Design and Pinch Analysis of a GFT Process for Production of Biojet Fuel from Biomass and Plastics

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Abstract: Environmental problems are frequently related to energy use, estimated to grow at 1.6% per year until 2035. The transport sector accounts for 30% of energy demand and aviation is growing around 2.6% per year. Thus, low-emissions policies promote the use of sustainable aviation fuels. This work simulates a gasification and Fischer-Tropsch process to obtain biojet fuel from biomass and plastic waste. Syngas obtained through cogasification is purified by amine scrubbing and subjected to a Fischer-Tropsch process to produce hydrocarbons, which are upgraded for optimal fuel properties. Pinch analysis is applied to minimize energy usage, while Rankine cycles and a cooling tower are designed to cover the demand of electricity and cooling water. Results show that mass yields of the process towards biofuels are 13.06%, with an output of 1697.45 kg/h of biojet fuel. Density, kinematic viscosity, pour and flammability points and the lower calorific value of the biojet fuel comply with the ASTM D7566 standard. Pinch analysis allows to reduce 41.58% and 100% of cooling and heating demands, respectively, using biomass as renewable energy for heating. Moreover, steam generation covers 38.73% of the required electricity. The produced biojet fuel emits 20.14 g CO₂eq/MJ and has a minimum selling price of 1.37 EUR/L.

Keywords: biojet fuel; cogasification; Fischer-Tropsch; upgrading; hydrocracking; pinch; thermodynamic cycle; cooling tower; economic analysis; Aspen; Epsilon

1. Introduction

Energy is the engine of society and one of the fundamental pillars of human progress. Global energy usage has increased significantly thanks to the large-scale incorporation of fossil fuels [1], which has led to a significant increase in living standards. Today, fossil fuels are still the main source of energy used worldwide, accounting for approximately 90% of energy demand [2]. However, the use of these raw materials as an energy source is the cause of the main environmental problems affecting the planet (climate change) and, due to their geographic location, has caused conflicts based on energy dependence and geopolitical strategies. According to the United Nations, at least 40% of violent conflicts in the last 60 years are related to the exploitation of strategic resources [3].

Renewable energies represent an alternative to conventional energy sources and biomass stands out among them, due to its ubiquity, availability, and low polluting nature [4]. Due to the increase in the price of fossil fuels and materials (in the United States the price of petrol between 2000 and 2021 has risen from 1.52 to 2.26 USD/gal [5]), in recent years, biorefineries present an interesting alternative, being able to efficiently convert renewable raw materials into a wide range of marketable products of biological origin.

Besides, nowadays plastic waste is another major environmental problem [6,7], as it ends up as waste that accumulates in landfills or is dumped into the environment. Plastics...
are resistant to decomposition, which makes them very versatile, but they need hundreds of years to be degraded in nature [8,9], leading to their accumulation, especially in the seas and oceans [10].

Plastic waste is sometimes shipped from developed countries to other countries, mainly Asian countries, for recycling, as exporting becomes cheaper than treating it in situ [9]. These practices are against circular economy and pose a double environmental problem. Firstly because of the transport of these plastics, and secondly because of the recycling treatments they receive in the destination countries since the legislation on their treatment and environmental regulations are much less restrictive than in the countries from which they originate. The final disposal of plastic waste in Europe [8] is as follows: landfill (52%), export (19%), recycling (18%), and incineration (11%).

An interesting option to reduce plastic dumping and export [11,12], is to convert plastic waste into fuels for transport sector, where the search of alternative fuels is a priority. This sector currently accounts for approximately 30% of global primary energy demand [13,14], of which more than 95% is obtained through the consumption of petroleum products [15].

In this context, aviation is the fastest way of transport for long distances and it covers 10% of the energy demand in the transport sector [15]. The number of flights is currently growing at 2.6% per year worldwide [16] and, in the European Union (EU), are expected to grow at 1.9% per year to 2040 [17]. Current aviation engine technology and regulations do not allow the commercial-scale use of hydrogen and electricity as energy sources; therefore, although regulations prevent the use of biofuel blends with traditional paraffin to exceed 50% by volume [18], the main alternative is biojet fuel.

There are several theoretical and experimental studies on biojet fuel production [19,20], and literature reviews depending on the feedstock and processes used [21]. The gasification and Fischer-Tropsch process (GFT) is based on reaction mechanisms whose kinetics and thermodynamic analysis are well known for a wide range of feedstocks [22–24]. However, no previous studies have been found that simulate reaction kinetics for cogasification of biomass and plastics. Once syngas is obtained, the industry already has mature technologies to convert it into fuels, such as CO₂ purification with amines [25,26], hydrocarbon synthesis via Fischer-Tropsch process [27,28] and final improvement of biojet fuel properties by hydrocracking (upgrading) [29–33].

The aims of this study are: (i) To simulate a cogasification of residual plastics and biomass (analysing the plant location to obtain input feedstock mass flow) to produce biojet fuel via GFT process, consisting of six units: a gasification unit, two amine scrubbing units, two reaction units (Fischer-Tropsch and upgrading), and a separation unit. (ii) To design a heat exchanger network, using the pinch method to reduce the demand of utilities (heating steam and cooling water). (iii) To design Rankine cycles and cooling tower to satisfy, as far as possible, the demand for steam, electricity, and fresh water required by the plant. (iv) Finally, to assess the technical viability of the biojet fuel, estimating combustion properties and CO₂eq emissions.

2. Materials and Methods

2.1. Location and Feedstock

In relation to sustainable aviation fuel, Europe is the continent that is making the most significant commitment [34], given its CO₂ emission reduction targets and its dependence on fossil fuels from other countries. While the geographical location of the plant has little influence on its design, it can play an important role in the economic analysis. The biojet fuel plant is located in Spain, because it is one of the main agricultural producers [35] and, therefore, a promising biojet fuel producer from biomass waste blended with plastics.

Residual biomass: In Spain, straw is the most abundant residual lignocellulosic biomass of agricultural origin [36]. Specifically, in the province of Huesca, wheat and barley straw production amounts to 178,002 and 579,448 tonnes per year (t/year), respectively. Although the total utilisation of wheat and barley residues available in the province is
optimistic, other types of residual lignocellulosic biomass are generated and must be considered. Therefore, the mass flow of this raw material is considered achievable.

Plastic waste: Spain produces 1.5 million tonnes of plastic waste per year, of which approximately 20% is exported to other countries [9]. In order to estimate the quantity and composition of the plastic used as raw material, the following assumptions are made:

- The amount of waste generated per inhabitant is homogeneous throughout Spain;
- The average composition of plastic waste is based on the type of polymers demanded in Europe [8];
- A total of 90% of the polyethylene (PE) and polypropylene (PP) that would be exported from the provinces of Huesca, Zaragoza, Navarra, and La Rioja are fed into the chemical process.

For a plant operating factor of 8000 h per year, the raw material quantity and composition by mass (wt%) are shown in Table 1:

| Raw material summary [8,9,36]. |
|------------------------------|
| wt% | wt% |
|-----|-----|
| 70  | 91  |
| 21  |     |
| 6   | 9   |
| 3   |     |

2.2. Process Simulation and Thermodynamic Models

Aspen Plus and Aspen HYSYS v10 have been used to simulate the process. The amount of raw material and the ratio between lignocellulosic biomass and plastic is based on Table 1. The biomass components (cellulose, hemicellulose, and lignin [37–40]) are entered as user-defined compounds using their molecular structure [4] for the software to estimate their physical properties. The software already contains polyethylene and polypropylene in its “APV100 POLYMER” database, which is used to simulate the plastic properties.

Furthermore, Aspen Plus has been used to model the physical properties of biomass and plastic applying NRTL [41] as thermodynamic model. Mass balance calculation for the distribution of pyrolysis products has been carried out by using Microsoft Excel. The gasification reactor and downstream processes have been simulated via Aspen HYSYS: using NRTL for gasification (unit 1, see Figure 1), FT process and upgrading (units 3 and 4, see Figure 2) [42]; Acid Gas—Chemical Solvents for amine scrubbing (unit 2, see Figure 1 and unit 5, see Figure 3) [43], and SRK for product separation (unit 6, see Figure 3) [44].

2.3. Heat Integration and Utilities

Energy integration between process streams has been studied using pinch analysis, performed via Aspen Energy Analyzer v10 software. Then, Rankine cycles (unit 7) were designed using Peng-Robinson [45], in Aspen HYSYS to cover part of the electrical demand, using the surplus steam generated.

Finally, EBSILON Professional v14.2 software was used to simulate a cooling tower. This software allows us to calculate the mass balance and the electrical power required by the equipment.
Figure 1. Gasification and amine syngas scrubbing (units 1 and 2).
Figure 2. Fischer-Tropsch and upgrading (units 3 and 4).
2.4. Economic Analysis

Total investment was estimated by the percentage method [46], based on equipment and raw materials costs. Minimum selling price (MSP) of biojet fuel and coproducts is assessed considering an internal rate of return (IRR) of 9% [47].

3. Results
3.1. Process Flow Diagram (PFD)

The chemical process starts in unit 1, shown in Figure 1 (refer to Table S9 of Supplementary Information to see the complete list of streams and equipment in PFD), where biomass (S101) and plastic (S102) are introduced into a fluidised bed boiler to be gasified in an
oxygen-poor atmosphere (S109) to produce syngas. Steam (S105) is introduced to adjust the amount of hydrogen (H\textsubscript{2}) generated. On one hand, the syngas leaves the boiler (S112) and is transported to unit 2. On the other hand, ashes and part of the bed-forming solids are removed from the boiler (S110).

