the incidence matrix to perform the thermoeconomic analysis [83].

2.5.3. Exergetic costs

The exergetic cost of a stream is equivalent to the required or consumed exergy to produce it; hence, each piece of equipment's outgoing streams is equal to the cost of all the incoming streams. The exergetic cost balance provided m equations to determine $n = m + 1$ exergetic costs; for this reason, more equations were required based on the productive structure from the $R/P/I$ classification [90]. The incidence matrix was complemented with an economic structure matrix (α) to build the cost square matrix ($A'_{n \times n}$) [91]. The exergetic costs were calculated using Eq. (11).

$$X^*_{(n \times 1)} = A'^{-1}_{(n \times n)} \times \Omega_{(n \times 1)} \quad (11)$$

The values of the $\Omega_{(n \times 1)}$ vector corresponded to zero to the first m elements, followed by appropriate terms corresponding to the additional equations, as shown in Fig. 4 [83].

Table 5
Exergy calculations for matter and energy streams.

Exergy	Equation	Ref
Physical	$X_{phys} = (h - h_0) - T_0(s - s_0)$	[85]
Chemical ^a	$X_{chem} = \sum y_i X_{chem,i} + RT_0 \sum y_i \ln y_i$	[86]
Pure compounds ^b	$\tilde{X}_{chem}(m) = \sum n_i \tilde{X}_{chem,i}(elements) + \Delta G_f^\circ(m)$	[87]
Heat	$X_q = \left(1 - \frac{T_0}{T}\right) \times \dot{Q}$	

^a Where y_i is the molar composition of the i compound.

^b Where n_i is the number of atoms.

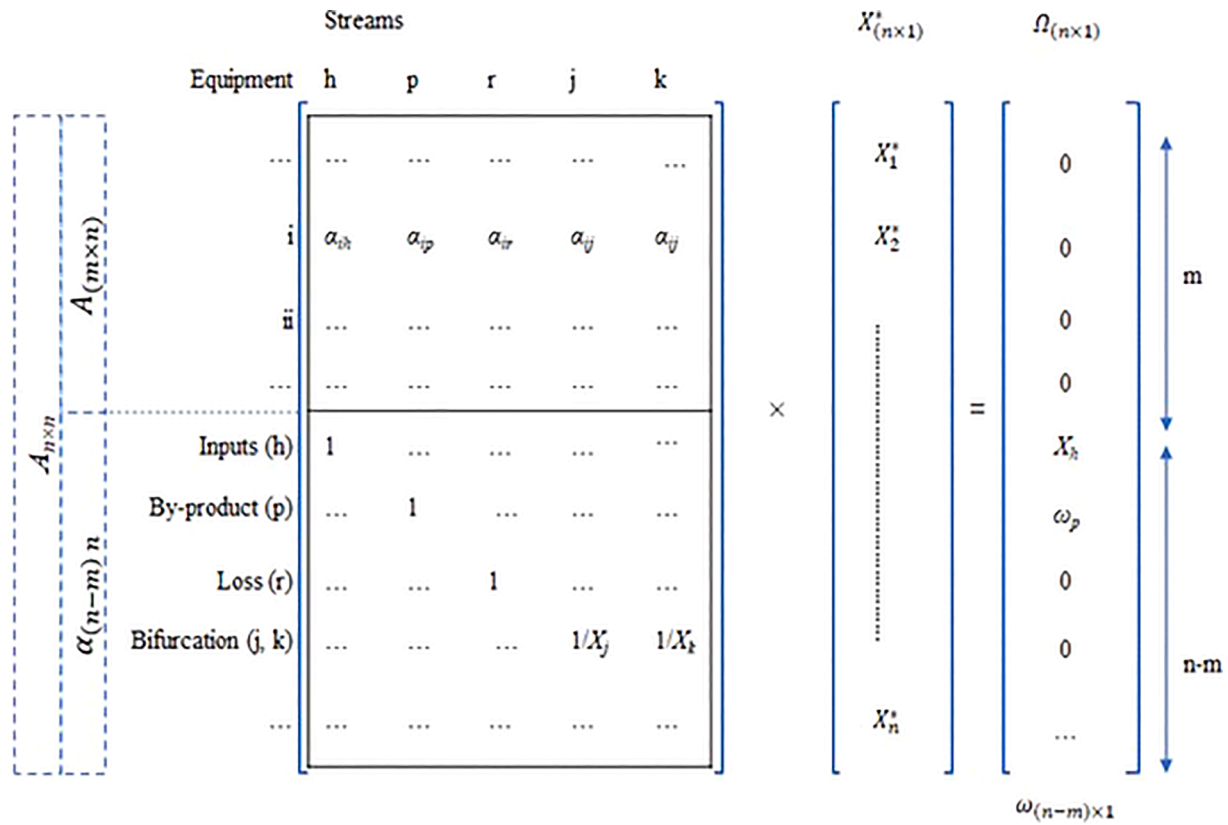


Fig. 4. Exergetic cost matrix.

2.5.4. Thermo-economic cost

The thermo-economic costs (Π) were calculated through the allocated thermo-economic costs (Φ), which are composed firstly of the assigned fixed cost flow (Z) to each piece of equipment from the total fixed costs based on the economic assumptions and its corresponding ($IC/\Sigma IC$) ratio, as shown in Eq. (12). Secondly, the provided thermo-economic costs ($-\Phi$) for the resources and by-products are defined in the complementary economic matrix, considering its variable cost (Table 4) and the mass flow. Waste/losses and bifurcations were considered zero [92,93].

$$\Pi_{(n \times 1)} = -A_{(n \times n)}^{-1} \times \Phi_{(n \times 1)} \quad (12)$$

Further information about the schematic assessment is fully described in the supplementary information SI7.

2.6. Life cycle assessment

LCA methodology was performed to evaluate and compare different environmental burdens, biosphere impacts, and resource consumption associated with the studied thermochemical routes. LCA identifies the environmental hotspots by compiling a thorough inventory of the inputs (feedstocks, fuels, and water) and quantifying the outputs (products, by-products, and emissions) [94]. An energy basis (1 MJ of biojet fuel produced) was employed as a functional unit in the LCA calculations. The LCA determined the life cycle GHG footprint and water consumption on each stage through the SimaPro® LCA v.9.0 modelling software. The system boundary is shown in Fig. 2. The environmental effects were quantified employing the mass and energy balance and the environmental impact categories “global warming potential” with a time scope of 100 years (GWP100) and “cumulative energy demand”. The produced GHG emissions were monetarized and taken into account in the variable operating costs in the TEA. Measured emissions affecting the global climate behaviour were homologated in equivalent CO_2 emissions ($\text{CO}_{2\text{eq}}$). The LCA models were complemented with the Ecoinvent v.3.3

database for process and materials previously developed. The model assumed an average three-stage in-situ wastewater treatment. The environmental burden allocation was partitioned between products and by-products streams based on guidelines from ISO 14044:2006 guidelines and mass (flow)-, energy (LHV)-, and market (€)-based methods [95]. In the ATJ and HEFA processes, the product was identified as a biojet fuel; nevertheless, some intermediate sub-systems generated by-products as green diesel and lignin (ATJ) and glycerol (HEFA). Biojet fuel combustion was disregarded in the analysis. Finally, the environmental effects were interpreted and compared between them and other ASTM biojet fuel approved routes, including conventional petroleum-derived Jet A-1 fuel with net GHG emissions of $94 \text{ gCO}_{2\text{eq}}/\text{MJ}$ [96].

2.7. Properties estimation

2.7.1. ASTM properties

The ASTM D7566 standard specification defines physico-chemical and thermodynamic parameters to describe traditional aviation turbine fuel quality and synthetic blending hydrocarbons. Seven properties were estimated for both types of biojet fuel derived from ATJ and HEFA pathways. A list of the bibliographic resources and group contribution methods employed in the estimations are detailed in Table 6.

The flash point (FP) is a volatility indicator. It was used to estimate the lowest temperature at which a spark or a flame may ignite the air-vapour mixture in equilibrium with the biojet fuel at atmospheric pressure. Biojet fuel density (ρ) and viscosity (ν) have an impact on combustion performance and emissions by primarily affecting atomization. The ρ influences the mean drop size, influencing the evaporation time, and hence, the reaction rates. On the other hand, the ν is closely related to pumpability and nozzle spray pattern; with the increase of ν , more massive drops, a smaller cone angle and reduced nozzle flow rates are expected [110]. Additionally, ρ is useful in empirical assessments of fuel metering (heating value) and aircraft flight range.

Table 6
Biojet fuel properties estimation.

Parameter	Estimation methods			
	Pure compound	Ref	Mixture ^a	Ref
Flash point ^b	Catoire-Naudet	[97]	$FP = 1.477 \times T_{b,mix}^{0.79686} \times \Delta H_{vap,mix}^{0.16845} \times n_{C,mix}^{-0.05948}$	[97]
Density	Rackett's equation	[98]	$\frac{1}{\rho} = \sum_i \frac{X_i}{\rho_i}$	[99]
Kinematic viscosity	Joback and Reid ^c	[100]	$\ln v = 1.17 \sum_i X_i \ln v_i - 0.22$	[101]
Freezing point	Constantinou and Gani	[102]	$T_f = \sum_i X_i T_{f,i}$	[103]
Lower heating value		[104, 105]	$LHV = \sum_i X_i LHV_i$	[106]
Smoke point ^d		[107, 108]	$\frac{MW_{mix}}{SP_{mix}} = \sum_i \frac{X_i MW_i}{SP_i}$	[109]

^a Where x_i corresponds to the molar fraction.

^b Where T_b is the boiling temperature (K) of the mixture at atmospheric pressure, $n_{C,mix}$ is average carbon number, and $\Delta H_{vap,mix}$ is the mixture's vaporization enthalpy (kJ mol⁻¹).

^c Dynamic viscosity.

^d MW is the molecular weight.

The freezing point (T_f) was calculated as a fluidity at a low-temperature indicator to preclude interference with biojet fuel distribution through the aircraft. The lower heating value (LHV) is the heat of combustion, which is crucial to efficient fuel consumption by quantifying the total energy released from the biojet fuel to perform useful work. The smoke point (SP) was estimated as the flame height achieved during fuel burn before smoke-producing when combustion efficiency is maximum [111]. Finally, a distillation curve was modelled in Aspen-Plus® by employing a RadFrac unit to ascertain the volatile substances content and easy vaporization at different temperatures and specific distilled volume (T_{10} , T_{30} , T_{50} , T_{70} , and T_{90}) [112].

2.7.2. Payload vs range

Payload vs range (Pv.R) analysis was carried out to determine the surrogate fuel's performance under specific flight conditions without conditioning the passenger and cargo capacity, nor flight range. The aircraft operability performance depends on the biojet fuel energy density (MJ/L); the lower the energy contained, the greater the fuel consumption, and the lesser the range. A high LHV and high-density increase the maximum power released during a specific fuel tank volume combustion. Because of the rapid expansion of airline operations worldwide, this study modelled a Boeing 737-800®, a short-haul commercial aircraft used by the most representative low-cost air company in Europe, for range calculations employing Eq. (13).

$$Range = \frac{V(L/D)}{g \times sfc_{AJF}} \ln \left(\frac{W_i}{W_f} \right) \quad (13)$$

Where L/D is the lift-drag ratio at cruise (16.3), V is the flight speed (237 m/s), g is the gravitational constant (9.8 m/s²), and W_f and W_i are the final and initial aircraft weight during the cruise stage [21]. The maximum take-off, landing, and payload weights were 79 t, 66 t, and 21 t, respectively. Distribution weight depends on the expected payload and fuel required for the flight range. Empty aircraft weight is 41 t, and fuel tank capacity is 26 m³. The specific fuel consumption ($sfc_{Biojet\ fuel}$) was defined as Eq. (14) shows.

$$sfc_{AJF} = sfc_{JetA1} \frac{LHV_{JetA1}}{LHV_{Biojetfuel}} \quad (14)$$

Where sfc_{JetA1} value corresponds to 10.76 mg/(N·s), fuel consumption during engine warm-up, take-off, and the climb is 4.5%.

