Sustainability Outlook of Thermochemical-Based Second-Generation Biofuel Production: Exergy Assessment

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Abstract: Since the last century, the idea of replacing traditional fossil sources with renewable alternatives has attracted much attention. As a result, auspicious renewable biofuels, such as biohydrogen or bio-oil, have emerged as suitable options. This study provides some knowledge on combining process design, modeling, and exergy analysis as a united framework to support decision making in energy-based projects. The assessment also included a final evaluation, considering sustainability indicators to evaluate process performance. Feedstock selection is crucial for producing bio-oil and hydrogen for process sustainability; this aspect is discussed, considering second-generation sources. Second-generation bio-oil and biohydrogen production are assessed and compared under the proposed framework. Process simulation was performed using ASPEN PLUS. Exergy analysis was developed using data generated in the process simulation stage, containing material and energy balances, thermodynamic properties, chemical reactions, etc. A mathematical formulation for the exergy analysis shows the exergy of utilities, waste, exergy efficiency, and exergy intensity of both processes, based on the same functional unit (1 kg of product). The sustainability evaluation included quantifying side parameters, such as the renewability index, energy efficiency, or global warming potential. The results indicate that pyrolysis obtained the highest resource exergy efficiency (11%), compared to gasification (3%). The exergy intensity shows that more exergy is consumed in the gasification process (4080.21 MJ/kg) than pyrolysis (18.64 MJ/kg). Similar results are obtained for total irreversibility (327.41 vs. 48.75 MJ/kg) and exergy of wastes (51.34 vs. 18.14 MJ/kg).

Keywords: exergy analysis; sustainability; pyrolysis; gasification; second-generation biomass; biofuels

1. Introduction

Renewable energy is an attractive alternative to start replacing fossil fuels, making this source more environmentally friendly. Biodiesel, bioethanol, and bio-oil are among the most explored biofuels obtained from different sources. Second-generation biofuels have started attracting more interest to use lignocellulosic material in biofuel production [1]. Most second-generation biofuel production technologies are currently unsustainable at a large scale, because of the lack of technology for the commercial exploitation of waste used as feedstock [2]. Most technologies transforming second-generation sources into biofuels are currently in lower technology readiness levels (TRLs) [3,4]. The combination of process analysis and exergy assessment is helpful to identify hotspots and improve the opportunities of using such biosources [5]. More research is needed to overcome the current limitations of second-generation biofuel production, regarding energy usage and resource intensity. It is worth mentioning that other researchers have explored other sources for fuel generation, such as sewage sludge [6] or plastics [7]. Still, more research is needed, in order to embrace broader perspectives in clean energy and sustainability.

Regarding biofuel production from biomass, feedstock selection is somewhat controversial because of the particular features of second-generation biofuels. Important
sustainability aspects, such as efficiency, environmental profile, and financials, must be considered [8]. Henceforward, using process analysis tools to compare the performance of second-generation technologies from different feedstocks become strategic. Biomass such as wood bagasse, leftovers, and others are sources of second-generation bio-oil [9]. These materials are abundant at a meager cost, due to their high availability. Direct combustion is traditionally used to generate energy from biomass conversion. thermochemical and biochemical pathways produce biofuels and biochemicals [10]. Second-generation biomass composition varies in different ranges. Its typical composition shows glucan within 40–50 wt.%, xylan 20–40 wt.%, and lignin 10–40 wt.% [11]. Pyrolysis is a suitable way of producing second-generation bio-oil and is a promising alternative to replace fossil fuels [12]. This process consists of a furnace or reactor to convert biomass into products, and condensing gases into liquid products [13].

Biohydrogen is a promising biofuel, and it is expected to play a role as a fuel that is clean, friendly with the environment, and energy-intensive. This component is also functional in fuel cells for electricity generation. A significant weakness in its commercial distribution involves its inflated cost [14]. Consequently, research and development activities are needed to increase TRLs for this kind of technology. This can lead to reaching more sustainable biofuel production [15]. Using lignocellulosic materials in hydrogen production can reduce expenditures, while improving the process’s environmental profile. Gasification is an appropriate technology for thermochemically transforming biomass into syngas and biohydrogen. The process adds a water gas shift (WGS) unit to enhance biohydrogen production [16]. Biomass gasification has also been used as an internal unit in a complete methanol production process in a combined scheme [17]. A significant issue in the thermochemical transformation processes (even more for second-generation sources) is their energy-intensity operations [18], making these technologies challenging to scale up and develop for commercial applications.