Syngas enters unit 2, shown in Figure 1, where it must be purified to reduce its concentration of carbon dioxide (CO\textsubscript{2}), as it poisons the Fischer-Tropsch reactor catalyst. Water (H\textsubscript{2}O) and other condensable compounds (S203) are first separated from the syngas in a flash chamber. Recovered water is taken to a treatment plant so that it can be reused in the process. Gases separated in this flash chamber (S202) are taken to an absorption column, where an aqueous solution of monoethanolamine (MEA) is used to absorb the CO\textsubscript{2} leaving at the bottom as rich amine (S208).

Rich amine is taken to a flash chamber (V-203) and a rectification tower (T-202), where the CO\textsubscript{2} is separated and emitted to the atmosphere (S218).

The regenerated amine, known as lean amine, leaves the distillation tower and is taken to a mixer, where its composition is adjusted by the introduction of water and fresh amine, conditioning it back to the absorption column (S206).

The purified gas stream leaves the absorption column at the top (S207) and is fed to a pressure swing adsorption (PSA) bed, where the ratio of H\textsubscript{2} to carbon monoxide (CO) is adjusted. The syngas (S226) is fed to unit 3, and the separated hydrogen (S225) to unit 4.

In unit 3, shown in Figure 2, syngas is brought to Fischer-Tropsch reactor operating conditions. In the reactor, syngas is transformed into water and straight-chain hydrocarbons (S305), which are transported to unit 4.

In unit 4, products obtained from unit 3 are taken to a 3-phase separator, where the gaseous products (S403) are sent to unit 5. The water generated is taken to the water treatment plant (S405), and the hydrocarbons (S404) to the upgrading reactor, to react with the hydrogen separated in the PSA of unit 2 (S225).

Final products are obtained in units 5 and 6. In unit 5 (see Figure 3), fuel gas from the three-phase separator of unit 4 (S403), with a high carbon dioxide content, is purified by procedures similar to those of unit 2. The purified gases (S503) are the final product.

Rich amine (S504) must be regenerated and, for this purpose, it enters a rectification column where CO\textsubscript{2} is separated and emitted to the atmosphere (S507). The lean amine leaves the equipment and is taken to a mixer where water and fresh amine are added in order to replace the losses produced in the unit and adjust its composition, before being recirculated to the absorption column.

Unit 6 consists of a set of columns that allow the separation of the different products obtained. These products are fuel gas (S610), petrol (S611), biojet fuel (S619), diesel (S627), and fuel oil (S629).

3.2. Chemical Process Design
3.2.1. Gasification (Unit 1)

Feedstock is fed into the gasification reactor, where the processes of pyrolysis, oxidation, and reforming take place. Pyrolysis is endothermic and starts at around 300 °C for biomass and 450 °C for plastic [22,48]:

\[
\text{Cellulose + Hemicellulose + Lignin} \rightarrow \text{Gas + Tar + Char}
\]

\[
\text{Plastic} \rightarrow \text{Gas + Tar}
\]

In the case of biomass, the gas stream is mainly composed by carbon monoxide, carbon dioxide, methane (CH\textsubscript{4}), ethylene (C\textsubscript{2}H\textsubscript{4}), and hydrogen. Char fraction is composed of carbon (C), ash, extractables and other solids. The tar is made up of hydrocarbons with an average composition of C\textsubscript{10}H\textsubscript{10} and oxygenated compounds with an average composition of C\textsubscript{4}H\textsubscript{10}O\textsubscript{3} [48].

In the case of plastics, the gas stream is considered to be composed of hydrogen, ethylene, and 1-butene (C\textsubscript{4}H\textsubscript{8}). The produced tar is of two types: primary tar, consisting of aromatic hydrocarbons equivalent to cyclohexane (C\textsubscript{6}H\textsubscript{12}), and secondary tar, consisting of olefins of average composition C\textsubscript{10}H\textsubscript{20} [48].
Pyrolysis mechanism is very fast and usually considered to occur instantaneously. Thus, a mass distribution of compounds formed after pyrolysis at 600 °C is calculated using the following equation [48]:

\[
(a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3),
\]

where \(a_0, a_1, a_2, \) and \(a_3\) are parameters from Table 2. Temperature \((T)\) is expressed in K for biomass and in °C for plastic.

### Table 2. Distribution of pyrolysis products.

| Compound (1) | \(a_0\) | \(a_1\) | \(a_2\) | \(a_3\) | Result (wt%) |
|--------------|---------|---------|---------|---------|--------------|
| Tar Biomass  | C\(_6\)H\(_{10}\)O\(_3\) | 19 | -0.1735 | 7.4 \times 10^{-5} | 0 | 0.10 |
|              | C\(_{10}\)H\(_{12}\) | 19 | -0.1735 | 7.4 \times 10^{-5} | 0 | 0.10 |
| Tar Plastic  | - | 2850 | -11.1 | 1.44 \times 10^{-2} | -6.22 \times 10^{-6} | 30.48 |
| Tar Primary  | C\(_6\)H\(_{12}\) | 87.037 | -0.52287 | 6.1991 \times 10^{-4} | 0 | 0.00 |
| Tar Secondary| C\(_{10}\)H\(_{20}\) | - | - | - | - | 30.48 |
| Char Biomass | C | 209 | -0.347 | 1.48 \times 10^{-4} | 0 | 0.19 |
| H\(_2\)      | 26 | -4.47 \times 10^{-2} | 4.54 \times 10^{-5} | 0 | 1.68 (5) |
|              | -49.816 | 0.13572 | -8.6478 \times 10^{-5} | 0 | 0.31 (6) |
| CO (5)       | 26 | 5.44 \times 10^{-2} | -3.88 \times 10^{-5} | 0 | 48.59 |
| CO\(_2\) (5) | 214 | -0.353 | 1.55 \times 10^{-4} | 0 | 42.27 |
| CH\(_4\)     | 1440.6 | 0.112 | -5.47 \times 10^{-5} | 0 | 7.08 (5) |
|              | -3.75 | 2.4997 \times 10^{-3} | 0 | 54.74 (6) |
| C\(_2\)H\(_4\) | -132 | 0.251 | -1.15 \times 10^{-4} | 0 | 0.00 (5) |
|              | -748.92 | 2.13 | -1.4122 \times 10^{-3} | 0 | 14.47 (6) |
| C\(_4\)H\(_8\) (6) | -529.15 | 1.4567 | -9.7835 \times 10^{-4} | 0 | 0.00 |

(1): Calculated for biomass and plastic separately. (2): Calculated as wt% of Tar\(_{plastic}\). (3): Calculated as the remaining Tar\(_{plastic}\). (4): Gas wt% is calculated as 100-wt% Tar+Char. For biomass, results are obtained as a volumetric composition (vol%) of gas and reconverted to wt%. For plastic, results are obtained as a wt% of gas. (5): Equation parameters and results for biomass. (6): Equation parameters and results for plastic.

Average specific heat \(c_p\) and specific enthalpy \(h\) of the species involved in the pyrolysis have been obtained from Aspen Plus (see Table 3). The mass of reactants is the mass of feedstock minus extractables and ash of S101 (see mass balances in Supplementary Information Section A):

### Table 3. Mass flow, specific heat, and enthalpy of pyrolysis species.

|          | kg/s | \(c_p\) (kJ/kg·K) | \(h\)\(_{600\degree C}\) (kJ/kg) |
|----------|------|-------------------|-------------------------------|
| Feedstock| 28.9 | 0.35              | -224.7                        |
| Reactants| 26.0 | -                 | -4088.3                       |

The heat required for pyrolysis reaction is calculated using the equation:

\[
H_{Pyrolysis} = m_{Feedstock} \cdot c_p \cdot (\Delta T) + m_{Reacting} \cdot \left(H_{Products} - H_{Reactives}\right),
\]

where \(\Delta T\) is the temperature difference between the pyrolysis (600 °C) and the reference temperature (25 °C). The heat required for the reaction is 106 MW, which is the minimum heat to be released during gasification to make the reactor autothermal.

After pyrolysis, the gasification takes place, in which the compounds shown in Table 2 react with each other and the gasifying agent to form syngas. In this study, a sufficient
amount of air is introduced so the exothermic mechanism of gasification compensates the endothermic mechanisms of pyrolysis and reforming [49,50].