3. Results and discussion

3.1. Process design

3.1.1. Simulation description

The feedstock streamflows ($S1_{ATJ}$ and $S2_{ATJ}$) of the ATJ sequentially go through hydrolysis, SSCF, dehydration, oligomerization, and hydro-processing. The HEFA feedstock ($S1_{HEFA}$, $S26_{HEFA}$ and $S10_{HEFA}$) are transformed through hydrolysis, decarboxylation and hydroprocessing reactions, as shown in Fig. 5.

The physico-chemical properties of all flow streams from the simulated biorefinery are summarized in the SI8 section. The mass and energy balances and the primary process results are described in Table 7.

The results indicate a higher specific biojet fuel mass ratio in the HEFA process since kernel oil and FAD have a more straightforward chemical structure and a higher effective hydrogen-carbon rate than the ATJ's lignocellulosic biomass [42]. Hence, the upgrading process was much direct; also, the FAD were entered directly in the decarboxylation stage. Nonetheless, the ATJ achieved a higher jet-to-fuel mass ratio (0.72 kg_{biojet fuel}/kg_{total fuels}) attributed to high purity ethanol production as an intermediate molecule and high C₉-C₁₂ hydrocarbons selectivity throughout oligomerization stages [55]. In addition, the azeotropic distillation reached around a 30% improvement in ethanol production rate compared to a conventional ethanol-water separation process employing scrubber and rectification columns [20].

In comparison, the dominant lauric acid (C₁₂H₂₄O₂) content in the kernel oil facilitates Jet A1 range alkanes selectivity of around 58%, increasing biojet fuel production rate, avoiding the formation of by-products such as diesel compared with other sorts of vegetable oils from residues [113,114]. Overall thermal efficiency or jet fuel-to-feed energy ratio estimated the remaining feedstock heat input at the biojet fuel product. The difference between processes is attributed to the complexity of the ATJ; the more elaborate the design, the greater the probability of energy loss.

Even though the ATJ energy demand is considerably higher than the HEFA, a significant amount of lignin suitable as heat and electricity feedstock is generated during ethanol production, projecting up to 45 MW of surplus electricity [20]. In contrast, the HEFA process needs combusting natural gas to attain electricity self-sufficiency. At the same time, specific hydrogen usage was 15.8 kg/t_{biojetfuel} and 52 kg/t_{biojetfuel} for ATJ and HEFA. Also, a comparison of energy consumption (heating, cooling, and electricity) determines the ethanol production stage as the primary contributor in the ATJ, despite a heat-exchangers net being implemented to optimize heat recovery.

3.1.2. Hydrolysis reaction

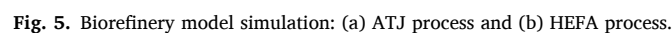
Calculated thermochemical properties for each condition are shown in Table 8.

Based on the Gibbs free energy, at state 1 (25 °C, 0.1 MPa), hydrolysis is an unfeasible endothermic reaction [117]. On the contrary, state 2 (250 °C, 5 MPa) overcame the activation energy barrier without catalyst, leading to water's higher solubility in the kernel oil phase [59]. Simultaneously, high pressure maintained the reactants in the liquid phase, yielding higher conversion rates [118]. The Gibbs free energy described the reaction as exothermic, becoming more attractive to its industrial scale-up. Thermodynamic results are in excellent agreement with experimentally obtained data [119].

3.2. Economic evaluation

The economic analysis results for biojet fuel production through the investigated pathways were calculated based on fixed and variable facilities costs under an average return of investment, capital depreciation, and an ordinary income tax. The results are summarized in Table 9.

During the ATJ route, two types of by-products are generated. Firstly, lignin from the lignocellulosic biomass pretreatment. Lignin is an



On the other hand, throughout the HEFA route, glycerol resulting from hydrolysis is catalogued as a by-product after its treatment with a 0.16 €/kg selling price. The capital costs of both processes are not

Table 7
Summary of results for investigated ASTM pathways.

Parameter		Process	
		ATJ	HEFA
Feedstock (t/h)	Lignocellulose	77.88	–
	Kernel oil	–	4.68
	FAD	–	1.46
Energy (MW)	Heating demand	117.98	4.22
	Cooling demand	123.63	6.31
	Electric power demand	30.58	1.85
Product (t/h)	Biojet fuel	10.99	4.74
By-products (t/h)	Unsaturated green diesel	4.38	–
	Lignin	20.27	–
	Glycerol	–	0.63
Intermediate		Ethanol	–
Specific biojet fuel production (kg/kg _{feedstock})		0.14 ^a /0.48 ^b	0.77
Specific by-products production (kg/kg _{feedstock})		0.32 ^a /0.17 ^b	0.10
Total fuel production (kg/kg _{feedstock})		0.46 ^a /0.65 ^b	0.87
Thermal efficiency from LHV (%)		26 % ^a /40 % ^b	65 %

^a The value refers to the production rate calculated assuming lignocellulosic biomass as feedstock.

^b The value ignores the ethanol production and assumes it as feedstock.

Table 8
Thermochemical properties of the studied components of triolein thermal hydrolysis.

Function	Unit	Compound	Formula	State	
				(25 °C, 0.1 MPa)	(250 °C, 5 MPa)
Enthalpy ΔH_f^0 (g) ^a	kJ·mol ⁻¹	Triolein	C ₅₇ H ₁₀₄ O ₆	–1841.18	–
		Water	H ₂ O	–241.83 ^b	–
		Oleic acid	C ₁₈ H ₃₄ O ₂	–650	–
		Glycerol	C ₃ H ₈ O ₃	–581.88	–
Entropy S^0 (g) ^c	J·mol ⁻¹ K ⁻¹	Triolein	C ₅₇ H ₁₀₄ O ₆	2548.42	–
		Water	H ₂ O	188.81	–
		Oleic acid	C ₁₈ H ₃₄ O ₂	0.8639	–
		Glycerol	C ₃ H ₈ O ₃	400.93	–
Departure enthalpy H^d	kJ·mol ⁻¹	Triolein	C ₅₇ H ₁₀₄ O ₆	–398.8	–137.36
		Water	H ₂ O	–45.92 ^d	–33.98 ^d
		Oleic acid	C ₁₈ H ₃₄ O ₂	–128.04	–92.84
		Glycerol	C ₃ H ₈ O ₃	–77.32	–64.32
Departure entropy S^d	J·mol ⁻¹ K ⁻¹	Triolein	C ₅₇ H ₁₀₄ O ₆	–413.83	–253.35
		Water	H ₂ O	–123.457 ^d	–94.41 ^d
		Oleic acid	C ₁₈ H ₃₄ O ₂	–217.92	–109.66
		Glycerol	C ₃ H ₈ O ₃	–55.24	–81.36
Heat capacity $C_p^0(T)^e$	J·mol ⁻¹ K ⁻¹	Triolein	C ₅₇ H ₁₀₄ O ₆	1315.31	2023.56
		Water	H ₂ O	417.58	646.15
		Oleic acid	C ₁₈ H ₃₄ O ₂	113.17	165.07
		Glycerol	C ₃ H ₈ O ₃	75.30	87.60
Reaction enthalpy ΔH	kJ·mol ⁻¹			114.79	–178.67
Reaction entropy ΔS	J·mol ⁻¹ K ⁻¹			68.77	47.64
Free Gibbs energy ΔG	kJ·mol ⁻¹			94.29	–192.87

^a Ideal gas enthalpy of formation was estimated using the method of Constantinou and Gani [102].

^b Entropy values obtained employing Benson's Group Method [115].

^c Reference value from the National Institute of Standards and Technology (NIST) Chemistry WebBook [116].

^d Values predicted in AspenPlus® by thermodynamics properties calculations.

^e Ideal gas heat capacity in function of T estimated through the Joback and Reid's group contribution method [100].

directly comparable due to the production ladder. This study comprehensively addresses the residues of an oleaginous crop. The ATJ is an industrial-scale biorefinery fed with lignocellulosic biomass. While the HEFA hydroprocessed the vegetable oil extracted from that

Table 9
Economic results summary.

Parameter	Units	Process	
		ATJ	HEFA
Biojet fuel production	(ML/year)	129.22	53.48
By-product production	(ML/year)	Unsaturated green diesel	43.26
			–
			–
Variable Operating Costs	(t/year)	Lignin	170.25
	(ML/year)		–
	(M€/year)		4.24
Fixed Operation Costs	(M€/year)	Feedstock	145.97
	(M€/year)	By-product credits	42.97
			8.10
TIC	(M€)		14.57
ΣIC	(M€)		22.07
FCI	(M€)		25.64
TCI	(M€)		42.73
MBSP	(€/kg _{biojet fuel})		1.43
			1.01

lignocellulosic biomass and the FAD produced during crude vegetable oil refining for biojet fuel production maximizing. Fig. 6 illustrates the capital costs distribution based on the installed equipment costs and the contribution process stages.

As demonstrated in Fig. 6, the main installed equipment costs for the ATJ process are determined as ethanol purification stage (30%) and oligomerization stage (20%). The lignocellulose to ethanol stages is demonstrated as more capital expenditure (CAPEX) intensive for the ATJ process, accounting for over 50%. The ATJ process also has a higher FCI due to more elaborate and sophisticated technology, such as azeotropic distillation and two-step ethylene oligomerization for biojet fuel upgrading [21]. On the other hand, the decarboxylation stage (45%) and hydrolysis stage (40%) are the primary installed equipment costs for the HEFA process. Notwithstanding, it is worth stressing that the facilities proposed and assessed may be challenged by higher contingency costs, as FOAK plants.

The ATJ converted 1800 t/day of dry lignocellulose into 294 ML/year of ethanol as an intermediate, producing 129 ML/year of biojet fuel as the final product. As a result, the calculated MBSP is 1.43 €/kg_{biojet fuel} or 1.03 €/L, significantly higher compared to the market jet fuel price (0.76 €/kg or 0.62 €/L in 2019). In this regard, ethanol bioconversion represents 49% of the MBSP (0.70 €/kg_{ethanol}). Nevertheless, it is similar to *n*-butanol and isobutanol minimum selling prices [122]. In contrast, the HEFA hydroprocessed 148 t/day of vegetable oil and FAD, producing 54 ML/year of biojet fuel. However, its MBSP (1.01 €/kg or 0.75 €/L) is relatively lower because the process requires a minimum amount of catalyst. At the same time, no enzymatic reactions were performed, reaching considerable savings compared to the ATJ [20]. Also, the decreasing kernel oil prices over the last decade and the thermodynamic improvements has contributed to efficient operating conditions.

The atmospheric pollutants released during biojet fuel refining were monetized based on the European Union emissions trading system (EU ETS). The EU ETS prices the CO₂ emissions at 52 €/t, respectively increasing 0.14 €/kg_{biojet fuel} and 0.03 €/kg_{biojet fuel} the MBSP of the ATJ and HEFA processes. Simultaneously, the Jet A1 selling price increases to 0.96 €/kg, approaching the MBSP of the HEFA process. Nevertheless, if only the emissions generated during the upgrade from ethanol to biojet are considered, the increase in the MBSP of the ATJ of 0.02 €/kg is worth noting. Furthermore, based on the current CO₂ emission cost, the techno-economic analysis concluded at least quadruple the emissions cost is necessary to balance the MBSP of the ATJ and the selling price of the Jet A1.