Computer-aided exergy analysis is a valuable tool to identify process hotspots from the energy viewpoint. Three processes for extracting microalgal oil from Chlorella sp. were examined using exergy analysis [19], and a maximum resource efficiency of 51% was reported, based on hexane extraction. Ojeda-Delgado et al. [20] assessed the energy profile for four ethanol processes through this method. They found that second-generation bioethanol could reach an exergy efficiency of 80% through steam-explosion, saccharification, fermentation and dehydration pathways. Ebrahimi and Ziabasharhag [21] analyzed the energy and exergy aspects of biomass gasification. They presented a new process setting with built-in heat, power, and liquified natural gas cogeneration. Recently, Reyes et al. [22] assessed pyrolysis processes based on different feedstock, in a semi-continuous reactor setting.

In addition to exergy evaluation, sustainability assessment emerges as a valuable tool for improving a process or system at the early design stage. Different methods and approaches are used to accomplish this purpose [23]. Among the reported frameworks, indicator-based methods have shown successful results, while keeping an uncomplex formulation. Ruiz-Mercardo et al. [24] presented a taxonomy for several sustainability indicators, to assess economy, environment, efficiency, and energy areas within a gate-to-gate approach. These scholars continued with this work to extend this methodology by identifying data needs to estimate these indicators. Estimating these indexes involves connecting the mathematical formulas based on data requirements [25]. The GREENSCOPE approach was successfully combined with design principles and computer-aided process engineering to show the advantages of coupling these tools in chemical process sustainability [26]. Exergy performance metrics have also been used in sustainability evaluation, as separate indicators in multiple-indicator analyses [27] and in aggregated approaches [28]. Still, many of these studies have focused on indicator-based analysis, but have not included a comprehensive framework that embodies all the aligned stages from feedstock selection to sustainability evaluation, involving exergy assessment in the process. In addition, there are still missing studies that comprehensively connect process...
simulation, analysis, and optimization from a sustainability perspective. The development of such methods could contribute to taking low/mid-TRL second-generation technologies to commercialization levels.

This work is aimed at the current needs of improving thermochemical technologies for second-generation biofuel production, including new know-how in the simultaneous application of process simulation and exergy analysis, to assess the performance of biofuels from lignocellulosic biomass. Besides, the approach enables process simulation and exergy analysis to be used in decision making, to compare thermochemical technologies. This method represents a new way of selecting and optimizing second-generation biofuel technologies that remain at low- to mid-TRL. The assessment is complemented by a further evaluation of sustainability indicators, based on process benchmarks, taking the assessment to the next level. The presented assessment is introduced to respond to the need and lack of comprehensive and straightforward studies for analyzing and improving bio-based processes from a broader sustainability dimension, by including exergy assessment. This approach is presented as a way of including exergy indicators in sustainable development, bringing new knowledge in process analysis for research and development in biomass transformation technologies. This work presented a practical framework that combines feedstock selection, process simulation, exergy analysis, and sustainability evaluation to compare pyrolysis and gasification as promising technologies to produce second-generation biofuels.

2. Materials and Methods

The method proposed in this work combines a feedstock selection task, process simulation of suitable thermochemical technologies (gasification and pyrolysis), and exergy analysis. Figure 1 shows the schematic representation of the proposed method to assess thermochemical-based biomass transformation processes under exergy assessment. This approach can identify energy hotspots and make comparisons between a set of alternatives. The method is also appropriate for low- to mid-TRL technologies since process simulation generates data to assess different systems considering the lack of industry data. The following subsections describe in more detail each step of the proposed methodology.

![Assessment Methodology used in this work.](image)