The reactions that take place in gasification and their kinetics are as follows (\(r\) is the reaction rate (kmol/(m\(^3\)·s)); the concentrations of referenced compounds are in kmol/m\(^3\); 
T (K); \(E_A\) is the activation energy (kJ/kmol) and \(p_{O_2}, p_{H_2O}\) is the partial pressure of \(O_2\) and \(H_2O\) (Pa));

- **Oxidation of gaseous compounds** [51]:
  \[
  CO + 0.5O_2 \leftrightarrow CO_2, \\
  r = 10^{10} \cdot e^{-\frac{526.68}{T}} \cdot [CO]^{0.5} \cdot [O_2]^{0.5} \cdot [CO_2]^{0.5}, 
  \]

- **Reforming** [48]:
  \[
  C + O_2 \leftrightarrow 2CO, \\
  \text{Direct } r = 1.51 \times 10^6 \cdot e^{-\frac{108.67}{T}} \cdot p_{O_2}, \\
  \text{Reverse } r = 5.3 \times 10^5 \cdot e^{-\frac{125}{T}} \cdot p_{O_2}^{0.53}, \\
  C + CO_2 \leftrightarrow 2CO, \\
  \text{Direct } r = 1.4 \times 10^{11} \cdot e^{-\frac{182.6}{T}}, \\
  C + H_2O \leftrightarrow CO + H_2, \\
  \text{Direct } r = 2.62 \times 10^{8} \cdot e^{-\frac{237}{T}} \cdot p_{H_2O}^{0.57}.
  \]

- **Tar oxidation** [48]:
  \[
  C_6H_{10}O_3 + 4O_2 \rightarrow 6CO + 5H_2O, \\
  r = 1.58 \times 10^{13} \cdot e^{-\frac{2910.75}{T}} \cdot [C_6H_{10}O_3] \cdot [O_2], \\
  C_{10}H_{10} + 7.5O_2 \rightarrow 10CO + 5H_2O, \\
  r = 9.2 \times 10^6 \cdot e^{-\frac{2605}{T}} \cdot [C_{10}H_{10}]^{0.5} \cdot [O_2], \\
  C_4H_{12} + 6O_2 \rightarrow 6CO + 6H_2O, \\
  r = 3.8 \times 10^7 \cdot e^{-\frac{5545}{T}} \cdot [C_4H_{12}] \cdot [O_2], \\
  C_{10}H_{20} + 10O_2 \rightarrow 10CO + 10H_2O, \\
  r = 6.04 \times 10^9 \cdot e^{-\frac{1804.19}{T}} \cdot [C_{10}H_{20}]^{0.25} \cdot [O_2]^{1.5}.
  \]

- **Char oxidation** [48]:
  \[
  2C + O_2 \leftrightarrow 2CO, \\
  \text{Direct } r = 1.51 \times 10^6 \cdot e^{-\frac{108.67}{T}} \cdot p_{O_2}, \\
  \text{Reverse } r = 5.3 \times 10^5 \cdot e^{-\frac{125}{T}} \cdot p_{O_2}^{0.53}, \\
  C + CO_2 \leftrightarrow 2CO, \\
  \text{Direct } r = 1.4 \times 10^{11} \cdot e^{-\frac{182.6}{T}}, \\
  C + H_2O \leftrightarrow CO + H_2, \\
  \text{Direct } r = 2.62 \times 10^{8} \cdot e^{-\frac{237}{T}} \cdot p_{H_2O}^{0.57}.
  \]

- **Reforming** [48]:
  \[
  CO + H_2O \leftrightarrow CO_2 + H_2, \\
  \text{Direct } r = 2.78 \times 10^3 \cdot e^{-\frac{12.6}{T}} \cdot [CO] \cdot [H_2O],
  \]

\[\text{[81x782]}\]
Reverse \( r = 0.07 \times 10^3 \cdot e^{\frac{-489.27}{R \cdot T}} \cdot [CO_2] \cdot [H_2O] \),

\[
CH_4 + H_2O \leftrightarrow CO_2 + 3H_2,
\]

\( r = 3 \times 10^5 \cdot e^{\frac{-1804.19}{R \cdot T}} \cdot [CH_4] \cdot [H_2O] \).

Once unit 4 (see Figure 2) has been simulated, the amount of steam to be introduced into the reactor to generate the hydrogen required is known to be 2600 kg/h. On the other hand, 38,200 kg/h of oxygen must be fed to make the reactor autothermal, producing 3.6 MW of heat that must be removed to maintain isothermal conditions.

3.2.2. Amine Scrubbing (Units 2 and 5)

There are two streams with a high concentration of carbon dioxide: the syngas from gasification and the Fischer-Tropsch produced gas. The syngas obtained after gasification (S112, see Figure 1), with 70.4 wt% CO\(_2\) that can poison the cobalt (Co) catalyst used in the Fischer-Tropsch (F-T) reactor [25]. On the other hand, the fuel gas obtained from F-T (S403, see Figure 3), with 62.4 wt% CO\(_2\) reduces the calorific value of the stream.

MEA is selected as it requires a flow rate several orders of magnitude lower than other amines [26] for keeping CO\(_2\) around 1 n/n% (mole percentage) in the clean gas stream. Before the recycle is introduced, the composition of the lean amine entering the absorption tower (S206/S502, see Figures 1 and 3) is supposed to be 25 wt% of MEA and 2 wt% of CO\(_2\). Next, the following parameters are adjusted in the absorption towers (T-201/T-501, see Figures 1 and 3): contact stages, operating pressure, and temperature, and lean amine flow rate.

Increase of pressure improves the absorption and favours the formation of syngas. Thus, taking into account the pressure drop between R-101 (see Figure 1) and T-201, an operating pressure of 65 bar is selected for the absorber. In the case of T-501, the selected pressure is 3 bar, which is the maximum discharge pressure of K-501 compressor for which the gas temperature is less than 100 °C, as this would cause the water in the amine solution to boil.

Regarding the operating temperature, absorption improves at low temperatures, so both absorption towers operate at a temperature of 50 °C. Absorbers (T-201/T-501, see Figures 1 and 3) are designed with 15 and 10 stages, respectively, to obtain less than 1 vol% CO\(_2\) in the clean gas.

In unit 2, a flash chamber (V-203, see Figure 1) can be used for CO\(_2\) separation, because there is a large pressure difference between the absorption tower and the regeneration tower (operating at a pressure of 2 bar). This separates 22.5 wt% of the CO\(_2\) (S210).

Regeneration towers (T-202/T-502, see Figures 1 and 3) operate at atmospheric pressure in the condensers and at 2 bar in the reboilers. These towers are designed for high CO\(_2\) and amine recovery while avoiding high reflux and vaporisation ratios in both condenser and reboiler.

Condensers of all rectification towers in the plant operate at full reflux and temperatures higher than 50 °C, so water from cooling tower can be used for refrigeration.

Table 4 lists the main operating parameters of the regeneration towers:

| Table 4. Main parameters of the regeneration towers (T-202/T-502). |
|-----------------|--------|--------|
| Stages          | 30     | 15     |
| \( T_{\text{Condenser (°C)}} \) | 70     | 102    |
| \( T_{\text{Reboiler (°C)}} \) | 122    | 124    |
| \( P_{\text{Condenser (bar)}} \) | 1.013  | 1.71   |
| \( P_{\text{Reboiler (bar)}} \) | 2.00   | 2.00   |
| Reflux ratio    | 0.75   | 1.00   |
In the amine syngas scrubbing unit (unit 2, see Figure 1), 98 n/n% of the carbon dioxide is recovered in the distillate, while 100 mol% of amine and 75 mol% of water are recovered in the residue. Sufficient water is generated in the process to replace these losses, so reducing the operating costs in the column is preferable to having a higher water recovery. The separated carbon dioxide (S214) is combined with the carbon dioxide obtained in V-203 (S210) and emitted to the atmosphere (S218). In the case of the amine fuel gas scrubbing unit (unit 5, see Figure 3), the carbon dioxide released is emitted directly.

After the regeneration towers, fresh water (S222/S513) and amine (S221/S514) are added in order to adjust the lean amine flow rate and composition. Then, lean amine (S206/S502) is conditioned and sent back to the absorption tower (T-201/T-501).

Following the absorption tower in unit 2, the clean syngas (S207) is sent to a PSA (V-202A/B, see Figure 1) which is used, on the one hand, to separate part of the hydrogen that is fed to the upgrading reactor (S225) and, on the other hand, to adjust the ratio of carbon monoxide to hydrogen in the syngas (S226) that is sent to the Fischer-Tropsch reactor.

3.2.3. Fischer-Tropsch Process (Unit 3)

The mass distribution of products obtained from this process (defined by Equation (19)) is calculated by the term “chain growth probability” (α) [28], which is a function of the type of catalyst used and the reaction conditions.

\[
wt\%_{\text{C}_n} = \left[ n \cdot \alpha^{n-1} \cdot (1 - \alpha)^2 \right] \cdot 100, \tag{19}
\]

where \( n \) is the carbon number in the paraffin formed [52]. The chain growth probability must be iterated in order to maximise the production of biojet fuel, as it determines whether the hydrocarbons formed are light or heavy.

Once 0.88 has been obtained as the optimal α value, the results obtained are summarised in Figure 4, where the “Products” series has been obtained by applying Equation (19). The width of rectangles in “Fractions” series resembles the carbon number of hydrocarbons considered to be contained in each fraction (C_8-C_16 for biojet fuel) and their height is the sum of the mass distribution of the hydrocarbons contained (44.76 wt% of biojet fuel).

![Figure 4. Products and fractions mass distribution.](image)

Reactions that take place for the production of straight-chain paraffins are:

\[
n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}. \tag{R15}
\]
Therefore, combining the probabilities of obtaining each hydrocarbon with the stoichiometry of each reaction, it is possible to calculate the optimal $\text{H}_2/\text{CO}$ mole ratio, which has been determined at 2.08.