Regarding conventional Jet A1 selling price, biojet fuel prices are expected to increase by 1.05 €/L and 0.37 €/L for the ATJ and HEFA routes [123]. Therefore, the produced biojet fuels bridge the gap in 61% and 75%, respectively. Although the determined MBSP for the ATJ is

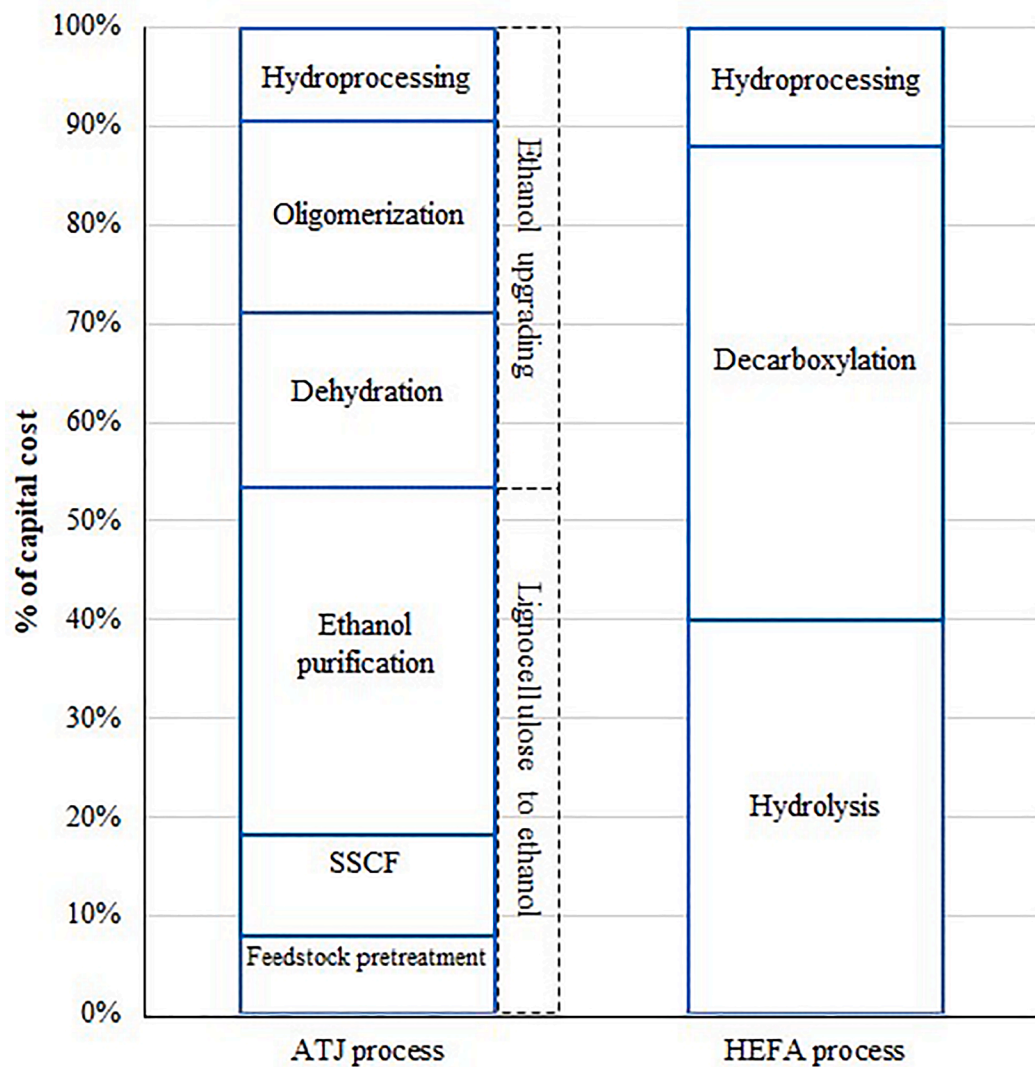


Fig. 6. Capital expenditure by stages.

similar to other alcohol-derived jet fuels, technological and biochemical improvements are required to lower production costs; otherwise, a competitive selling price will not be possible [21]. Nonetheless, if the additional fee corresponding to implementing the produced biojet fuel in a regular 1000 km flight is allocated among passengers, the ticket fare will rise between 1.20 € to 4.30 € [2].

3.3. Exergetic analysis

The exergy analyses employed an appropriate level of aggregation.

Table 10
Exergy results for the analyzed sub-systems.

System	Sub-system	Index						
		X_R (MW)	X_P (MW)	X_I (MW)	X_d (MW)	d_r (%)	X_d/X_R	E_{ff}
ATJ	Feedstock pretreatment	2489	2341	143	5.90	0.02	0.002	0.94
	SSCF	2325	2247	4	74.11	0.62	0.032	0.97
	Ethanol purification	648	484	138	27.07	0.23	0.042	0.75
	Dehydration	429	427	0	2.77	0.02	0.006	0.97
	Oligomerization	1034	1021	0	12.14	0.10	0.012	0.97
	Hydro-processing	369	367	0	1.47	0.01	0.004	0.98
HEFA	Hydrolysis	199	198	0	0.21	0.22	0.001	0.97
	Decarboxylation	315	314	0.23	0.37	0.38	0.001	0.97
	Hydro-processing	124	124	0	0.37	0.39	0.003	0.95

to the saccharification reactor (B9) with an exergetic efficiency (eff) of 82%. Irreversibilities were generated because of the relatively lower conversion efficiency of *gluco*-oligomer (C6) to glucose and fructose and *xylo*-oligomer (C5) to xylose, evidencing the necessity of an enzymatic improvement to detect potential hosts [124]. Consequently, fermentation yield was also impaired. Biochemical conversions yield are directly related to irreversibility generation—the lower the conversion yield, the more significant exergy destruction [125]. In addition, hemicellulose degradation and lignin solubility throughout lignocellulosic biomass pretreatment directly affecting the SSCF efficiency [46]. The neutralization reaction after the acid hydrolysis generated 62% of the irreversibilities in the pretreatment sub-system. Ethanol purification also contributed to an appreciable amount of exergy destruction due to high energy consumption.

Nevertheless, the exergy destruction in both distillation columns compared to the exergy of the resources consumed (X_d/X_R) is barely 4%. A relatively low exergy destruction ratio is expected throughout the systems, considering an oleaginous crop residues transformation into biojet fuel [126]. In contrast, ethanol dehydration and ethylene oligomerization were exergetically more efficient, achieving 97% by implementing a heat exchanger net to reduce losses regarding harsh operating conditions. The developed ATJ biorefinery's calculated efficiency was 89%, significantly improved from 66% of other biomass-based biorefineries [127,128].

On the other hand, the HEFA system irreversibility was 990 kW with an exergetic efficiency of 71%. The X_d is essential, but so is the ratio between equipment destruction and total exergy destroyed in the system. The relative exergy destruction (d_r) was similar in decarboxylation and hydro-processing sub-systems (~40%), the high-power consumption (heat and work) attended by an inefficient hydrogen recovery unit and reactors losses. The triglycerides hydrolysis exergetic efficiency and the exergy destruction ratio at the operating conditions previously evaluated in section 2.3.1 vary from 28%/78% in (T_1 , P_1) to 85%/11% (T_2 , P_2), improving 19% and 10%, respectively, compared to enzymatic hydrolysis of lignocellulose biomass [129].

3.4. Thermoeconomic analysis

The thermo-economic analysis results evaluated the effect of Z on the exergetic results of each piece of equipment for the optimization of both systems and costs minimization. The calculated indexes are summarized in Table 11.

The thermoeconomic cost of the products (Π_P) varied from the resources thermoeconomic cost (Π_R) proportionately to the Z costs. In the ATJ instance, the elevated Z is attributed to the ethanol purification and oligomerization sub-systems. The ethanol preconcentration and azeotropic distillation columns (C1 and C2, respectively) are complex and large equipment, requiring high temperatures because of low-pressure conditions to operate [130]. Similarly, the C3 fractionating column bottom streams require a high temperature due to the oligomerized reaction product's high molecular weight, demanding more complicated

and expensive fired heaters. Furthermore, a much larger oligomerization reactor (B2) and distillation column (C3) were required to handle the increased volumetric flow because of the high rate of recycling using more separation/fractionation energy, and hence more associated conservation elements [55]. There were no substantial variations concerning the HEFA process; however, the decarboxylation stage contributes the most because of the implementation of gaseous and effluents recovery and energy conservation units.

In addition to the unit exergoeconomic cost ($C_j = \Pi_j/X_j$) of the resources (C_R), the unit exergoeconomic costs of the products (C_P) added the Z values and the losses/waste and exergy destruction costs of the equipment. These added values of thermodynamic character are defined as the relative overcost ($(C_P - C_R)/C_R$), which calculates the increase rate between products and resources [126]. Interestingly, despite the fact that the SSCF accumulate more irreversibilities, the ethanol purification achieved a higher relative overcost due to energy losses and wastewater generation from the dehydration and azeotropic distillation columns. However, energy efficiency (60%) could significantly improve by replacing the traditional adiabatic column with a non-adiabatic distillation column [131]. Therefore, compared to the TEA results, it does not surprise the elevated production cost of ethanol. In contrast, the products' thermoeconomic cost ($C_R \cdot X_P$) was calculated, assuming the exergy destruction, losses, and fixed costs are zero. The difference between ($C_R \cdot X_P$) and (Π_P) resulted in the absolute overcost ($C_P - X_R$) $\cdot X_P$, where the thermodynamic contribution is decomposed in the thermoeconomic costs of the exergy losses ($C_R \cdot X_I$) and the thermoeconomic costs of the exergy destruction ($C_R \cdot X_d$) [83].

Finally, the exergoeconomic factor (f) of the equipment was calculated to determine the influence of the economic contributions (Z) on the total overcost ($Z + C_R \cdot X_I + C_R \cdot X_d$). If the achieved f is low, a cost improvement could be reached by incrementing thermodynamic efficiency. But if the calculated f is high, a simplification in the equipment design would be required, even though this implies more significant exergy destruction [86]. The sub-systems achieved an f value below 0.5, evidencing the mild impact of Z on the total costs; thus, variable costs are far more critical. However, with further precision, the ATJ sub-systems require an equipment simplification based on the thermodynamic improvements; i.e., if the exergetic efficiency is low with a high exergy destruction rate without contributing to costs minimization, then the equipment should be eliminated. The hydrolysis f value is slightly higher in the HEFA system because of elevated exergy destruction in the preconditioning equipment P1 and H1. As mention before, at 250 °C and 5 MPa, the reaction becomes very exothermic, losing energy proportionately, increasing operating costs despite the exergetic efficiency, and lower Z .

3.5. Life cycle assessment

The resulting life cycle GHG emissions for the ATJ and HEFA routes were 75 gCO_{2eq} and 18 gCO_{2eq} for each MJ of biojet fuel produced, respectively. At the same time, the life cycle fuel consumption was 47.5

Table 11
Thermoeconomic results for the processes equipment (Total cost).

System	Sub-system	Index Z (€/s)	Π_R (€/s)	Π_P (€/s)	C_R (€/MWh)	C_P (€/MWh)	$C_R \cdot X_P$ (€/s)	$C_R \cdot X_I$ (€/s)	$C_R \cdot X_d$ (€/s)	$(C_P - C_R) \cdot X_P$ (€/s)	$(C_P - C_R)/C_R$	f
ATJ	Feedstock pretreatment	0.10	21.73	21.83	31.42	33.57	20.43	1.25	0.05	1.40	0.07	0.49
	SSCF	0.12	29.75	29.87	46.06	47.86	28.75	0.05	0.95	1.12	0.04	0.06
	Ethanol purification	0.42	11.87	12.29	65.91	91.49	8.86	2.52	0.50	3.44	0.39	0.30
	Dehydration	0.07	14.73	14.81	123.52	124.91	14.64	0.00	0.09	0.17	0.01	0.27
	Oligomerization	0.41	37.70	38.11	131.32	134.31	37.26	0.00	0.44	0.85	0.02	0.31
	Hydro-processing	0.13	35.41	35.48	345.60	347.69	35.27	0.00	0.14	0.21	0.01	0.32
HEFA	Hydrolysis	0.01	10.02	10.02	181.58	181.93	10.00	0.00	0.01	0.02	0.00	0.44
	Decarboxylation	0.01	22.37	22.38	255.95	256.55	22.33	0.02	0.03	0.05	0.00	0.19
	Hydro-processing	0.00	11.74	11.74	339.66	340.76	11.70	0.00	0.04	0.04	0.00	0.07

MJ/kg_{biojet fuel} and 5 MJ/kg_{biojet fuel} for each route. In this regard, the ATJ emissions compare well with sugarcane-derived ethanol and *n*-butanol ATJ routes. Contrastingly, the HEFA shows an improvement relative to palm oil and jatropha oil, as shown in Fig. 7.