2.1. Feedstock Selection

An optimum biomass selection for chemical design is fundamental for chemical process sustainability. The principles for selecting feedstock depend on numerous aspects, e.g., availability, transportation, logistics, supply chain, and cellulosic content. Different biomasses have been investigated for industrial production. Food security issues restrict edible biomass as bio-based feedstock, even though these are economical and technically viable in biorefinery design [29]. However, first-generation biomasses are initially discarded. Lignocellulosic biomass has emerged as a suitable source of biomass, considering its residual origin. Therefore, one can avoid food security issues using this type of biomass.
Lignocellulosic biomass refers to agricultural and forestry residues and biowaste streams (e.g., municipal solid waste). These materials are highly available as co-products (even as not-desired ones) from economic activities in productive agricultural chains [30]. There are still some disposal issues associated with these substances. They might result in higher environmental and ecological effects, increased transportation expenditures, and low bulk compactness [31]. Globally, yucca is produced with a projected 60 million tons per year, generating approximately an equal amount of yucca peels and stems (YPS) [32]. Other crop wastes are also widely accessible as by-products of agricultural activities, such as rice straw (RS) and cocoa pod husk (CCH). The banana market is even bigger than yucca, rice, and cocoa, with 116 million tons produced by 2019. EBFB, RS, CCH, and YPS are attractive feedstock considering their high availability in Northern Colombia. The whole production chain for agricultural products also includes land use and harvesting. There are differences between crops in terms of the productivity yield per area of land used for harvesting. This feature becomes a crucial issue since it is more desirable to have high efficiency of this variable, translated into more availability while decreasing environmental burdens to the soil.

2.2. Process Simulation

The first step for simulating a chemical process technology involves designating the task in terms of viable product(s), available raw materials, and adequate processing pathways. Then, these layers are interconnected to generate a flowsheet containing all these elements, showing how the task is accomplished [33]. Finally, the method continues with setting chemical substances/components, thermodynamic model, and equation of state. Besides, this step includes setting production capacity and considering inlet conditions of mass and energy balances, generation and consumption of resources, operating process conditions, such as temperature or pressure, chemical reaction kinetics, fractional yields, and stoichiometry [34].

This work employed ASPEN PLUS® software to model the selected topological pathways based on thermochemical technologies for biomass transformation into biofuels. Aspen Tech (United States) developed this process engineering software and it is the leading tool in process engineering design, analysis, and optimization [35]. Input data are entered into the software to perform simulations. This modeling includes information about chemical substances, property models, mass balances, processing units, and others. However, some components (cellulose, hemicellulose, etc.) are missing in the software. The National Energy Renewable Laboratory (NERL) developed a biomass-based database for to simulate bio-processes in ASPEN PLUS software [36]. Besides, the program included a subroutine in calculating thermodynamic properties, which can be temperature-dependent or scalar. The Gibbs energy of formation, heat capacity, heat formation, or viscosity are estimated. The following assumptions are employed for modeling pyrolysis and gasification processes to produce biofuels (biohydrogen and bio-oil):

- Steady-state modeling;
- Solid carbon is used as char;
- Tar formation is not considered;
- Biomass was created as a mixture of components (cellulose, hemicellulose, lignin, ash, and acetate);
- Temperature changes and profiles were not considered in the gasification reaction;
- Volatile reactions follow stoichiometric equations and reported fractional yields.

2.2.1. Biomass Gasification for Hydrogen Production

The first simulated thermochemical process was gasification for biohydrogen production. This process is performed taking the following four raw materials into account: (i) CS, (ii) RS, (iii) BEFB, and (iv) CCH. These are identified in the process flowsheet simulation diagram (see Figure 2) as streams 1, 2, 3, and 4, respectively. Table 1 reports the chemical
composition and mass flow rate of the primary raw materials for the gasification process. In this sense, the total feedstock flow was 52,289.80 kg/h of combined biomasses.

![Process flowsheet diagram of the gasification process.](image)

**Figure 2.** Process flowsheet diagram of the gasification process.

**Table 1.** Chemical composition and mass flow rate of raw materials in the gasification process.

| Biomass | Mass Flow (kg/h) | Cellulose (%wt.) | Hemicellulose (%wt.) | Xylan (%wt.) |
|---------|------------------|-------------------|----------------------|--------------|
| CS      | 25,742.20        | 0.29              | 0.20                 | 0.13         |
| RS      | 19,242.20        | 0.29              | 0.25                 | 0.18         |
| BEEF    | 7001.80          | 0.42              | 0.13                 | 0.12         |
| CCH     | 303.60           | 0.28              | 0.29                 | 0.12         |

These streams are mixed to follow the dryer unit to reduce the moisture content below 10%. This operation is developed before entering the gasification reactor (RX-1). This process is carried out in the gasifier, which operates at 750 °C and 1 atm. Generally, the products of complete combustion are substances containing nitrogen, water vapor, carbon dioxide, among others. The reaction mechanism in the gasifier involves transforming biomass into coal, and it is transformed into CO and H₂ [37]. First, the outlet reactor stream is sent to the cyclone unit (CYC-1) to separate solids and fluids. The gas-phase flow is cooled down in HX-1 to 15 °C. As a result, a large amount of water is condensed. Next, the mainstream is sent to an injector (IY-1) to remove dissolved CO₂, in which water is used as the porous medium. Finally, the flow is compressed to 6 bar (CM-1) and sent to a separator (SP-1) to remove water along with the dissolved CO₂ [38].