The operating temperature of the reactor is calculated taking into account the partial pressure of each species in the reactor, as shown in Equation (20):

$$\alpha = [1 - 0.039 \cdot (T - 533)] \left[ 0.2332 \cdot \left( \frac{n_{\text{H}_2}}{n_{\text{CO}}} \right)_{\text{opt}} + 0.663 \right],$$

(20)

where $\left( \frac{n_{\text{H}_2}}{n_{\text{CO}}} \right)_{\text{opt}}$ is the optimal $\text{H}_2/\text{CO}$ mole ratio in the syngas. Therefore, the optimum operating temperature is 211 °C.

Mass composition of products from the Fischer Tropsch reactor (R-301, see Figure 2) is given in Table 5:

Table 5. Composition of S305 (see Figure 2).

| Compound | wt% | Compound | wt% | Compound | wt% |
|----------|-----|----------|-----|----------|-----|
| $\text{H}_2\text{O}$ | 53.93 | $\text{C}_8\text{H}_{18}$ | 1.62 | $\text{C}_{17}\text{H}_{36}$ | 2.29 |
| $\text{CO}_2$ | 3.63 | $\text{C}_9\text{H}_{20}$ | 1.80 | $\text{C}_{18}\text{H}_{38}$ | 2.26 |
| $\text{CH}_4$ | 0.07 | $\text{C}_{10}\text{H}_{22}$ | 1.95 | $\text{C}_{19}\text{H}_{40}$ | 2.21 |
| $\text{C}_2\text{H}_4$ | 0.12 | $\text{C}_{11}\text{H}_{24}$ | 2.08 | $\text{C}_{20}\text{H}_{42}$ | 2.15 |
| $\text{C}_2\text{H}_6$ | 0.23 | $\text{C}_{12}\text{H}_{26}$ | 2.17 | $\text{C}_{21}\text{H}_{44}$ | 2.09 |
| $\text{C}_3\text{H}_8$ | 0.45 | $\text{C}_{13}\text{H}_{28}$ | 2.24 | $\text{C}_{22}\text{H}_{46}$ | 2.02 |
| $\text{C}_4\text{H}_{10}$ | 0.69 | $\text{C}_{14}\text{H}_{30}$ | 2.28 | $\text{C}_{23}\text{H}_{48}$ | 1.94 |
| $\text{C}_5\text{H}_{12}$ | 0.94 | $\text{C}_{15}\text{H}_{32}$ | 2.31 | $\text{C}_{24}\text{H}_{50}$ | 1.86 |
| $\text{C}_6\text{H}_{14}$ | 1.19 | $\text{C}_{16}\text{H}_{34}$ | 2.31 | $\text{C}_{25}\text{H}_{52}$ | 1.77 |
| $\text{C}_7\text{H}_{16}$ | 1.41 |  |  |  |  |

Finally, using the enthalpy of the inlet and outlet streams and eliminating the sensible heat term in Equation (2), the heat given off in the reactor is estimated as 51 MW, which must be removed to maintain isothermal conditions.

3.2.4. Upgrading (Unit 4)

Linear hydrocarbons are taken to the upgrading reactor, where hydrocracking and isomerization take place, increasing the yield of light products and improving their properties for their commercialisation [53].

Inside the reactor, operating at 250 °C and 30 bar, the following reactions (with the correspondent mass yield $\eta$) occur [29]:

- Hydrocracking:

\[
\eta = 5.8\% \quad \text{C}_{13}\text{H}_{28} + \text{H}_2 \rightarrow \text{C}_{10}\text{H}_{22} + \text{C}_3\text{H}_8,
\]

(R16)

\[
\eta = 61.7\% \quad \text{C}_{14}\text{H}_{30} + \text{H}_2 \rightarrow \text{C}_{11}\text{H}_{24} + \text{C}_3\text{H}_8,
\]

(R17)

\[
\eta = 51.3\% \quad \text{C}_{15}\text{H}_{32} + \text{H}_2 \rightarrow \text{C}_{12}\text{H}_{26} + \text{C}_3\text{H}_8,
\]

(R18)

\[
\eta = 37.1\% \quad \text{C}_{16}\text{H}_{34} + \text{H}_2 \rightarrow \text{C}_{13}\text{H}_{28} + \text{C}_3\text{H}_8,
\]

(R19)

\[
\eta = 50.4\% \quad \text{C}_{17}\text{H}_{36} + \text{H}_2 \rightarrow \text{C}_{14}\text{H}_{30} + \text{C}_3\text{H}_8,
\]

(R20)

\[
\eta = 4.9\% \quad \text{C}_{18}\text{H}_{38} + \text{H}_2 \rightarrow \text{C}_{15}\text{H}_{32} + \text{C}_3\text{H}_8,
\]

(R21)

\[
\eta = 17.3\% \quad \text{C}_{17}\text{H}_{36} + \text{H}_2 \rightarrow \text{C}_9\text{H}_{20} + \text{C}_8\text{H}_{18},
\]

(R22)

\[
\eta = 41.9\% \quad \text{C}_{18}\text{H}_{38} + \text{H}_2 \rightarrow \text{C}_{10}\text{H}_{22} + \text{C}_8\text{H}_{18},
\]

(R23)

\[
\eta = 2\% \quad \text{C}_{17}\text{H}_{36} + \text{H}_2 \rightarrow \text{C}_{10}\text{H}_{22} + \text{C}_7\text{H}_{16},
\]

(R24)

\[
\eta = 13.9\% \quad \text{C}_{18}\text{H}_{38} + \text{H}_2 \rightarrow \text{C}_{11}\text{H}_{24} + \text{C}_7\text{H}_{16},
\]

(R25)
η = 18% C₁₆H₃₄ + H₂ → 2C₈H₁₈, \hspace{1cm} (R26)

η = 23.2% C₁₈H₃₈ + H₂ → 2C₈H₂₀, \hspace{1cm} (R27)

- Isomerization:
  \begin{align*}
  \eta &= 90\% \quad n-C₈H₁₈ \rightarrow i-C₈H₁₈, \hspace{1cm} (R28) \\
  \eta &= 88\% \quad n-C₉H₂₀ \rightarrow i-C₉H₂₀, \hspace{1cm} (R29) \\
  \eta &= 90\% \quad n-C₁₀H₂₂ \rightarrow i-C₁₀H₂₂, \hspace{1cm} (R30) \\
  \eta &= 90\% \quad n-C₁₁H₂₄ \rightarrow i-C₁₁H₂₄, \hspace{1cm} (R31) \\
  \eta &= 90\% \quad n-C₁₂H₂₆ \rightarrow i-C₁₂H₂₆, \hspace{1cm} (R32) \\
  \eta &= 90\% \quad n-C₁₃H₂₈ \rightarrow i-C₁₃H₂₈, \hspace{1cm} (R33) \\
  \eta &= 53.9\% \quad n-C₁₄H₃₀ \rightarrow i-C₁₄H₃₀, \hspace{1cm} (R34) \\
  \eta &= 27.2\% \quad n-C₁₅H₃₂ \rightarrow i-C₁₅H₃₂, \hspace{1cm} (R35) \\
  \eta &= 6\% \quad n-C₁₆H₃₄ \rightarrow i-C₁₆H₃₄, \hspace{1cm} (R36) \\
  \eta &= 12.6\% \quad n-C₁₇H₃₆ \rightarrow i-C₁₇H₃₆, \hspace{1cm} (R37) \\
  \eta &= 18.9\% \quad n-C₁₈H₃₈ \rightarrow i-C₁₈H₃₈. \hspace{1cm} (R38)
\end{align*}

The amount of remaining reactants and formed products are estimated from mass yields and stoichiometric ratio of the different reactions. It is assumed that all isoparaffins formed have a single branch, with the methyl group on the second carbon of the chain [30–33,54,55].

Finally, using Equation (2) for the upgrading reactor (R-401, see Figure 2), the heat that must be removed to maintain isothermal conditions is estimated as 196 kW.

3.2.5. Product Separation (Unit 6)

The objective of the unit is to maximise the biojet fuel fraction, which comprises hydrocarbons from C₈ to C₁₆. However, n-octane (n-C₈) and isooctane (i-C₈) improve the properties of petrol, which contains hydrocarbons from C₅ to C₁₁. Therefore, in the first column (T-601, see Figure 3) the aim is to recover n-C₇, which forms part of the petrol, and n-C₉, which forms part of the biojet fuel (both are set to 99.5 n/n%). Under these conditions, the column has a certain flexibility of operation in which 90.7 n/n% of the C₈ is obtained in the distillate.

Light fractions are led to a flash chamber (V-601) to separate petrol from fuel gas, while heavier hydrocarbons are taken to two other rectification towers (T-602 and T603). T-602 is used to separate the biojet fuel from the heavier compounds; so, the recovery of i-C₁₆ in the distillate and n-C₁₇ in the residue is close to 100 n/n%. Finally, T-603 is used to separate diesel (C₁₅–C₂₀/2₅) from fuel oil (C₂₀+), setting the recovery of n-C₁₉ (head) and n-C₂₁ (bottom) at 90 n/n%.