The emissions related to cultivation (11 gCO_{2eq}/MJ_{biojet fuel}) were not considered in the biojet fuel LCA. Furthermore, based on the EU directive on promoting energy use from renewable sources, the environmental burdens of the feedstocks are zero because they are waste [4]. Besides, it was considered 100 km of distance between the vegetable oil processing plant and the biorefinery regarding transportation. Transport from one place to another was carried out by train and truck, in a proportion of 85% and 15% respectively. The GHG emissions generated in the lignocellulose-to-ethanol biochemical conversion constitute 88% of the overall process, mainly attributed to the ethanol purification stage. Nevertheless, the dehydration and azeotropic columns' total heat duty is approximately 15% higher than a combined double column and molecular sieve adsorption unit [122]. On the ethanol upgrade to biojet fuel, most of the emissions (7.2 gCO_{2eq}/MJ_{biojet fuel}) occur in the dehydration and oligomerization stages, primarily caused by energy consumption.

Life cycle GHG emissions and fossil fuel consumption through the ATJ route are elevated. Nonetheless, GHG reductions were estimated applying the EU Renewable Energy Directive II (RED II) methodology for by-product displacement credit. Otherwise, the process would breach the mandatory GHG emissions target reduction of 65%,

compared to petroleum-derived Jet A1 (94 gCO_{2eq}/MJ) for facilities starting operation after January 2021 [4]. The ATJ model corresponded to a 2G biorefinery employing residual biomass. The ethanol production stage was designed following a specific standard configuration, comprising steam explosion pretreatment, an internal heat provision by lignin combustion, and C₅-C₆ co-fermentation to meet the minimum GHG saving requirements [132].

The remaining lignin from the SSCF stage is an essential component in valorizing lignocellulosic biomass. Lignin versatility as a by-product due to its lower heating value (24.07 MJ/kg) makes it suitable for efficient heat and electricity conversions. While the TEA assumes the sale of lignin as a value-added by-product, it could be used as an in-situ energy source. For example, high-pressure steam could be obtained through a fluidised bed combustor, supplying the demand for the pretreatment reactor and distillation columns. Furthermore, converting excess into electricity to encounter biorefinery's utility requirements, avoiding a significant amount of emissions and natural gas consumption [133].

The electricity surplus displaced an equivalent amount of the marginal grid electricity (1:1 kWh), generating a net GHG emissions reduction of 110 gCO_{2eq}/MJ_{biojet fuel}, as defined by the Ecoinvent database. The marginal electricity mix played an important role, considering the elevated coal-fired electricity import share [132,134]. Besides, the RED II grants GHG emissions credits when petroleum-derived CO₂ is replaced, i.e., one kg of green diesel produced at the oligomerization stage displaced 1 kg of petroleum-derived diesel equivalent to 4.09

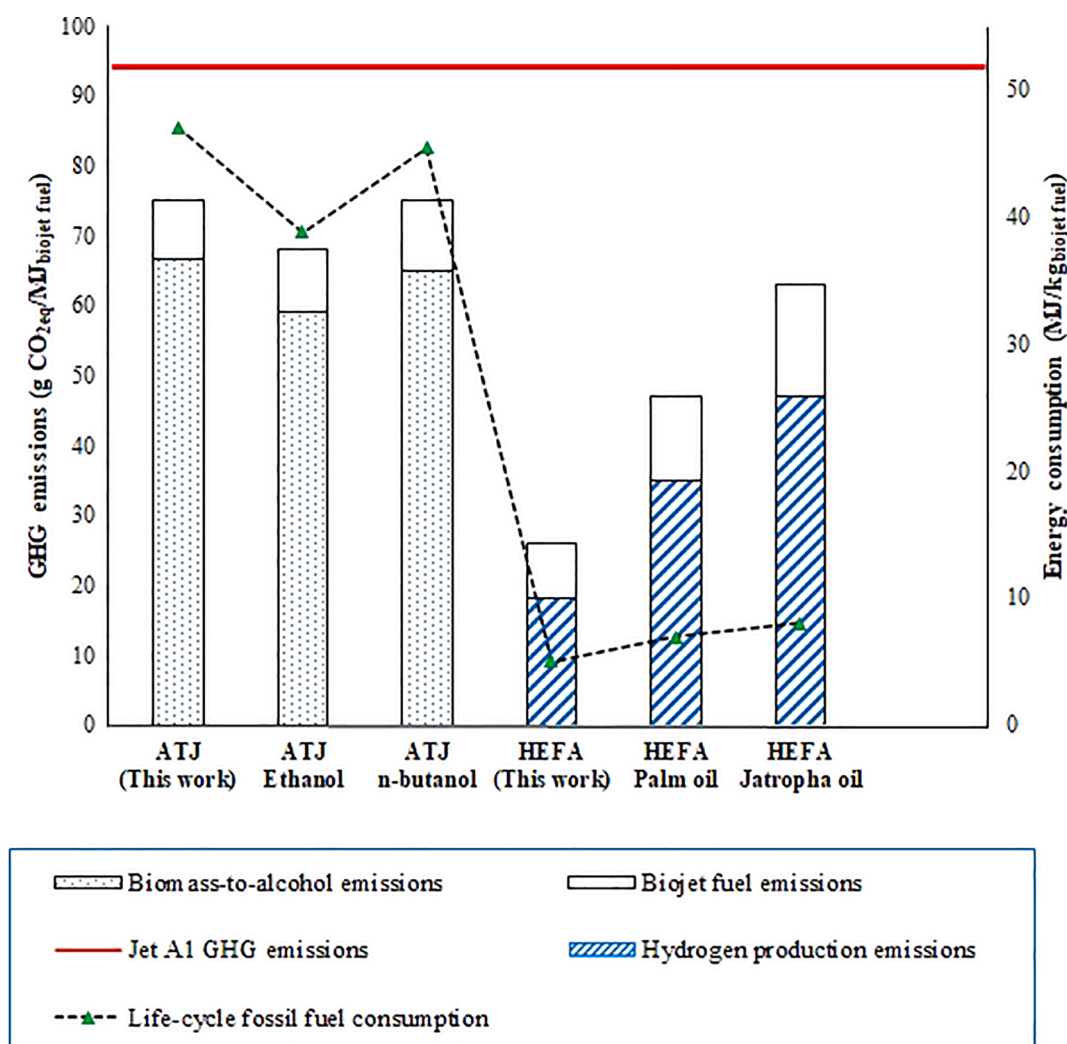


Fig. 7. Comparison of net GHG emissions between studied and similar process varying the feedstock.

kgCO_{2eq}/kg_{diesel} [122].

On the other hand, the GHG footprint of the HEFA process is significantly influenced by the hydrogen source and its consumption during the decarboxylation and hydroprocessing stages. Lower net GHG emissions can be achieved by replacing the steam methane reforming of natural gas with its biomass-derived counterpart (off-gas) to produce in-situ hydrogen. Accordingly, the gasification process leads to a carbon footprint reduction in the entire chain of 65%, mainly due to the absorption of CO₂ during biomass growing (total CO₂ capture of 29.8 kg CO_{2eq}/kg_{hydrogen} was assumed in this context) [135,136]. Compared to the fossil reference, the GHG reduction is over the RED II threshold, which agrees with the other biojet fuels from the ASTM D7566 [123,137]. Regarding the energy consumption, the HEFA achieved a highly efficient process attributed to the heat exchanger net implemented on each stage.

3.6. Properties estimation

3.6.1. ASTM properties

The calculated physico-chemical properties of both biojet fuels and the ASTM standard specifications are listed in Table 12.

The *FP* of the HEFA is acceptable, while the ATJ is slightly lower than the specification since the lower volatility component primarily dictates the *FP* indicator. However, a considerable improvement in volatility content is expected when Jet A1 blending occurs. In both cases, the ρ parameter is inside the requirement; nevertheless, none of them could be considered a Jet A1 surrogate on its own. The density of a biojet fuel is crucial to obtain a stable blend since the lower the difference between them, the smaller the chance of separation. Both fuels' kinematic viscosity is within the acceptable range, even though the ATJ is much lower, leading to better atomization and combustion and pumping ease. The T_f of both biojet fuels overpasses the ASTM reference and the experimental Jet A1 value due to its composition based on straight and branched carbon chains and its low level of polyunsaturates. The T_f must be low enough to ensure the fuel fluency at high-altitude reached temperatures during a flight. In both cases, the *LHV* measure is similar and is above the specification, which is in excellent agreement with the Jet A1 reference. As mention before, both biojet fuels are composed of a significant amount of *iso*-alkanes (~80%); for that reason, the achieved virtual *SP* is higher than the specification and the Jet A1. *Iso*-alkanes

Table 12
Standard physico-chemical requirements.

Property	Unit	ASTM D7566 ^a	Jet fuel		
			ATJ	HEFA	Jet A1 ^c
Flash point	°C	min 38	32	62	42
Density at 15 °C	kg/m ³	730 to 770/ 775 to 840 ^b	730.2	757.5	798.0
Kinematic viscosity at -20 °C	mm ² /s	max 8	2.63	5.27	4.63
Freezing point	°C	max -40/max -47 ^b	-76	-54	-52
Lower heating value	MJ/kg	min 42.8	44.33	44.21	43.52
Smoke point	mm	min 25	65.8	75.4	24.0 ^d
Distillation					
T ₁₀	°C	max 205	146	181	179
T ₅₀	°C	report	180	217	204
T ₉₀	°C	report	209	275	238
Final boiling point	°C	max 300	250	287	254
T ₉₀ -T ₁₀	°C	min 22/min 40 ^b	63	94	59

^a Requirements for the ATJ and HEFA biojet fuels are described in Annex 2 and Annex 5, respectively.

^b Specification to biojet fuel/Jet A1.

^c Physico-chemical properties of an average Jet A1 [138].

^d Experimental data obtained through the ASTM D86 methodology for atmospheric distillation curve [139].

have a relatively high *SP* due to their low sooting tendency. The flame height difference between biojet fuels is ascribed to its primary C₁₂ and C₁₁ isoalkane composition; the shorter the carbon chain, the higher the smoke point.

The volatility of both biojet fuels determines their combustion properties. As was expected from the *FP* calculation, the distillation curve of the ATJ evidences an overly volatile compound compared to the HEFA (see Fig. 8).

High flammable fuel is prone to evaporative losses at high altitude, so low volatility might not ignite readily during combustion [138]. Thus, in both cases, the combustion efficiency is reduced, and the emissions increased. Notwithstanding, the biojet fuels met all the ASTM specifications and can be blended up to a 50:50 ratio with Jet A1.

3.6.2. Payload vs range

The ATJ and HEFA fuels' energy density was 32.4 MJ/L and 32.8 MJ/L, while the Jet A1 reached 34.7 MJ/L. Hence, to maximize range when the biojet fuels are implemented, the aircraft's payload capacity will be conditioned by the size of the fuel tanks and not exceed the maximum structural load. Besides, the *Pv.R* calculations considered at least 20% fuel remaining at the end of the flight to meet safety requirements. The results diagram is plotted in Fig. 9.