The WGS (RX-2) increased biohydrogen production based on H₂ and CO₂ formation from CO and H₂O. The equilibrium is favorable to the products when the system performs at 205 °C and 32 atm. The reactor was simulated as a Rstoic model in ASPEN PLUS, considering reported thermodynamic parameters and performance of the equilibrium reactions under the described conditions [39]. Due to the formation of CO₂ in WGS, this substance is highly mixed in the mainstream with H₂ (stream 27). Thus, a filter/membrane (FT-1) was used, which according to Veenstra et al. [40], produces hydrogen with 99% purity operating at 5 bar and 430 °C. It is worth highlighting that this device is operative for up to one year, at which it needs a replacement. In this process, hydrogen is produced with a mass flow rate of 1666.8 kg/h; this traduced into global biomass to product yield of 3.20%. Besides, this process consumed energy with a rate of 4,096,267 MJ/h and a total freshwater supply of 410,360 kg/h.
2.2.2. Biomass Pyrolysis for Bio-Oil Production

Bio-oil is produced from BEFB and CS through the biomass pyrolysis pathway. The raw material is thermally converted through energy-intensive operations involving reactor section and downstream [41]. There is a mass flow of 2600 kg/h and 7800 t/h of CS and BEFB, for a total processing capacity of 10,400 kg/h. This topology produces 3900 kg/h of bio-oil, showing a total yield of 0.38 kg/kg of biomass. Figure 3 shows a flowsheet diagram of the biomass pyrolysis process. BEFB and CS are sent to an initial process handling and conditioning stage (MIX-1). Then, the mixture is heated up and dried to reduce water content below 10%. The steam leaves drying unit (DRY-1). This stage is developed at 110 °C. After this conditioning, biomass is ready to be sent to the pyrolysis reactor. This stage decomposes lignocellulosic biomass at 500 °C. Gases such as H₂, CO, CH₄ and char are generated in this system [42].

Figure 3. Process flowsheet diagram of the pyrolysis process.

The reaction followed the stoichiometric modeling described by Dussan et al. [43]. It contains the kinetic modeling of the pyrolysis process considering the described conditions. The product stream of the pyrolysis reactor is sent to a complete extraction process, composing a cyclone unit for solid separation (CYC-1). The gas stream contains bio-oil components and persisting impurities. Later, non-pure bio-oil follows additional purification units to reject undesirable components. A separator rejects these remaining impurities. The outlet stream is chilled to 60 °C and subsequently fed into a flash drum (FL-1). A portion of produced bio-oil is extracted at this point. The other portion is recovered by removing unwanted gases in a flash separator (FL-2) at 25 °C.

Graphite content extracted during the cyclone stage is combusted together with ashes and gases. This allows heat to be generated and reduces energy supply. This approach is strategic to improve energy performance and exergetic profile of the process [44]. Sand and compressed air (at 2 atm) are fed together into the combustion reactor. The output stream reaches 1380 °C. This steam is directed to the cyclone unit for an additional solid–gas extraction (SEP-2). Gases leave this unit while the solid stream is cooled to 600 °C. This setting lets the generated energy from this stream to be used in order to decrease energy needs. Finally, the solid stream leaves the system. Product streams of both flash separators are directed to a vessel and cooled at 28 °C, and finally, bio-oil is stored. Final bio-oil contains a significant portion of water (73%), hydrocarbons (26.5%), and gases (0.5%).

2.3. Formulation of Exergy Analysis

Thermodynamics and energy transference principles are fundamental in chemical process design, also applicable to bio-based thermochemical technologies. From an energetic viewpoint, exergy assessment means a methodology to surpass the limitations of the 1st law of thermodynamics to recognize critical energy outflow sources [45]. This feature defines its capacity to screen energy hotpots to improve overall process efficiency.
Exergy analysis quantifies chemical process system performance from a thermodynamic perspective. Exergy gives the maximum theoretical useful work (or energy) once a system reaches its thermodynamic equilibrium with the surroundings [46]. Some considerations are considered for performing exergy analysis, and these include the following aspects:

- Steady-state conditions;
- Kinetic and potential (energy) exergy flows as neglected;
- Reference temperature and pressure of 25 °C and 1 atm, respectively.