Table 6 lists the main parameters of the rectification columns:

| Column | T-601 | T-602 | T-603 |
|--------|-------|-------|-------|
| Stages | 25    | 25    | 30    |
| T<sub>Condenser</sub> (°C) | 135   | 252   | 349   |
| T<sub>Reboiler</sub> (°C) | 305   | 438   | 438   |
| P<sub>Condenser</sub> (bar) | 4.00  | 5.00  | 1.71  |
| P<sub>Reboiler</sub> (bar) | 6.00  | 2.50  | 3.50  |
| Reflux ratio | 1.15  | 1.30  | 2.90  |
3.2.6. Overall Mass Balance

The mass flow between units is shown in Figure 5 and Table 7 (see Figures 1–3 for stream identification):

![Figure 5. Overall mass balance.](image)

**Table 7. Overall mass balance.**

| Stream             | kg/h  | Stream             | kg/h  |
|--------------------|-------|--------------------|-------|
| Straw              | 94,681| S405               | 17,160|
| PE + PP            | 9312  | S408               | 24    |
| S103               | 2600  | S412               | 12,940|
| O₂                 | 38,200| S503               | 646   |
| Ash                | 13,753| S507               | 1936  |
| S112               | 130,959| S511             | 0     |
| S205               | 7843  | S513               | 780   |
| CO₂                | 105,337| S514              | 0     |
| S219               | 2     | Other Biofuels (1) | 1697  |
| S221               | 1     |                    | 1590  |
| S222               | 14,094|                    |       |
| S225               | 45    |                    |       |
| S226               | 31,831| Biojet fuel        | 5676  |
| S305               | 31,880| H₂Ofresh           | 1991  |
| S403               | 1802  | H₂O_blowdown       | 7742  |

(1) Fuel gas (S503 + S602), petrol (S611), diesel (S627) and fuel oil (S629), see SI E-F for detailed information.

As shown, 103,994 kg/h of biomass and plastic are used as raw material, which is converted into 1207 kg/h of fuel gas, 1590 kg/h of petrol, 5676 kg/h of biojet fuel, 1697 kg/h of diesel, and 3416 kg/h of fuel oil, which means a yield of 13.06% towards products. This yield could be slightly improved by adjusting the supply of oxygen as a gasifying agent, since CO₂ production has been increased to make the reactor autothermal.

All mass balance data sheets of the chemical process can be found in Supplementary Information Sections A–F.

3.3. Heat Integration

Aspen Energy Analyzer is used to optimize energy demand. Stream properties were imported from Aspen HYSYS. The heat load released or given off by reactors, which require cooling or heating, is calculated for a difference of 1 °C from the operating temperature (see Supplementary Information Table S1). Prior to the pinch analysis, the heating and cooling demands are, respectively, 55,098 and 296,573 kW.

For the simulation of heat exchanger networks, Aspen Energy Analyzer allows the input of additional parameters such as viscosity (µ), thermal conductivity (k), and density (ρ), which have been obtained directly from Aspen HYSYS. These parameters and the
flow velocity through the exchanger (v) are used to calculate the individual heat transfer coefficient of the fluid. This velocity is set to 15 m/s for gases and 3 m/s for liquids or phase changes (see Supplementary Information Table S2).

Hot streams, whose temperature need to decrease and require cooling, form the Hot Composite Curve (HCC). Cold streams, whose temperature need to increase and require heating, form the Cold Composite Curve (CCC). Plotting both curves in a T-H diagram (see Figure 6), there is a maximum approach, represented in green, which is given by the minimum admissible temperature difference \( (\Delta T_{\text{min}}) \) in the heat exchangers [56]. This approach marks the optimal heating and cooling demands, from a thermodynamic point of view [57].

![Figure 6. Composite curves.](image)

The design of the heat exchanger network and, therefore, the potential energy integration, implies the need to fix this minimum temperature difference \( (\Delta T_{\text{min}}) \), so the heat exchanged is maximised without the size of equipment being excessive [58]. Using the Aspen Energy Analyzer software, the relationship between fixed and operating costs related to heat exchangers and utilities can be estimated, as shown in Figure 7:

![Figure 7. Selection of \( \Delta T_{\text{min}} \) in heat exchangers.](image)

Figure 6 shows that the whole CCC lies below the HCC, which means that there exists at least one heat exchanger network that fully satisfies the heating demand of the system. The excess heat from the process could be used for steam generation, which can be sold, so total costs shown in Figure 7 are negative, which indicate that the design of a heat exchanger network will have a positive impact on the economics of the project, which is an improvement to the GFT process. A \( \Delta T_{\text{min}} \) of 6 °C is selected as economically optimal (see Figure 7) [57].

Once the \( \Delta T_{\text{min}} \) is selected, the Grand Composite Curve (GCC) is drawn in Figure 8. The GCC allows to know pinch temperature (847 °C), and thermodynamically optimal demands (0 MW for heating and 170 MW for cooling):
In addition, the GCC is used to select the utilities for the heat exchanger network, as shown in Table 8:

Table 8. Utilities for the heat exchanger network.

| Utility                          | Conditions at Heat Exchanger Inlet | Conditions at Heat Exchanger Outlet |
|---------------------------------|-----------------------------------|-------------------------------------|
| For heating                     |                                    |                                     |
| Very high-pressure steam (HHPS) | Saturated steam at 260 °C          | Saturated liquid at 259 °C          |
| High-pressure steam (HPS)       | Saturated steam at 250 °C          | Saturated liquid at 249 °C          |
| For cooling (1)                 |                                    |                                     |
| Very high-pressure steam generation | Saturated liquid at 259 °C      | Superheated steam at 270 °C         |
| High-pressure steam generation  | Saturated liquid at 249 °C          | Superheated steam at 260 °C         |
| Medium-pressure steam (MPS) generation | Saturated liquid at 174 °C   | Superheated steam at 185 °C         |
| Low-pressure steam (LPS) generation | Saturated liquid at 124 °C     | Superheated steam at 135 °C         |
| Water from cooling tower        | Subcooled liquid at 28 °C          | Subcooled liquid at 42 °C           |

(1) Given the high temperatures, it is possible to have steam generation. Steam is superheated 10 °C to avoid condensation during transport due to heat losses, so this heat is assumed to be dissipated.

Thus, knowing the demands, flow rates and properties of all streams and temperature of utilities, the heat exchange network is designed using the Aspen Energy Analyzer software (see Supplementary Information Figure S10).

The steam demanded by the cold streams is generated from the hot streams, so that the final heating and cooling demands of the chemical process are set at 173 MW for cooling (2.12% higher than the optimal) and 0 kW for heating; thus, the network manages to reduce the initial demands by 41.58 and 100%, respectively. By oversizing the necessary cooling water flow by 10%, the required mass flow rate of this utility is 6,830,113 kg/h.

3.4. Thermodynamic Cycles and Cooling Tower

3.4.1. Thermodynamic Cycles (Unit 7)

The excess steam generation, obtained from the heat exchanger network, is used to partially cover the electricity demand of the plant, calculated as 26,146 kW (see Supplementary Information Section L and unit 8 electricity demands in Section 3.4.2. Aspen HYSYS is used to design the different Rankine cycles for each steam pressure.
All cycles start in a heat exchanger where steam is generated (E-950, E-G_{HPS}, E-G_{MPS} and E-949, see Figure 9). This steam is taken, if required, to the heat exchanger network (E-939, E-952) and pumped (P-701, P-703) to the operating pressure of steam generators.

The rest of the steam is used to generate electricity in the turbines (ST-701, ST-702, ST-703, ST-704), cooled in the condensers (E-701, E-702, E-703, E-704), pumped (P-702, P-704, P-705, P-706) to the operating pressure of steam generators and sent to the heat exchanger network, closing the cycle.

Table 9 shows heat used as an input for evaporators:

| Cycle                        | Heat Exchanged (kW) | Evaporators                  |
|------------------------------|---------------------|-------------------------------|
| Very high-pressure steam     | 311                 | E-950                        |
| High-pressure steam          | 40,487              | E-927, E-928, E-944, E-945 and E-951 (E-G_{HPS}) |
| Medium-pressure steam        | 38,641              | E-953 and E-954 (E-G_{MPS})   |
| Low-pressure steam           | 312                 | E-949                         |

Likewise, the inlet and outlet temperatures for the steam at the different pressures are used as initial data: 259–270 °C for HHPS, 249–260 °C for HPS, 174–185 °C for MPS and 124–135 °C for LPS. For each steam type, the pressure at which evaporation occurs (at 260, 250, 175, and 125 °C respectively), is set at the steam outlet after the pressure drop in the evaporator.
In the high and very high-pressure cycles, flow dividers are used as part of the steam is sent for heating. A cooler is used to simulate 10 °C of temperature loss in transport. Moreover, exchangers that demand the steam are placed downstream, where the heat exchanged is introduced as an input, so that Aspen HYSYS can calculate the ratio of steam to be turbined and sent as utility.

The pressure drop in the turbine is limited so steam fraction at the turbine outlet is higher than 90%, or the outlet pressure higher than 0.4 bar.