During a flight with the maximum payload capacity, the biojet fuel reached a range improvement of approximately 3% compared to traditional Jet A1; however, it required 6% more fuel tank capacity. On the other hand, an optimal weight breakeven is achieved when the fuel tank is filled with biojet fuel, enabling a higher payload capacity of 1.7 t upper than Jet A1, but 1000 km of autonomy is lesser. In contrast, the closer the payload approaches zero, the more significant the difference in long-range achieved by Jet A1 owing to its high energy density.

The global crisis regarding the SARS-CoV-2 has significantly impacted the air transport sector, reducing nearly 25% of the operations during 2020 compared to 2019. Countless layoffs and bankrupted companies are expected throughout the world. In addition to the sparse demand for flights, the extra costs that the pandemic implies must be added; the airlines must invest more in cleaning and disinfection, spending more time on the ground than flying. Hence, the air industry can implement sustainable initiatives that contribute economically to overcome the pothole being left by the health emergency. The biojet fuel *Pv.R* performance is on par with its petroleum-derived counterpart; nevertheless, the optimal weight balance to improve range occurs in short-haul distance flights with a payload and fuel tank capacity just under the maximum limit (15% and 5%, respectively), implying a reduction in operating costs and physical distancing between passengers preventing contagion inside the aircraft. For instance, running the 10,800 flights per year route (round trip) between Madrid and London involves travelling 1246 km per flight. The ATJ and HEFA fuel consumption to complete the journeys is 3% more efficient than Jet A1, accomplishing another 335 and 283 additional flights. The extra flights are equivalent to approximately 0.7 M€/year from fuel savings, compensating for reducing payload due to current biosafety regulations. Further savings are expected concerning refuelling associated costs.

4. Conclusions

The simulated processes for biojet fuel production from lignocellulosic biomass through the ATJ and HEFA thermochemical routes achieved a highly efficient production rate. From the techno-economic analysis, it is concluded that even though the HEFA process has better performance than the ATJ route in terms of carbon utilization and thermal efficiency, the minimum biojet fuel selling price remains higher than the Jet A1 price. On the other hand, the ATJ minimum selling price almost double Jet A1 price attributed to the higher CAPEX, especially in the ethanol processing stage. Nevertheless, further development of microorganisms dedicated to simultaneous saccharification and co-fermentation regarding potential hosts detection might enhance the

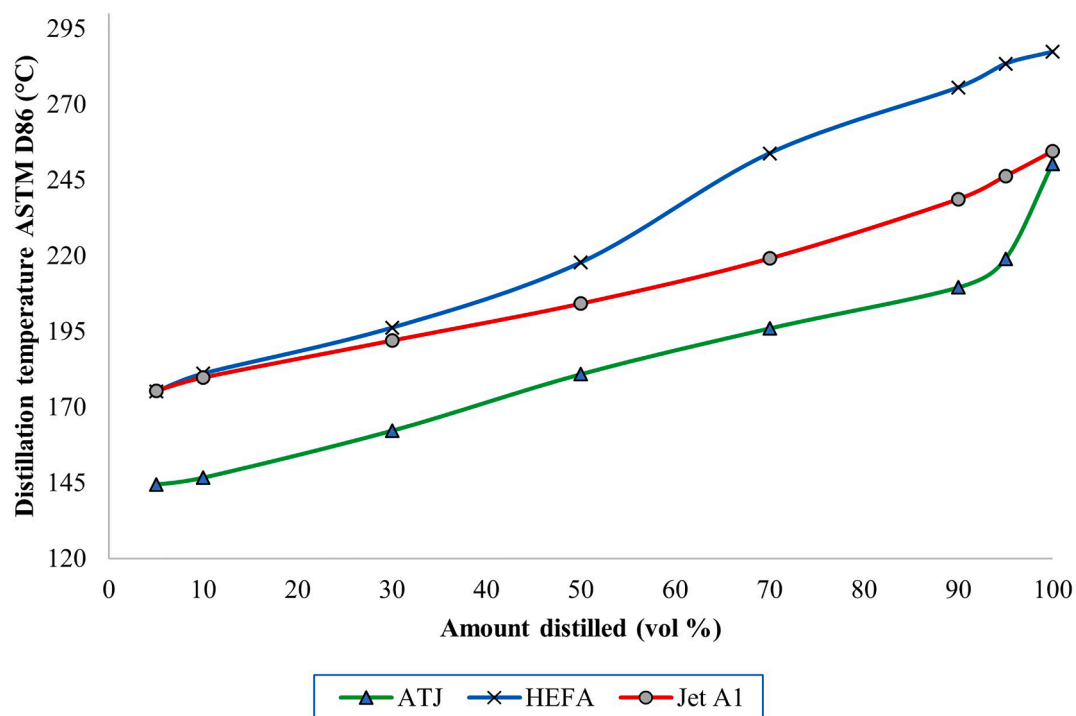


Fig. 8. Biojet fuel distillation curves.

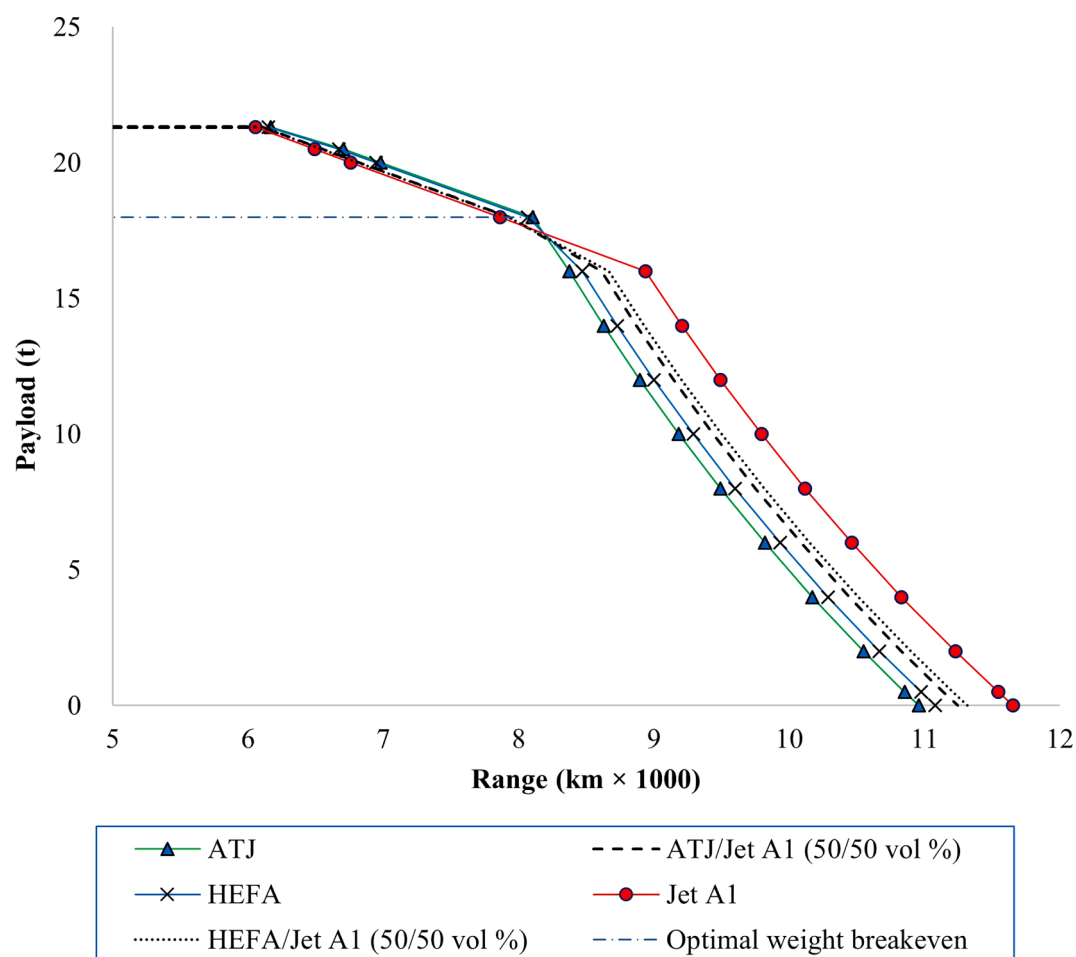


Fig. 9. Payload vs Range diagram performance of the produced biojet fuels in a Boeing 737-800®.

concept's competitiveness. At the same time, higher selectivity catalysts would reduce the recycling stream, reducing the equipment size and lowering CAPEX. Furthermore, it is worth mentioning the azeotropic distillation equipment as more CAPEX intensive; thus, more attention should be given in future studies.

Exergetic calculations identified irreversibilities on each piece of equipment, while the thermoeconomic analysis quantified them. In this sense, the ethanol purification sub-system requires thermodynamic improvements. Otherwise, it would be more profitable to substitute the azeotropic distillation with another purification technology. The potential of lignin as a by-product has the most significant impact on reducing the GHG footprint of the life cycle assessment when its conditioned and used as an in-situ power source. As long as policies and design improvements in ethanol processing were implemented, the entire process's GHG footprint decreased. Furthermore, the produced biojet fuels are suitable as jet fuel blending components; their combustion behaviour meets the requirements for commercial flights. In this regard, the chemical composition of feedstocks directly affects biojet fuel volatility.

The combined research discussed in this manuscript takes a quantitative and qualitative approach to biojet fuel production from ethanol and vegetable oil, pinpointing innovations needed to make the process technically, economically, and environmentally feasible. Nonetheless, it is imperative to further studies on producing an entire replacement for petroleum-derived jet fuel (e.g. outputting naphtha and reforming it to produce the needed aromatics). Finally, the logistics and seasonality of feedstock could be studied in further works.