Table 2 shows governing equations of the exergetic analysis. The exergy balance does not follow the energy/material conservation principle. There is always a loss of exergy connected to unavoidable irreversibilities. These are an estimation of destroyed exergy flows within a chemical process [47].

| Equations       | Formula                                      | Description                                                                 |
|-----------------|----------------------------------------------|-----------------------------------------------------------------------------|
| Exergy balance  | \( \dot{E}_{\text{loss}} = \dot{E}_{\text{mass}} + \dot{E}_{\text{heat}} + \dot{E}_{\text{work}} \) | \( \dot{E}_{\text{loss}} \) is exergy loss, \( \dot{E}_{\text{mass}} \) mass exergy, \( \dot{E}_{\text{heat}} \) heat exergy, \( \dot{E}_{\text{work}} \) work exergy |
| Heat exergy     | \( \dot{E}_{\text{heat}} = (1 - T_0/T)Q \)  | \( T_0 \) is reference temperature, \( T \) stream temperature, \( Q \) heat flow |
| Exergy of work  | \( \dot{E}_{\text{work}} = W \)            | \( W \) system work                                                        |
| Mass exergy     | \( \dot{E}_{\text{mass}} = \dot{E}_{\text{phy}} + \dot{E}_{\text{che}} \) | \( \dot{E}_{\text{phy}} \) physical exergy, \( \dot{E}_{\text{che}} \) chemical exergy |
| Chemical exergy | \( \dot{E}_{\text{ch}} = \Delta G^0_{f - i} + \sum v_j \dot{E}_{\text{ch}}^{0 - j} \) | \( \Delta G^0_{f - i} \) Gibb's energy, \( \dot{E}_{\text{ch}}^{0 - j} \) estimated chemical exergy |
| Physical exergy | \( \dot{E}_{\text{phy}} = (H - H_0) - T_0(S - S_0) \) | \( \dot{E}_{\text{phy}} \) physical exergy \( H \) enthalpy, \( H_0 \) enthalpy at reference conditions, \( S \) entropy, \( S_0 \) entropy at reference conditions |

For ideal gases, the physical exergy flow is determined by (7). Here, heat capacity \( (C_p) \) is considered as a constant. For a solid–liquid mixture, physical exergy is calculated using (7).

\[ \dot{E}_{\text{phy}} = C_p(T - T_0) - T_0(C_p \ln T/T_0 - \ln P/P_0) \]  

The physical exergy is estimated using ASPEN PLUS. The exergy balance formulation contains all inlet exergy flows by material streams or utilities. The balance is formulated with the following:

\[ \dot{E}_{\text{in}} = \dot{E}_{\text{stream}} + \dot{E}_{\text{utilities}} \]  

\( \dot{E}_{\text{in}} \) gives the total inlet exergy, \( \dot{E}_{\text{stream}} \) is the exergy flow of process streams, and \( \dot{E}_{\text{utilities}} \) represents the exergy of utility. The total outlet exergy embraces products and waste streams produced throughout production. Equation (9) gives the mathematical formula of this variable.

\[ \dot{E}_{\text{out}} = \sum \dot{E}_{\text{product--out}} + \sum \dot{E}_{\text{residues--out}} \]  

\( \dot{E}_{\text{out}} \) is the total outlet exergy flow, \( \sum \dot{E}_{\text{product--out}} \) is the summation of product exergy, \( \sum \dot{E}_{\text{residues--out}} \) represents the exergy of waste flows. This formulation of the exergy...
analysis determines the thermodynamic inefficiencies or irreversibility of a system. It also includes the underuse work and energy efficiency [48].

\[
\dot{E}_{\text{loss}} = \sum \dot{E}_{\text{in}} - \sum \dot{E}_{\text{product-out}}
\] (10)

\(\dot{E}_{\text{loss}}\) represents process irreversibilities. The exergy efficiency \(\eta_{\text{exergy}}\) provides the thermodynamic yield of the process. This analysis also considers calculating the influence of each process on the irreversibilities of the process \(% \dot{E}_{\text{product-out}}\).

\[
\eta_{\text{exergy}} = 1 - \left( \frac{\dot{E}_{\text{loss}}}{\sum \dot{E}_{\text{in}}} \right)
\] (11)

\[
% \dot{E}_{\text{loss-k}} = \left( \frac{\dot{E}_{\text{loss-k}}}{\sum \dot{E}_{\text{in}}} \right) \times 100%
\] (12)

According to the described mathematical structure, the formulation is normalized in a functional unit (1 kg of product). This setting lets a direct comparison be made between different projects with different sizes and settings.