Condensers (E-701, E-702, E-703, E-704, see Figure 9) use cooling water (CW) from the tower, so the inlet and outlet temperatures are assumed to be 28 and 42 °C, respectively. The data shown in Tables 10 and 11 are obtained after the simulation of the cooling tower (unit 8, see Figure 10):

### Table 10. Design of condensers for Unit 7.

| Exchanger | HS (1)  | $T_{\text{inHS}}$ (°C) | $T_{\text{outHS}}$ (°C) | CS (2) | $T_{\text{inCS}}$ (°C) | $T_{\text{outCS}}$ (°C) | $H$ (kW) |
|-----------|---------|------------------------|-------------------------|--------|------------------------|------------------------|----------|
| E-701     | HHPS    | 164                    | 164                     | CW     | 28                     | 42                     | 254      |
| E-702     | HPS     | 153                    | 152                     | CW     | 28                     | 42                     | 31,823   |
| E-703     | MPS     | 90                     | 40                      | CW     | 28                     | 42                     | 33,191   |
| E-704     | LPS     | 76                     | 71                      | CW     | 28                     | 42                     | 279      |

(1) Hot stream; (2) Cold stream.

### Table 11. Design of condensers for Unit 7 (cont.).

| Exchanger | $U$ (kW/(m²·K)) | LMTD (°C) | $F_T$ | $S$ (m²) | $S_{\text{Overs. 10\%}}$ (m²) | $m_{\text{CW}}$ (kg/h) |
|-----------|-----------------|-----------|-------|----------|-----------------------------|------------------------|
| E-701     | 0.17            | 129       | 1.00  | 11.9     | 8.3                         | 15,662                 |
| E-702     | 1.25            | 117       | 1.00  | 217.9    | 677.7                       | 1,963,629              |
| E-703     | 1.34            | 26        | 1.00  | 969.5    | 1066.5                      | 2,048,032              |
| E-704     | 0.15            | 38        | 1.00  | 48.9     | 24.1                        | 17,210                 |

Figure 10. Cooling tower (unit 8).

Cooling water flow required by the cycle, oversized by 10%, reaches 4,448,986 kg/h, which is added to the 6,830,113 kg/h demanded by the chemical process, so that the total flow of water to be cooled by the cooling tower is 11,279,099 kg/h.
After simulating the cycles in Aspen HYSYS, the net power required is 10,431 kW, which means that the steam generated does not cover all the electrical demand of the chemical process equipment, so 16,698 kW must be purchased.

3.4.2. Cooling Tower (Unit 8)

This unit (see Figure 10) is simulated using Ebsilon Professional and a mechanical forced draft tower with countercurrent flow [59].

The hot water enters the cooling tower (S801, see Figure 10), is atomised, and then flows down. Air (S802), at ambient conditions, is introduced at the bottom and flows upwards, gets in contact with hot water and leaves the tower as saturated air (S803), cooling the liquid water, which falls into a pool at the bottom. The water losses increase the concentration of salts in the cycle over time, so part of the cooled water (S804) must be purged. The rest is recirculated (S805) and mixed with fresh water (S806) to make up for the losses, restarting the cycle.

Atmospheric pressure and a temperature of 25 °C for all raw materials are used as input. In addition, the average relative humidity of the air is assumed to be 75% [60]. Results of the cooling tower simulation are shown in Table 12:

| Water Flow to be cooled (kg/h) | 11,279,099 |
|--------------------------------|------------|
| Blowdown flow (kg/h)          | 53,932     |
| Water makeup flow (kg/h)      | 270,230    |
| \( T_{\text{In hot water}} \) \(^\circ\text{C}\) | 42         |
| \( T_{\text{Out cooled water}} \) \(^\circ\text{C}\) | 28         |
| \( P_{\text{Overs. 10\% (P-801)}} \) (kW) | 343        |
| \( P_{\text{Overs. 10\% (fan)}} \) (kW) | 641        |

The flow of fresh water taken from the medium represents approximately 3% of the refrigerated water flow. The mass balance data sheets of the thermodynamic cycles and the cooling tower can be found in SI G-H.

3.5. \( \text{CO}_2 \) Equivalent Emissions and Biojet Fuel Properties

On the one hand, emissions from biomass combustion are considered biogenic and not accounted in the biojet fuel life cycle. On the other hand, the gasification reactor is fed with 9 wt% of plastic waste (see Table 1), so 8227 kg/h of the carbon dioxide emitted has a non-renewable origin. These emissions are imputed to 13,586 kg of products; with an impact of 0.61 kg\( \text{CO}_2\text{eq}/\text{kg Biofuel} \). It should be noted that emissions could be reduced if the \( \text{CO}_2 \) captured from amine scrubbing were stored or transformed in different products [61].

In Spain, 0.2 t of carbon dioxide are emitted for each MWh demanded [62]. Thus, 0.25 kg\( \text{CO}_2\text{eq}/\text{kg Biofuel} \) are caused by the usage of 16.7 MW of electricity. Taking into account a default value of 0.085 kg\( \text{CO}_2\text{eq}/(\text{t} \cdot \text{km}) \) [63] for truck transportation (transport of the waste to the production plant and the fuel to the airports) and a distance of 200 km, transportation produces 0.02 kg\( \text{CO}_2\text{eq}/\text{kg Biofuel} \). The sum of \( \text{CO}_2 \) equivalent emissions is 0.9 kg\( \text{CO}_2\text{eq}/\text{kg Biofuel} \), which is considerably lower than in the case of conventional fuels [64], around 3 kg\( \text{CO}_2\text{eq}/\text{kg Fuel} \) (production) and 0.9 kg\( \text{CO}_2\text{eq}/\text{kg Fuel} \) (consumption).

The low heating value of biojet fuel produced is 43.1 MJ/kg, therefore, around 20 g\( \text{CO}_2\text{eq}/\text{MJ} \) are emitted; complying with the 65% mandatory reduction stated in the European Directive 2018/2001 [65].

Biojet fuel properties are estimated using the analysis tools offered by Aspen HYSYS, to check whether it meets the requirements specified in ASTM D7566-20c standard [66]. Results are shown in Table 13:
Table 13. Properties of biojet fuel compared to ASTM D7566 standard.

| Parameter                          | GFT Biojet Fuel | ASTM D7566          |
|------------------------------------|----------------|---------------------|
| Density at 15 °C (kg/m³)           | 742            | 730 to 770          |
| Kinematic viscosity at –20 °C (cSt)| 4              | lower than 8        |
| Pour point (°C)                    | –66            | lower than –40      |
| Flammability point (°C)            | 97             | greater than 38     |
| Lower calorific value (MJ/kg)      | 43.1           | greater than 42.8   |

All estimated parameters comply with the standard. Other parameters (not estimated) could also comply, due to the nature of the fuel produced. Aromatic and naphthalene content is negligible, since the biojet fuel produced contains straight and branched chain hydrocarbons. Moreover, there is no sulphur (and, therefore, no mercaptan content), which together with water, acids, and carbon dioxide, is one of the main causes of corrosion and high electrical conductivity [67]. Distillation curve temperatures should also be met, since the hydrocarbons that make up the biojet fuel match those that make up conventional paraffin (see Figure 4). Finally, the smoke point requirement should not cause problems, since paraffins and isoparaffins (with higher H/C ratio than other hydrocarbons) reduce the amount of smoke produced [67].

Therefore, the estimated properties of the produced biojet fuel fulfill the standard. Experimental tests should be performed to ensure that it could be blended up to 50% with conventional jet fuel [66].

3.6. Economic Analysis

Fixed and variable costs are taken into account to estimate the minimum selling price of the biojet fuel produced and assess if the pinch analysis and the use of Rankine cycles makes the process economically more attractive.

3.6.1. Cost of Equipment

The cost the equipment is calculated using equations of Table 14:

Table 14. Cost of equipment [46].

| Equipment            | Cost Equation (EUR)          | Equation Number |
|----------------------|------------------------------|-----------------|
| Pumps (1)            | $C_{2007}^{\text{pumps}} = 6900 + 206 \cdot V^{0.9}$ | (21)            |
| Compressors (2)      | $C_{2007}^{\text{compressors}} = 490,000 + 16,800 \cdot P^{0.6}$ | (22)            |
| Heat exchangers (3)  | $C_{2007}^{\text{heat exchangers}} = 22,080 + 46 \cdot S^{1.2}$ | (23)            |
| Furnace (4)          | $C_{2007}^{\text{furnace}} = 180,000 \cdot H$ | (24)            |
| Cooling tower (5)    | $C_{2007}^{\text{cooling tower}} = 250,000 + 1300 \cdot V^{0.9}$ | (25)            |
| Steam turbines (6)   | $C_{2007}^{\text{steam turbines}} = 14,500 \cdot P^{0.452}$ | (26)            |

(1) V is the volumetric flow rate in L/s. The cost is doubled, as pumps are installed with a spare. (2) P is the power in kW. (3) S is the exchange surface in m². (4) H is the heat produced by F-101 in millions of kcal/h (9.45 million kcal/h). (5) V is the flow of water to be cooled (S801) in L/s. (6) P is the power generated in kW.