CRediT authorship contribution statement

Nicolas Vela-García: Conceptualization, Methodology, Software, Investigation, Writing - review & editing. **David Bolonio:** Conceptualization, Methodology, Validation, Visualization, Project administration. **María-Jesús García-Martínez:** Methodology, Software, Resources, Formal analysis. **Marcelo F. Ortega:** Software, Resources, Formal analysis. **Daniela Almeida Streitwieser:** Conceptualization, Investigation, Writing - review & editing. **Laureano Canoira:** Supervision, Validation, Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] International Air Transport Association. Annual Review. 76th Annual General Meeting, 2020.
- [2] Deane JP, Pye S. Europe's ambition for biofuels in aviation - A strategic review of challenges and opportunities. *Energy Strateg Rev* 2018;20:1–5. <https://doi.org/10.1016/j.esr.2017.12.008>.
- [3] Rojo C, Vancassel X, Mirabel P, Ponche J-L, Garnier F. Impact of alternative jet fuels on aircraft-induced aerosols. *Fuel* 2015;144:335–41. <https://doi.org/10.1016/j.fuel.2014.12.021>.
- [4] European Union. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources. vol. 5. 2018.
- [5] Mawhood R, Gazis E, de Jong S, Hoefnagels R, Slade R. Production pathways for renewable jet fuel: a review of commercialization status and future prospects. *Biofuels Bioprod Biorefining* 2016;10(4):462–84. <https://doi.org/10.1002/bbb.2016.10.issue-410.1002/bbb.1644>.
- [6] Hammond GP, Seth SM. Carbon and environmental footprinting of global biofuel production. *Appl Energy* 2013;112:547–59. <https://doi.org/10.1016/j.apenergy.2013.01.009>.
- [7] Kong S-H, Loh S-K, Bachmann RT, Rahim SA, Salimon J. Biochar from oil palm biomass: A review of its potential and challenges. *Renew Sustain Energy Rev* 2014;39:729–39. <https://doi.org/10.1016/j.rser.2014.07.107>.
- [8] Cai J, He Y, Yu Xi, Banks SW, Yang Y, Zhang X, et al. Review of physicochemical properties and analytical characterization of lignocellulosic biomass. *Renew Sustain Energy Rev* 2017;76:309–22. <https://doi.org/10.1016/j.rser.2017.03.072>.
- [9] Colombo CA, Chorfi Berton LH, Diaz BG, Ferrari RA. Macauba: a promising tropical palm for the production of vegetable oil. *OCL* 2018;25(1):D108. <https://doi.org/10.1051/ocl/2017038>.
- [10] Khatun R, Reza MIH, Moniruzzaman M, Yaakob Z. Sustainable oil palm industry: the possibilities. *Renew Sustain Energy Rev* 2017;76:608–19. <https://doi.org/10.1016/j.rser.2017.03.077>.
- [11] Mohammed MAA, Salmiaton A, Wan Azlina WAKG, Mohammad Amran MS, Fakhru'l-Razi A, Taufiq-Yap YH. Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia. *Renew Sustain Energy Rev* 2011;15(2):1258–70. <https://doi.org/10.1016/j.rser.2010.10.003>.
- [12] Rahman SHA, Choudhury JP, Ahmad AL. Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid. *Biochem Eng J* 2006;30(1):97–103. <https://doi.org/10.1016/j.bej.2006.02.009>.
- [13] Atsonios K, Kougiumtzis M-A, D. Panopoulos K, Kakaras E. Alternative thermochemical routes for aviation biofuels via alcohols synthesis: Process modeling, techno-economic assessment and comparison. *Appl Energy* 2015;138:346–66. <https://doi.org/10.1016/j.apenergy.2014.10.056>.
- [14] Gupta KK, Rehman A, Sarviya RM. Bio-fuels for the gas turbine: a review. *Renew Sustain Energy Rev* 2010;14(9):2946–55. <https://doi.org/10.1016/j.rser.2010.07.025>.
- [15] Wise M, Muratori M, Kyle P. Biojet fuels and emissions mitigation in aviation: an integrated assessment modeling analysis. *Transp Res Part D Transp Environ* 2017;52:244–53. <https://doi.org/10.1016/j.trd.2017.03.006>.
- [16] Gupta KK, Rehman A, Sarviya RM. Bio-fuels for the gas turbine: a review. *Renew Sustain Energy Rev* 2010;14:2946–55. <https://doi.org/10.1016/j.rser.2010.07.025>.
- [17] de Klerk A. Aviation Turbine Fuels Through the Fischer–Tropsch Process. *Biofuels Aviat., Elsevier*; 2016, p. 241–59. <https://doi.org/10.1016/B978-0-12-804568-8.00010-X>.
- [18] Pires APP, Han Y, Kramlich J, Garcia-Perez M. Chemical composition and fuel properties of alternative jet fuels. *BioResources* 2018;13:2632–57. <https://doi.org/10.15376/biores.13.2.2632-2657>.
- [19] Chiaromonte D, Prussi M, Buffi M, Tacconi D. Sustainable bio kerosene: Process routes and industrial demonstration activities in aviation biofuels. *Appl Energy* 2014;136:767–74. <https://doi.org/10.1016/j.apenergy.2014.08.065>.
- [20] Diederichs GW, Ali Mandegari M, Farzad S, Görgens JF. Techno-economic comparison of biojet fuel production from lignocellulose, vegetable oil and sugar cane juice. *Bioresour Technol* 2016;216:331–9. <https://doi.org/10.1016/j.biortech.2016.05.090>.
- [21] Vela-García N, Bolonio D, Mosquera AM, Ortega MF, García-Martínez M-J, Canoira L. Techno-economic and life cycle assessment of triisobutane production and its suitability as biojet fuel. *Appl Energy* 2020;268:114897. <https://doi.org/10.1016/j.apenergy.2020.114897>.
- [22] Atsonios K, Christodoulou C, Koytsoumpa E-I, Panopoulos KD, Kakaras E. Plant design aspects of catalytic biosyngas conversion to higher alcohols. *Biomass Bioenergy* 2013;53:54–64. <https://doi.org/10.1016/j.biombioe.2013.01.035>.
- [23] Hannon JR, Lynd LR, Andrade O, Benavides PT, Beckham GT, Biddy MJ, et al. Technoeconomic and life-cycle analysis of single-step catalytic conversion of wet ethanol into fungible fuel blendstocks. *Proc Natl Acad Sci* 2020;117(23):12576–83. <https://doi.org/10.1073/pnas.1821684116>.
- [24] Klein BC, Chagas MF, Junqueira TL, Rezende MCAF, Cardoso TdF, Cavaletto O, et al. Techno-economic and environmental assessment of renewable jet fuel production in integrated Brazilian sugarcane biorefineries. *Appl Energy* 2018;209:290–305. <https://doi.org/10.1016/j.apenergy.2017.10.079>.
- [25] Eagan NM, Kumbhalkar MD, Buchanan JS, Dumesic JA, Huber GW. Chemistries and processes for the conversion of ethanol into middle-distillate fuels. *Nat Rev Chem* 2019;3(4):223–49. <https://doi.org/10.1038/s41570-019-0084-4>.
- [26] Wang X, Hu X, Song C, Lux KW, Namazian M, Imam T. Oligomerization of Biomass-Derived Light Olefins to Liquid Fuel: Effect of Alkali Treatment on the HZSM-5 Catalyst. *Ind Eng Chem Res* 2017;56(42):12046–55. <https://doi.org/10.1021/acs.iecr.7b0231610.1021/acs.iecr.7b02316.s001>.
- [27] Galadima A, Muraza O. Zeolite catalysts in upgrading of bioethanol to fuels range hydrocarbons: A review. *J Ind Eng Chem* 2015;31:1–14. <https://doi.org/10.1016/j.jiec.2015.07.015>.
- [28] Saavedra Lopez J, Dagle RA, Dagle VL, Smith C, Albrecht KO. Oligomerization of ethanol-derived propene and isobutene mixtures to transportation fuels: catalyst and process considerations. *Catal Sci Technol* 2019;9(5):1117–31. <https://doi.org/10.1039/C8CY02297F>.
- [29] Sun J, Wang Y. Recent Advances In Catalytic Conversion Of Ethanol To Chemicals. *ACS Catal* 2014;4(4):1078–90. <https://doi.org/10.1021/cs4011343>.
- [30] Michailos S, Bridgwater A. A comparative techno-economic assessment of three bio-oil upgrading routes for aviation biofuel production. *Int J Energy Res* 2019;er.4745. <https://doi.org/10.1002/er.4745>.
- [31] Natelson RH, Wang W-C, Roberts WL, Zering KD. Technoeconomic analysis of jet fuel production from hydrolysis, decarboxylation, and reforming of camelina oil.

- Biomass Bioenergy 2015;75:23–34. <https://doi.org/10.1016/j.biombioe.2015.02.001>.
- [32] Goh BHH, Chong CT, Ge Y, Ong HC, Ng J-H, Tian Bo, et al. Progress in utilisation of waste cooking oil for sustainable biodiesel and biojet fuel production. *Energy Convers Manag* 2020;223:113296. <https://doi.org/10.1016/j.enconman.2020.113296>.
- [33] Neste® 2021. <https://www.neste.com/sustainability/sustainable-supply-chain/raw-material-sourcing#ccb25303>.
- [34] Allami HA, Tabasizadeh M, Rohani A, Farzad A, Nayebzadeh H. Precise evaluation the effect of microwave irradiation on the properties of palm kernel oil biodiesel used in a diesel engine. *J Clean Prod* 2019;241:117777. <https://doi.org/10.1016/j.jclepro.2019.117777>.
- [35] Radzuan MN, Banat IM, Winterburn J. Production and characterization of rhamnolipid using palm oil agricultural refinery waste. *Bioresour Technol* 2017; 225:99–105. <https://doi.org/10.1016/j.biortech.2016.11.052>.
- [36] Tanzil AH, Brandt K, Wolcott M, Zhang X, Garcia-Perez M. Strategic assessment of sustainable aviation fuel production technologies: Yield improvement and cost reduction opportunities. *Biomass Bioenergy* 2021;145:105942. <https://doi.org/10.1016/j.biombioe.2020.105942>.
- [37] Torres Ortega JA, Contento Rubio OF, Herrera OI. Análisis de ciclo de vida para una biorefinería derivada de residuos agrícolas de palma aceitera (Elaeis guineensis). *Publicaciones e Investig* 2018;11:13–36. <https://doi.org/10.22490/25394088.2251>.
- [38] Bond JQ, Upadhye AA, Olcay H, Tompsett GA, Jae J, Xing R, et al. Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass. *Energy Environ Sci* 2014;7(4):1500–23. <https://doi.org/10.1039/C3EE43846E>.
- [39] Petersen AM, Farzad S, Görgens JF. Techno-economic assessment of integrating methanol or Fischer-Tropsch synthesis in a South African sugar mill. *Bioresour Technol* 2015;183:141–52. <https://doi.org/10.1016/j.biortech.2015.02.007>.
- [40] Derman E, Abdulla R, Marbawi H, Sabullah MK. Oil palm empty fruit bunches as a promising feedstock for bioethanol production in Malaysia. *Renew Energy* 2018;129:285–98. <https://doi.org/10.1016/j.renene.2018.06.003>.
- [41] Zabeed H, Sahu JN, Boyce AN, Faruq G. Fuel ethanol production from lignocellulosic biomass: An overview on feedstocks and technological approaches. *Renew Sustain Energy Rev* 2016;66:751–74. <https://doi.org/10.1016/j.rser.2016.08.038>.
- [42] Itthibenchapong V, Srifa A, Kaewmeesri R, Kidkhunthod P, Faungnawakij K. Deoxygenation of palm kernel oil to jet fuel-like hydrocarbons using Ni-MoS₂/Al₂O₃ catalysts. *Energy Convers Manag* 2017;134:188–96. <https://doi.org/10.1016/j.enconman.2016.12.034>.
- [43] Chongkhong S, Tongurai C, Chetpattananondh P, Bunyakan C. Biodiesel production by esterification of palm fatty acid distillate. *Biomass Bioenergy* 2007; 31(8):563–8. <https://doi.org/10.1016/j.biombioe.2007.03.001>.
- [44] Badgujar KC, Bhanage BM. Factors governing dissolution process of lignocellulosic biomass in ionic liquid: Current status, overview and challenges. *Bioresour Technol* 2015;178:2–18. <https://doi.org/10.1016/j.biortech.2014.09.138>.
- [45] Tao L, Aden A, Elander RT, Pallapolu VR, Lee YY, Garlock RJ, et al. Process and techno-economic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass. *Bioresour Technol* 2011;102(24): 11105–14. <https://doi.org/10.1016/j.biortech.2011.07.051>.
- [46] Ojeda K, Ávila O, Suárez J, Kafarov V. Evaluation of technological alternatives for process integration of sugarcane bagasse for sustainable biofuels production—Part 1. *Chem Eng Res Des* 2011;89(3):270–9. <https://doi.org/10.1016/j.cherd.2010.07.007>.
- [47] Kumar B, Bhardwaj N, Agrawal K, Chaturvedi V, Verma P. Current perspective on pretreatment technologies using lignocellulosic biomass: an emerging biorefinery concept. *Fuel Process Technol* 2020;199:106244. <https://doi.org/10.1016/j.fuproc.2019.106244>.
- [48] Fockink DH, Sánchez JH, Ramos LP. Comprehensive analysis of sugarcane bagasse steam explosion using autocatalysis and dilute acid hydrolysis (H₃PO₄ and H₂SO₄) at equivalent combined severity factors. *Ind Crops Prod* 2018;123: 563–72. <https://doi.org/10.1016/j.indcrop.2018.07.017>.
- [49] Crawford JT, Shan CW, Budsberg E, Morgan H, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: techno-economic assessment. *Biotechnol Biofuels* 2016;9:141. <https://doi.org/10.1186/s13068-016-0545-7>.
- [50] Vasconcelos CJG, Wolf-Maciel MR. Dynamic and control of high purity heterogeneous azeotropic distillation process. *Comput. Aided Chem. Eng.* Elsevier 2000;8:217–22. [https://doi.org/10.1016/S1570-7946\(00\)80038-3](https://doi.org/10.1016/S1570-7946(00)80038-3).
- [51] Kagymanova AP, Chumachenko VA, Korotkiikh VN, Kashkin VN, Noskov AS. Catalytic dehydration of bioethanol to ethylene: Pilot-scale studies and process simulation. *Chem Eng J* 2011;176–177:188–94. <https://doi.org/10.1016/j.cej.2011.06.049>.
- [52] Haishi T, Kasai K, Iwamoto M. Fast and quantitative dehydration of lower alcohols to corresponding olefins on mesoporous silica catalyst. *Chem Lett* 2011; 40(6):614–6. <https://doi.org/10.1246/cl.2011.614>.
- [53] Meng X, Zhang L, Chen Y, Jiang T. Silane-bridged diphosphine ligands for nickel-catalyzed ethylene oligomerization. *React Kinet Mech Catal* 2016;119(2):481–90. <https://doi.org/10.1007/s11444-016-1056-z>.
- [54] Mahdavi SH, Parvati M, Soudbar D. Ethylene dimerization by a homogeneous Ti-based three-component catalyst system: process evaluation and optimization of parametric performance. *Procedia Eng* 2012;42:616–22. <https://doi.org/10.1016/j.proeng.2012.07.454>.
- [55] Kuechler KH, Brown SH, Jaensch H, Mathys GM, Luo S, Cheng JC. Olefin oligomerization to produce hydrocarbon compositions useful as fuels. US7678954B2, 2010.
- [56] Why ESK, Ong HC, Lee HV, Gan YY, Chen W-H, Chong CT. Renewable aviation fuel by advanced hydroprocessing of biomass: Challenges and perspective. *Energy Convers Manag* 2019;199:112015. <https://doi.org/10.1016/j.enconman.2019.112015>.
- [57] Chen Y-K, Hsieh C-H, Wang W-C. The production of renewable aviation fuel from waste cooking oil. Part II: Catalytic hydro-cracking/isomerization of hydro-processed alkanes into jet fuel range products. *Renew Energy* 2020;157:731–40. <https://doi.org/10.1016/j.renene.2020.04.154>.
- [58] Wang W-C, Thapaliya N, Campos A, Stikeleather LF, Roberts WL. Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. *Fuel* 2012;95:622–9. <https://doi.org/10.1016/j.fuel.2011.12.041>.
- [59] Wang W-C, Natelson RH, Stikeleather LF, Roberts WL. CFD simulation of transient stage of continuous countercurrent hydrolysis of canola oil. *Comput Chem Eng* 2012;43:108–19. <https://doi.org/10.1016/j.compchemeng.2012.04.008>.
- [60] Roberts WL, Lamb H, Stikeleather, Larry F. Turner TL. Process for conversion of biomass to fuel. US7816570B2, 2011.
- [61] Reid RC, Sherwood TK, Street RE. The properties of gases and liquids. *Phys Today* 1959;12(4):38–40. <https://doi.org/10.1063/1.3060771>.
- [62] Constantinou L, Gani R, O'Connell JP. Estimation of the acentric factor and the liquid molar volume at 298 K using a new group contribution method. *Fluid Phase Equilib* 1995;103(1):11–22. [https://doi.org/10.1016/0378-3812\(94\)02593-P](https://doi.org/10.1016/0378-3812(94)02593-P).
- [63] Peng D-Y, Robinson DB. A new two-constant equation of state. *Ind Eng Chem Fundam* 1976;15(1):59–64. <https://doi.org/10.1021/i160057a011>.
- [64] Gong S, Shinozaki A, Shi M, Qian EW. Hydrotreating of jatropha oil over alumina based catalysts. *Energy Fuels* 2012;26(4):2394–9. <https://doi.org/10.1021/ef300047a>.
- [65] Abhari Ramin, Tomilson L, Havlik P JN. Process for co-producing jet fuel and LPG from renewable sources. US7846323B2, 2010.
- [66] Sun J, Li Yi, Mu C, Wei J, Zhao Y, Ma X, et al. Supported heteropolyacids catalysts for the selective hydrocracking and isomerization of n-C16 to produce jet fuel. *Appl Catal A Gen* 2020;598:117556. <https://doi.org/10.1016/j.apcata.2020.117556>.
- [67] Robota HJ, Alger JC, Shafer L. Converting algal triglycerides to diesel and HEFA jet fuel fractions. *Energy Fuels* 2013;27(2):985–96. <https://doi.org/10.1021/ef301977b>.
- [68] 2019 Chemical Engineering Plant Cost Index annual average. *Chem Eng Mag* 2021. <https://www.chemengonline.com/2019-chemical-engineering-plant-cost-index-annual-average/>.
- [70] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA, Bhattacharyya D. Analysis, Synthesis and Design of Chemical Processes by R. Turton, R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz. Prentice Hall: New Jersey, 1999. 814 pp. ISBN 0-13-570565-70. £66. *Org Process Res Dev* 1999;3:494–494. <https://doi.org/10.1021/op990061d>.
- [71] Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, Schoen P, Lukas J, Olthoff B, Worley M, Sexton D, Dudgeon D. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. Golden, CO (United States): 2011. <https://doi.org/10.2172/1013269>.
- [72] Lang HJ. Simplified approach to preliminary cost estimates. *Chem Eng* 1948;55: 112–3.
- [73] Baasel WD. Preliminary chemical engineering plant design. 2nd ed. New York: New York Van Nostrand; 1990.
- [74] Lim CH, Lam HL. Biomass supply chain optimisation via novel Biomass Element Life Cycle Analysis (BELCA). *Appl Energy* 2016;161:733–45. <https://doi.org/10.1016/j.apenergy.2015.07.030>.
- [75] Pérez-Uresti S, Adrián-Mendiola J, El-Halwagi M, Jiménez-Gutiérrez A. Techno-economic assessment of benzene production from shale gas. *Processes* 2017;5:33. <https://doi.org/10.3390/pr5030033>.
- [76] Wang W-C, Tao L, Markham J, Zhang Y, Tan E, Batan L, Warner E, Biddy M. Review of Biojet Fuel Conversion Technologies. Golden, CO (United States): 2016. <https://doi.org/10.2172/1278318>.
- [77] Embong NH, Maniam GP, Ab. Rahim MH, Lee KT, Huisingh D. Utilization of palm fatty acid distillate in methyl esters preparation using SO₄²⁻/TiO₂-SiO₂ as a solid acid catalyst. *J Clean Prod* 2016;116:244–8. <https://doi.org/10.1016/j.jclepro.2015.12.108>.
- [78] Rubio-Maya C, Uche-Marcuello J, Martínez-Gracia A, Bayod-Rújula AA. Design optimization of a polygeneration plant fuelled by natural gas and renewable energy sources. *Appl Energy* 2011;88(2):449–57. <https://doi.org/10.1016/j.apenergy.2010.07.009>.
- [79] Harahap F, Silveira S, Khatawada D. Cost competitiveness of palm oil biodiesel production in Indonesia. *Energy* 2019;170:62–72. <https://doi.org/10.1016/j.energy.2018.12.115>.
- [80] Index Mundi Commodity prices indices: 2020 Palm kernel oil price 2020. <https://www.indexmundi.com/commodities/?commodity=palm-oil&months=60¤cy=eur&commodity=palm-kernel-oil>.
- [81] Kevin Kenney, Kara G. Cafferty, Jacob J. Jacobson, Ian J. Bonner, Garold L. Gresham, William A. Smith, David N. Thompson, Vicki S. Thompson, Jaya Shankar Tumuluru, Neal Yancey. Feedstock Supply System Design and Economics for Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Conversion Pathway: Biological Conversion of Sugars to Hydrocarbons The 2017 Design Case. 2013. <https://doi.org/10.2172/1130548>.