- Plastic and biomass feed hoppers and mixers:

They are calculated as vessels. A length to diameter (L/D) ratio of 5 gives the minimum cost. Applying Equation S3 (see SI L) and a residence time of 15 min, the hoppers volume can be calculated, which is oversized by 100%:

A total of 3 mm of corrosion allowance (C.A.), carbon steel as construction material, and a design pressure of 3.5 kg/cm² are used for the following calculations, as lean amine and raw materials are assumed to be non-corrosive:

$$D = \sqrt[3]{\frac{4 \cdot V}{\pi \cdot \left(\frac{L}{D}\right)}}$$ (27)
\[ L = D \cdot \left( \frac{L}{D} \right), \]

\[ t = C.A. + P_D \cdot \left( \frac{D}{2} \right) \cdot \frac{1000}{St \cdot E - 0.6 \cdot P_D}, \]

\[ W = 0.0246 \cdot D \cdot (L + 0.8 \cdot D) \cdot (t + x), \]

\[ \text{Cost}_{2007} = 13,014 \cdot W^{0.92} \cdot \left( \frac{L}{D} \right)^{-0.15} \cdot \left( \frac{t}{8} \right)^{-0.21}, \]

where:

- \( D \) is the diameter of the vessel (m);
- \( V \), volume (m\(^3\));
- \( L \), length (m);
- \( t \), thickness (mm);
- \( C.A. \), corrosion allowance (mm);
- \( P_D \), the design pressure (kg/cm\(^2\));
- \( St \), a dimensionless factor depending on the material, pressure and temperature conditions. This value is set to 1055 when using carbon steel and moderate conditions;
- \( E \), modulus of elasticity of carbon steel, which is 0.85 GPa;
- \( W \), weight of the equipment (t);
- \( X \), a complexity factor, considered 2 for simple equipment;

- **Flash chambers:**
  
  Thickness, mass, and cost of flash chambers are calculated using the following equations:

  \[ t = t_{\text{Shell}} + C.A., \]

  \[ m = \pi \cdot \rho \cdot L \cdot D \cdot e, \]

  \[ \text{Cost}_{2007} = 10,000 + 29 \cdot m^{0.85}, \]

  where data such as shell thicknesses (\( t_{\text{Shell}} \)), corrosion allowances, lengths, diameters, and densities of the materials have been obtained from Aspen HYSYS, using a liquid volume in the vessels of 50%.

- **Distillation columns:**
  
  Their cost is calculated as the sum of vessel and trays cost:

  \[ \text{Cost}_{\text{Vessel \ 2007}} = 17,640 \cdot D^{1.066} \cdot L^{0.802}, \]

  \[ \text{Cost}_{\text{Trays \ 2007}} = 0.92 \cdot \left( 290 + 550 \cdot D^{1.9} \cdot N_{\text{Trays}} \right). \]

  Sections and heights are sized and trays are selected using Aspen HYSYS, so the fluid dynamics in each plate and all parameters are in a normal operating range. Columns are divided into sections and the cost is calculated as the sum of each individual section.

  In addition, the installed cost of PSAs for oxygen (to be fed to F-101) and hydrogen purification (V-202A/B), and the R-301 and R-401 reactors, is calculated using the exponent (exp) method and their respective installation factors:

  \[ \text{Cost}_{\text{Installed}} = 0.92 \cdot F_{\text{Installation}} \cdot \text{Cost}_{\text{Base}} \cdot \left( \frac{\text{Cap}}{\text{Cap}_{\text{Base}}} \right)^{\text{exp}}, \]

  where the base capacities (\( \text{Cap}_{\text{Base}} \)) are the following [28]:

  - For oxygen separation PSA, the air flow rate obtained (t/h);
  - For hydrogen separation PSA, the flow rate of hydrogen separated (kg/h);
  - For the Fischer-Tropsch reactor, the feed flow rate (kmol/h);
  - For the upgrading reactor, the feed flow rate (kg/h).
The capacity (Cap) of the equipment and costs are shown in Table 15:

Table 15. Cost of PSAs (V-202A/B, see Figure 1) and reactors (R-301/R-401, see Figure 2).

| Equipment | Cap_{Base} | Cost_{Base} (USD) | Year | Exp | Cap | F_{Installation} | Cost_{Installed} (EUR) |
|-----------|------------|--------------------|------|-----|-----|------------------|------------------------|
| R-301     | 3186       | 10,500,000         | 2003 | 0.72| 2955.4 | 1               | 9,151,283              |
| R-401     | 4355       | 5,021,074          | 2011 | 0.65| 12,940.0 | 3              | 28,126,803             |
| PSA Air   | 24         | 24,552,000         | 2002 | 0.75| 38.2   | 1               | 32,008,387             |
| V-202A/B  | 8665       | 4,855,471          | 2002 | 0.6 | 44.8   | 2.47            | 468,393                |

For the rest of the equipment, the installation factor (F_{Installation}) is unique and is calculated from different factors, such as material (f_M, carbon steel), equipment placement (f_{ER}), piping cost (f_P), instrumentation and control (f_I), electricity (f_{EI}), civil works (f_C), buildings and structures (f_S), and thermal insulation and painting (f_L), whose values are 1, 0.3, 0.8, 0.3, 0.2, 0.3, 0.2, and 0.1 respectively [46].

To obtain the cost of installed equipment, the following equation is applied:

\[
\text{Cost}_{\text{Installed}} = \text{Cost} \cdot (1 + \text{Cost}) \cdot f_M + (f_{ER} + f_P + f_I + f_{EI} + f_C + f_S + f_L) .
\]  (38)

The equipment costs are calculated and updated using the following expression, where the chemical plant cost index (CEPCI) of the year 2007 (former) is 525.4 and for 2018 (current) is 603.1 [45]:

\[
\text{Cost}_{\text{Updated}} = \frac{\text{Cost}_{\text{Installed}} \cdot \text{CEPCI}_{\text{Current}}}{\text{CEPCI}_{\text{Former}}} .
\]  (39)

Table 16 lists the cost of all equipment:

| Equipment          | Cost_{Purchase} 2007 (EUR) | Cost_{Installed} 2007 (EUR) | Cost_{Installed} 2018 (EUR) |
|--------------------|---------------------------|-----------------------------|-----------------------------|
| Trays              | 485,804                   | 485,804                     | 557,649                     |
| Pumps              | 5,544,448                 | 17,742,233                  | 20,366,084                  |
| Compressors        | 10,840,115                | 34,688,369                  | 39,818,339                  |
| Heat exchangers    | 2,384,730                 | 7,631,136                   | 8,759,684                   |
| Furnace            | 17,014,877                | 54,447,606                  | 62,499,717                  |
| Hoppers and mixers | 243,213                   | 778,283                     | 893,381                     |
| Flash chambers     | 296,036                   | 947,314                     | 1,087,410                   |
| Tower vessels      | 2,791,047                 | 8,931,351                   | 10,252,184                  |
| Cooling tower      | 2,071,034                 | 6,627,309                   | 7,607,404                   |
| Steam turbines     | 1,537,455                 | 4,919,856                   | 5,647,441                   |
| **Total**          |                           |                             | 253,468,920                 |

3.6.2. Cost of Raw Materials and Products

Costs for cooling water (S806), process water (S001), fuel oil (S629), and electricity have been obtained for the year 2015, while that for biomass (S101) has been obtained for the year 2007, so they must be updated using Equation (47); knowing that the CEPCI for the year 2015 was 556.8 [68]. The material balance for the calculation of the fresh process water flow rate is calculated in Supplementary Information Section I.

Thus, Table 17 is obtained [69]:
The cost of raw materials is 42,698,867 EUR/year and the amount obtained from the sale of products is 50,453,213 EUR/year.

3.6.3. Minimum Selling Price

The percentage method (see Table 18) is used to obtain a reference value for the fixed and working capital, based on the total cost of equipment [46]:

\[ ISBL = E + M + D.E. + P.E. + Con. + Con.S, \]  
\[ F.C. = ISBL + Ut. + O.S. + S.C. + U.C., \]  
\[ W.C. = 0.2 \cdot C.I. \]
The lifespan is 20 years, from years 3 to 22 and inflation is considered to be 4% per year. Thus, fixed capital is updated:

$$F.C._{\text{Updated}} = \%_{\text{Invested}} \cdot F.C. \cdot (1 + I)^{\text{Year}}.$$  \hspace{1cm} (43)

The working capital is invested at the end of the project in the third year at the updated cost, and that amount is recovered in year 22.

$$W.C._{\text{Updated}} = W.C. \cdot (1 + I)^{\text{Year}},$$  \hspace{1cm} (44)

$$T.I. = F.C._{\text{Updated}} + W.C._{\text{Updated}}.$$  \hspace{1cm} (45)

During plant operation years, there is no investment, only the profits or losses from the sale and purchase of products and raw materials. In this scenario, 45 employees will be paid an average of 1800 EUR per worker [70], 1,134,000 EUR in total. Insurance is assumed to be 2% [46] of the fixed capital, 19,281,762 EUR. Both costs are added to the cost of raw materials to be purchased. These costs (C.) and sales profits (S.) are updated annually:

$$S_{\text{Updated}} = S \cdot (1 + I)^{\text{Year}},$$  \hspace{1cm} (46)

$$C_{\text{Updated}} = C \cdot (1 + I)^{\text{Year}}.$$  \hspace{1cm} (47)

During the first 10 years of plant operation, depreciation (D.) for the fixed capital invested in the project is accounted as:

$$D_{\text{Updated}} = F.C. \cdot \frac{I \cdot (1 + I)^{\text{Year}}}{(1 + I)^{\text{Year} - 1}}.$$  \hspace{1cm} (48)

This depreciation has a value of 0 for the remaining years of operation, and allows tax deductions (T.), as these are calculated as 35% of the pre-tax profits (P.T.P.):

$$P.T.P. = C_{\text{Updated}} - S_{\text{Updated}} - D_{\text{Updated}},$$  \hspace{1cm} (49)

$$T. = 0.35 \cdot P.T.P.$$  \hspace{1cm} (50)

Profit after tax (P.A.T.) is calculated as the difference between profit before tax and tax. Finally, funds generated (F.G.) and cash flow (C.F.) are calculated:

$$P.A.T. = P.T.P. - T.,$$  \hspace{1cm} (51)

$$F.G. = D_{\text{Updated}} + P.A.T.,$$  \hspace{1cm} (52)

$$C.F. = F.G. - T.$$  \hspace{1cm} (53)

Results are shown in Supplementary Information Table S10.

From the cash flow obtained for each year, a sensitivity analysis is performed by taking each year’s cash flow and updating it for a chosen rate of return (RoR):

$$C.F._{\text{Updated}} = \frac{C.F.}{(1 + \text{RoR})^{\text{Year}}}.$$  \hspace{1cm} (54)

The sum of cash flows gives the net present value (NPV) of the plant.

Bioproducts selling prices need to be higher than conventional petroleum fuels prices for the plant to be profitable. Thus, if an internal rate of return (IRR) of 9% is used, [47], bioproducts MSP are shown in Table 19:
Table 19. MSP of biofuels for the studied process.

| Product       | MSP   | EUR/kg | EUR/L |
|---------------|-------|--------|-------|
| Natural gas   | 0.51  | 0.54   |
| Petrol        | 1.71  | 1.16   |
| Biojet fuel   | 1.85  | 1.37   |
| Diesel        | 1.90  | 1.45   |
| Fuel oil      | 1.42  | 1.09   |

These prices are 3.47 times higher than conventional fuels prices (see Table 17), but similar to prices found in other studies for biojet fuel [18,21,28]. EU sets a tax of approximately 25 EUR/t CO$_2$eq [18] to penalise CO$_2$ emissions, which would increase the price of biojet fuel by around 0.02 EUR/kg, which increases the fossil jet fuel by 0.10 EUR/kg. CO$_2$ emissions price can significantly increase in the coming years [71], and could help the biojet fuel become economically competitive. According to Deane et al. [72], this would add near 5 EUR to the ticket’s price per passenger of a regular 1000 km flight. Thus, it is worth noting that the use of this biojet fuel will not have a significant impact on the final consumer.

4. Conclusions

Production of biojet fuel from the cogasification of biomass and plastic (GFT-J process) has been described in detail, considering the design of a heat exchanger network, thermodynamic cycles, cooling tower, and an economic analysis. The following conclusions can be drawn:

The addition of plastic to biomass gasification improves the volatility of the mixture and reduces tar and char residues, so the yield of raw materials toward products is 13.06%, where the mass distribution of products is: 8.88% fuel gas; 11.7% petrol; 41.8% biojet fuel; 12.5% diesel, and 25% fuel oil. According to Aspen HYSYS properties estimation, the produced biojet fuel complies with the requirements established by the standard ASTM D7566. Thus, it could be blended up to 50% with traditional jet fuel.

Pinch analysis reveals that steam can be generated using the caloric power of hot streams, so 38.73% of electricity, 41.58% of cooling, and 100% of heating demand can be covered with renewable energy (waste biomass) of the process, and the design of a heat exchanger network reduces the total cost of the GFT process.

Biojet fuel MSP (1.37 EUR/L) is higher than conventional jet fuel price, however, the rise of CO$_2$ emission taxes could help biojet fuel to be more competitive. The produced biojet fuel emits 20.14 gCO$_2$eq/MJ, a significant reduction compared to 94 gCO$_2$eq/MJ emitted by fossil fuels. Moreover, emissions caused by electricity consumption during biojet fuel production could be further reduced by the change to a more renewable electricity mix.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14196035/s1, Figure S1: Simulation of unit 1, Figure S2: Simulation of unit 2, Figure S3: Simulation of unit 3, Figure S4: Simulation of unit 4, Figure S5: Simulation of unit 5, Figure S6: Simulation of unit 6, Figure S7: Simulation of unit 7, Figure S8: Simulation of unit 8, Figure S9: Water treatment plant, Figure S10: Heat exchanger network (unit 9), Table S1: Chemical process stream demands, Table S2: Viscosity, density and thermal conductivity of streams, Table S3: Heat exchangers parameters, Table S4: Power demand of mixers, Table S5: Power demand of process pumps, Table S6: Power demand of the pumps upstream of the reboilers, Table S7: Power demand by tower reflux booster pumps, Table S8: Power demand by compressors, Table S9: List of streams and equipment, Table S10: Annual economic balance.

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**Abbreviations**

The following are abbreviations, units, and acronyms used in the article.

- $\alpha$: Probability of chain growth
- $\Delta$: Variation, difference
- $\Delta T_{\text{min}}$: Pinch temperature of a heat exchanger
- $\eta$: Yield
- $\nu$: Stoichiometric coefficient
- $\rho$: Density
- $\mu$: Viscosity
- $[x]$: Concentration of compound x
- $^\circ$C: Degree(s) centigrade(s)
- bar: Bar(s)
- BTU: British thermal unit(s)
- C.: Cost(s)
- C.A.: Corrosion allowance
- C.F.: Cash flow
- cal: Calorie(s)
- Cap: Capacity
- CCC: Cold composite curve
- CEPCI: Chemical plant cost index(es)
- cm: Centimetre
- Con: Condenser
- Con.: Construction
- Con. S.: Construction supervision
- cP: Centipoise
- $c_p$: Specific heat
- CS: Cold stream
- CW: Cooling water
- $C_x$: Hydrocarbon of x number of carbons
- $C_{x+}$: Hydrocarbon with number of carbons greater than x
- D.: Depreciation
- D.E.: Detailed engineering
- E: Modulus of elasticity, cost of equipment; as indicated
- E-: Heat exchanger
- $E_A$: Activation energy
- EUR: Euro(s)
- F: Factor
- F.C.: Fixed cost(s)
- F.G.: Funds generated
- F-: Furnace
- F-T: Fischer-Tropsch
- $f_C$: Civil works factor
- $f_{EI}$: Electricity factor
- $f_{ER}$: Equipment placement factor
- $f_i$: Instrumentation and control factor
- $f_l$: Thermal insulation and painting factor
- $f_M$: Material factor
- $f_p$: Piping cost factor
- $f_S$: Buildings and structures factor
- $F_T$: Correction factor in a heat exchanger
g  Gravitational acceleration
Gen.  Generation
GFT-J  Gasification and Fischer-Tropsch synthesis to jet fuel
GPa  Gigapascals
h  Hour(s), specific enthalpy; as indicated
H  Enthalpy, heat
HCC  Hot composite curve
HHPS  Very high-pressure steam
HPS  High-pressure steam
HS  Hot stream
HTFT  High temperature Fischer-Tropsch
Hx  Height of x
I  Inflation
i-Cx/i-Cy  Isoparaffin of x number of carbons
Inv.  Invested
IRR  Internal rate of return
ISBL  Inside battery limits
J  Joule(s)
K  Kelvin(s)
K-  Compressor
kg  Kilogram(s)
kJ  Kilojoule(s)
kmol  Kilomol(es)
kWh  Kilowatt(s) hour
L  Litre(s)
LPS  Low-pressure steam
LTFT  Low temperature Fischer-Tropsch
m  Meter(s)
M  Material cost(s)
M.W.  Molecular weight
M-  Mixer
MEA  Monoethanolamine
min  Minimum
mm  Milimeter
MPS  Medium-pressure steam
MW  Megawatt(s)
MWh  Megawatt(s) hour
N  Number
N(x)  Molar flow rate of component x
n-Cx/n-Cy  Paraffin of x number of carbons
n/n%  Mole distribution
NPV  Net present value
O.S.  Off-sites
OSBL  Outside battery limits
Overs.  Oversized
P  Pressure, power; as indicated
P.E.  Licenses and process engineering costs
P&ID  Piping and instrumentation diagram
P-  Pump
P.A.T.  Profit after tax
Pa  Pascal(s)
P_D  Design pressure
PE  Polyethylene
PP  Polipropylene
PSA  Pressure swing adsorption
P.T.P. Pre-tax profits
$p_x$ Partial pressure of compound x
$r$ Reaction speed
$R$ Ideal gas constant
$R_{-yxx}$ Reactor
$Reb$ Reboiler
$RoR$ Rate of return
$s$ Second(s)
$s$ Surface
$s$. Sales
$S.C.$ Start-up cost(s)
$SI$ Supplementary Information
$SI_{X}$ Supplementary Information Section X
$SI_{X-Y}$ Sections X to Y of Supplementary Information
$ST-$ Steam turbine
$S_{xxx}$ Stream xxx
$t$ Time, tonne(s), thickness; as indicated
$T$ Temperature
$T.$ Tax(es)
$T^*$ Modified temperature
$T.$- Distillation tower
$T.I.$ Total invested
$T_{in}$ Temperature at inlet
$T_{out}$ Temperature at outlet
$t_{R}$ Residence time
$U$ Overall heat transfer coefficient in a heat exchanger
$U.C.$ Unforeseen contingencies
$USD$ US dollar(s)
$v$ Velocity
$V$ Volume, volumetric flow; as indicated
$V.$- Vessel
$vol\%$ Volumetric composition
$W$ Watt(s), weight; as indicated
$W.C.$ Working capital
$wt\%$ Mass composition
$x$ Complexity factor

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