- [82] Bunker fuel selling price in Spain 2021. <https://geoportalgasolineras.es/#/Inicio>.
- [83] Querol E, Gonzalez-Regueral B, Ramos A, Perez-Benedito JL. Novel application for exergy and thermoeconomic analysis of processes simulated with Aspen Plus®. *Energy* 2011;36(2):964–74. <https://doi.org/10.1016/j.energy.2010.12.013>.
- [84] Hinderink AP, Kerkhof FPJM, Lie ABK, De Swaan Arons J, Van Der Kooi HJ. Van Der Kooi HJ. Exergy analysis with a flowsheeting simulator—I. Theory; calculating exergies of material streams. *Chem Eng Sci* 1996;51(20):4693–700. [https://doi.org/10.1016/0009-2509\(96\)00220-5](https://doi.org/10.1016/0009-2509(96)00220-5).
- [85] Tsatsaronis G. Definitions and nomenclature in exergy analysis and exergoeconomics. *Energy* 2007;32(4):249–53. <https://doi.org/10.1016/j.energy.2006.07.002>.
- [86] Montes Villalon JM, Garcia Torrent J, Querol Aragon E. *Termoeconomía y optimización energética*. Madrid: Fundación Gómez Pardo en colaboración con el Consejo Superior de Colegios de Ingenieros de Minas. 2009.
- [87] Szargut J, Morris D. Standard chemical exergy of some elements and compounds on the planet earth. *Energy* 1986;11(8):733–55. [https://doi.org/10.1016/0360-5442\(86\)90013-7](https://doi.org/10.1016/0360-5442(86)90013-7).
- [88] Irwin L, Stekli J, Pfefferkorn C, Pitchumani R. Thermochemical energy storage for concentrating solar thermal (CST) systems. *Adv. Conc. Sol. Therm. Res. Technol., Elsevier* 2017;247–67. <https://doi.org/10.1016/B978-0-08-100516-3.00011-3>.
- [89] Tsatsaronis G. Thermoeconomic analysis and optimization of energy systems. *Prog Energy Combust Sci* 1993;19(3):227–57. [https://doi.org/10.1016/0360-1285\(93\)90016-8](https://doi.org/10.1016/0360-1285(93)90016-8).
- [90] Paulus DM, Tsatsaronis G. Auxiliary equations for the determination of specific exergy revenues. *Energy* 2006;31(15):3235–47. <https://doi.org/10.1016/j.energy.2006.03.003>.
- [91] Lozano MA, Valero A. Theory of the exergetic cost. *Energy* 1993;18(9):939–60. [https://doi.org/10.1016/0360-5442\(93\)90006-Y](https://doi.org/10.1016/0360-5442(93)90006-Y).
- [92] Valero A, Lozano MA, Bartolomé JL. On-line monitoring of power-plant performance, using exergetic cost techniques. *Appl Therm Eng* 1996;16(12):933–48. [https://doi.org/10.1016/1359-4311\(95\)00092-5](https://doi.org/10.1016/1359-4311(95)00092-5).
- [93] Querol E, Gonzalez-Regueral B, García-Torrent J, Ramos Alberto. Available power generation cycles to be coupled with the liquid natural gas (LNG) vaporization process in a Spanish LNG terminal. *Appl Energy* 2011;88(7):2382–90. <https://doi.org/10.1016/j.apenergy.2011.01.023>.
- [94] Ubando AT, Rivera DRT, Chen W-H, Culaba AB. A comprehensive review of life cycle assessment (LCA) of microalgal and lignocellulosic bioenergy products from thermochemical processes. *Bioresour Technol* 2019;291:121837. <https://doi.org/10.1016/j.biortech.2019.121837>.
- [95] Standardization IO for. Environmental management: Life cycle assessment; requirements and guidelines. ISO Geneva; 2006.
- [96] Capaz RS, Posada JA, Osseweijer P, Seabra JEA. The carbon footprint of alternative jet fuels produced in Brazil: exploring different approaches. *Resour Conserv Recycl* 2021;166:105260. <https://doi.org/10.1016/j.resconrec.2020.105260>.
- [97] Catoire L, Naudet V. A unique equation to estimate flash points of selected pure liquids application to the correction of probably erroneous flash point values. *J Phys Chem Ref Data* 2004;33(4):1083–111. <https://doi.org/10.1063/1.1835321>.
- [98] Rackett HG. Equation of state for saturated liquids. *J Chem Eng Data* 1970;15(4):514–7. <https://doi.org/10.1021/jc60047a012>.
- [99] Koekemoer LR, Badenhorst MJG, Everson RC. Determination of viscosity and density of Di-(2-ethylhexyl) phosphoric acid + aliphatic kerosene. *J Chem Eng Data* 2005;50(2):587–90. <https://doi.org/10.1021/jc049664510.1021/jc0496645.s001>.
- [100] Joback KG, Reid RC. Estimation of pure-component properties from group-contributions. *Chem Eng Commun* 1987;57(1-6):233–43. <https://doi.org/10.1080/00986448708960487>.
- [101] Llamas A, García-Martínez MJ, Al-Lal AM, Canoira L, Lapuerta M. Biokerosene from coconut and palm kernel oils: Production and properties of their blends with fossil kerosene. *Fuel* 2012;102:483–90. <https://doi.org/10.1016/j.fuel.2012.06.108>.
- [102] Constantinou L, Gani R. New group contribution method for estimating properties of pure compounds. *AIChE J* 1994;40(10):1697–710. [https://doi.org/10.1002/\(ISSN\)1547-590510.1002/aic.v40.1010.1002/aic.690401011](https://doi.org/10.1002/(ISSN)1547-590510.1002/aic.v40.1010.1002/aic.690401011).
- [103] Hwang G, Lee J, Jeong S, Weisend JG. Estimation of freezing point of hydrocarbon and hydrofluorocarbon mixtures for mixed refrigerant JT cryocooler. *AIP Conf. Proc., Am Inst Phys AIP*; 2010;1218:95–102. <https://doi.org/10.1063/1.3422466>.
- [104] Llamas A, Lapuerta M, Al-Lal AM, Canoira L. Oxygen extended sooting index of FAME blends with aviation kerosene. *Energy Fuels* 2013;27(11):6815–22. <https://doi.org/10.1021/ef401623t>.
- [105] Bolonio D, García-Martínez M-J, Ortega MF, Lapuerta M, Rodríguez-Fernández J, Canoira L. Fatty acid ethyl esters (FAEEs) obtained from grapeseed oil: A fully renewable biofuel. *Renew Energy* 2019;132:278–83. <https://doi.org/10.1016/j.renene.2018.08.010>.
- [106] Mehta PS, Anand K. Estimation of a lower heating value of vegetable oil and biodiesel fuel. *Energy Fuels* 2009;23(8):3893–8. <https://doi.org/10.1021/ef900196r>.
- [107] Haas FM, Qin A, Dryer FL. “Virtual” Smoke Point Determination of Alternative Aviation Kerosenes by Threshold Sooting Index (TSI) Methods. 50th AIAA/ASME/SAE/ASEE Jr. Propuls. Conf., Reston, Virginia: American Institute of Aeronautics and Astronautics; 2014:1–9. <https://doi.org/10.2514/6.2014-3468>.
- [108] Won SH, Veloo PS, Dooley S, Santner J, Haas FM, Ju Y, et al. Predicting the global combustion behaviors of petroleum-derived and alternative jet fuels by simple fuel property measurements. *Fuel* 2016;168:34–46. <https://doi.org/10.1016/j.fuel.2015.11.026>.
- [109] Yan S, Eddings EG, Palotas AB, Pugmire RJ, Sarofim AF. Prediction of sooting tendency for hydrocarbon liquids in diffusion flames. *Energy Fuels* 2005;19(6):2408–15. <https://doi.org/10.1021/ef050107d>.
- [110] Sundararaj RH, Kumar RD, Raut AK, Sekar TC, Pandey V, Kushari A, et al. Combustion and emission characteristics from biojet fuel blends in a gas turbine combustor. *Energy* 2019;182:689–705. <https://doi.org/10.1016/j.energy.2019.06.060>.
- [111] Chen DH, Alphones A. Characterization of the incipient smoke point for steam-/air-assisted and nonassisted flames. *J Air Waste Manage Assoc* 2019;69(1):119–30. <https://doi.org/10.1080/10962247.2018.1525443>.
- [112] Das DD, St. John PC, McEnally CS, Kim S, Pfefferle LD. Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale. *Combust Flame* 2018;190:349–64. <https://doi.org/10.1016/j.combustflame.2017.12.005>.
- [113] Sousa FP, Silva LN, de Rezende DB, de Oliveira LCA, Pasa VMD. Simultaneous deoxygenation, cracking and isomerization of palm kernel oil and palm olein over beta zeolite to produce biogasoline, green diesel and biojet-fuel. *Fuel* 2018;223:149–56. <https://doi.org/10.1016/j.fuel.2018.03.020>.
- [114] Sangar SK, Lan CS, Razali SM, Farabi MSA, Taufiq-Yap YH. Methyl ester production from palm fatty acid distillate (PFAD) using sulfonated cow dung-derived carbon-based solid acid catalyst. *Energy Convers Manag* 2019;196:1306–15. <https://doi.org/10.1016/j.enconman.2019.06.073>.
- [115] Cohen N, Benson SW. Estimation of heats of formation of organic compounds by additivity methods. *Chem Rev* 1993;93(7):2419–38. <https://doi.org/10.1021/cr00023a005>.
- [116] National Institute of Standards and Technology (NIST) Chemistry WebBook 2021. <https://webbook.nist.gov/chemistry/name-ser/>.
- [117] Moquin PHL, Temelli F. Kinetic modeling of hydrolysis of canola oil in supercritical media. *J Supercrit Fluids* 2008;45(1):94–101. <https://doi.org/10.1016/j.supflu.2007.11.018>.
- [118] Barnebey HL, Brown AC. Continuous fat splitting plants using the Colgate-Emery process. *J Am Oil Chem Soc* 1948;25(3):95–9. <https://doi.org/10.1007/BF02579733>.
- [119] Wang W-C, Natelson RH, Stikeleather LF, Roberts WL. Product sampling during transient continuous countercurrent hydrolysis of canola oil and development of a kinetic model. *Comput Chem Eng* 2013;58:144–55. <https://doi.org/10.1016/j.compchemeng.2013.06.003>.
- [120] Baral NR, Kavvada O, Mendez-Perez D, Mukhopadhyay A, Lee TS, Simmons BA, et al. Techno-economic analysis and life-cycle greenhouse gas mitigation cost of five routes to bio-jet fuel blendstocks. *Energy Environ Sci* 2019;12(3):807–24. <https://doi.org/10.1039/C8EE03266A>.
- [121] Demirbas A. Higher heating values of lignin types from wood and non-wood lignocellulosic biomasses. *Energy Sources, Part A Recover Util Environ Eff* 2017;39(6):592–8. <https://doi.org/10.1080/15567036.2016.1248798>.
- [122] Tao L, Tan ECD, McCormick R, Zhang M, Aden A, He X, et al. Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. *Biofuels Bioprod Biorefining* 2014;8(1):30–48. <https://doi.org/10.1002/bbb.1431>.
- [123] Wang W-C, Tao L. Bio-jet fuel conversion technologies. *Renew Sustain Energy Rev* 2016;53:801–22. <https://doi.org/10.1016/j.rser.2015.09.016>.
- [124] Griggs AJ, Stickel JJ, Lischke JJ. A mechanistic model for enzymatic saccharification of cellulose using continuous distribution kinetics II: cooperative enzyme action, solution kinetics, and product inhibition. *Biotechnol Bioeng* 2012;109(3):676–85. <https://doi.org/10.1002/bit.v109.310.1002/bit.23354>.
- [125] Ensinas AV, Modesto M, Nebra SA, Serra L. Reduction of irreversibility generation in sugar and ethanol production from sugarcane. *Energy* 2009;34(5):680–8. <https://doi.org/10.1016/j.energy.2008.06.001>.
- [126] Tsatsaronis G, Moran MJ. Exergy-aided cost minimization. *Energy Convers Manag* 1997;38:1535–42. [https://doi.org/10.1016/S0196-8904\(96\)00215-4](https://doi.org/10.1016/S0196-8904(96)00215-4).
- [127] Aghbashlo M, Mandegari M, Tabatabaei M, Farzad S, Mojarab Soufian M, Görgens JF. Exergy analysis of a lignocellulosic-based biorefinery annexed to a sugarcane mill for simultaneous lactic acid and electricity production. *Energy* 2018;149:623–38. <https://doi.org/10.1016/j.energy.2018.02.063>.
- [128] Tock L, Gassner M, Maréchal F. Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. *Biomass Bioenergy* 2010;34(12):1838–54. <https://doi.org/10.1016/j.biombioe.2010.07.018>.
- [129] Palacios-Bereche R, Mosqueira-Salazar KJ, Modesto M, Ensinas AV, Nebra SA, Serra LM, et al. Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane. *Energy* 2013;62:46–61. <https://doi.org/10.1016/j.energy.2013.05.010>.
- [130] Kiss AA, Suszwalak DJPC. Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns. *Sep Purif Technol* 2012;86:70–8. <https://doi.org/10.1016/j.seppur.2011.10.022>.
- [131] de Koeijer G, Rivero R. Entropy production and exergy loss in experimental distillation columns. *Chem Eng Sci* 2003;58(8):1587–97. [https://doi.org/10.1016/S0009-2509\(02\)00627-9](https://doi.org/10.1016/S0009-2509(02)00627-9).
- [132] Buchspies B, Kaltschmitt M, Neuling U. Potential changes in GHG emissions arising from the introduction of biorefineries combining biofuel and electrofuel production within the European Union – A location specific assessment. *Renew Sustain Energy Rev* 2020;134:110395. <https://doi.org/10.1016/j.rser.2020.110395>.
- [133] Staples MD, Malina R, Olcay H, Pearson MN, Hileman JI, Boies A, et al. Lifecycle greenhouse gas footprint and minimum selling price of renewable diesel and jet

- fuel from fermentation and advanced fermentation production technologies. *Energy Environ Sci* 2014;7(5):1545–54. <https://doi.org/10.1039/C3EE43655A>.
- [134] Largarita R, Duarte R, Hewings G, Sánchez-Chóliz J. Testing European goals for the Spanish electricity system using a disaggregated CGE model. *Energy* 2019; 179:1288–301. <https://doi.org/10.1016/j.energy.2019.04.175>.
- [135] Vásquez MC, Martínez A, Castillo EF, Silva EE. Holistic approach for sustainability enhancing of hydrotreated aviation biofuels, through life cycle assessment: a Brazilian case study. *J Clean Prod* 2019;237:117796. <https://doi.org/10.1016/j.jclepro.2019.117796>.
- [136] Moreno J, Dufour J. Life cycle assessment of hydrogen production from biomass gasification. Evaluation of different Spanish feedstocks. *Int J Hydrogen Energy* 2013;38(18):7616–22. <https://doi.org/10.1016/j.ijhydene.2012.11.076>.
- [137] Neuling U, Kaltschmitt M. Techno-economic and environmental analysis of aviation biofuels. *Fuel Process Technol* 2018;171:54–69. <https://doi.org/10.1016/j.fuproc.2017.09.022>.
- [138] Chuck CJ, Donnelly J. The compatibility of potential bioderived fuels with Jet A-1 aviation kerosene. *Appl Energy* 2014;118:83–91. <https://doi.org/10.1016/j.apenergy.2013.12.019>.
- [139] Chung H, Ku M-S, Lee J-S. Comparison of near-infrared and mid-infrared spectroscopy for the determination of distillation property of kerosene. *Vib Spectrosc* 1999;20(2):155–63. [https://doi.org/10.1016/S0924-2031\(99\)00034-X](https://doi.org/10.1016/S0924-2031(99)00034-X).