2.4. Sustainability Assessment

The sustainability evaluation is developed considering a multiple-indicator approach to cover more improvement areas towards a more sustainable design. Ruiz-Mercado et al. [49] described a straightforward way to evaluate sustainability by assessing technical indicators. These are defined in four different sustainability areas, including economics, efficiency, environment, and energy. An advantage of this approach is viewed through the evaluation of technical parameters between best and worst targets. The percent score provides a dimensionless scale to evaluate each indicator based on benchmarks and stakeholder’s expectations (see Equation (13)).

\[
\text{Percent score} = P\% = \frac{I_C - I_W}{I_B - I_W} \times 100%
\] (13)

\(I_C\) is the current indicator, \(I_W\) is the worst target, and \(I_B\) is the best target. \(P\%\) represents the percent score of the indicator. Another feature of this method is its capacity to compare dissimilar systems under the same limits. The practitioner has the freedom to select indicators based on different criteria, such as decision-maker expectations, process nature, or convenience. This study did not consider economic indicators since calculating these parameters involves performing a techno-economic analysis and is beyond this study’s scope. The sustainability evaluation was focused on environmental, efficiency, energy, and exergy indicators. Table 3 shows selected indicators for performing sustainability assessment and their corresponding best and worst targets.

| Area          | Indicator                   | Formula                              | Worst | Best |
|---------------|-----------------------------|--------------------------------------|-------|------|
| Environment   | Renewability index          | \(RI = \frac{\text{Renewable inputs}}{\text{Total inputs}}\) | 0     | 1    |
|               | Global warming potential    | \(\text{GWP} = \frac{\text{Total CO}_2 \text{ eq.}}{\text{Mass of product}}\) | All waste | 0    |
| Efficiency    | Production yield            | \(y = \frac{\text{Mass of product}}{\text{Feedstock input}}\) | 0     | 1    |
| Energy        | Energy efficiency           | \(\eta_E = \frac{\text{Energy content of product}}{\text{Energy content of input}}\) | 0     | 1    |
| Exergy        | Exergy efficiency           | \(\eta_{\text{energy}} = \frac{\text{Exergy of product}}{\text{Total input energy}}\) | 0     | 1    |

3. Results

Exergy analysis was performed based on the proposed method. Gasification and pyrolysis processes were assessed under this framework. Chemical and physical exergies were estimated, to obtain the mass exergy of flow streams. Table 4 reports specific chemical
exergies for components involved in the simulation of both processes. The total power for gasification was 18 kW/kg of product, with the corresponding exergy of work of 64.79 MJ/kg. The total heat flow for this process was 3696.22 MJ/kg of product (exergy of heat flow: 3538.62 MJ/kg of product). The corresponding exergy of utilities count both work and heat streams, which resulted in a total flow of 3603.42 MJ/h.

Table 4. Chemical exergy of active components.

| Components       | Chemical Exergy (kJ/kg) |
|------------------|-------------------------|
| Acetaldehyde     | 51,402.00               |
| Acetate          | 15,120.00               |
| Acetic Acid      | 15,120.00               |
| Acetone          | 46,229.00               |
| Acrylic acid     | 39,382.00               |
| Ash              | 1965.00                 |
| Carbon           | 34.16                   |
| Carbon dioxide   | 433.87                  |
| Carbon monoxide  | 9807.40                 |
| Ethylene         | 79,735.00               |
| Formaldehyde     | 40,195.00               |
| Furfural         | 24,341.00               |
| Glucan           | 20,996.00               |
| Hydrogen         | 118,095.00              |
| Lignin           | 28,123.00               |
| Methane          | 106,199.00              |
| Nitrogen         | 25.71                   |
| Nitrogen         | 25.71                   |
| Oxygen           | 124.06                  |
| Silicon Dioxide  | 2.20                    |
| Water            | 50.00                   |
| Xylan            | 21,395.00               |

Otherwise, the results for the pyrolysis process evidence a better energetic profile, with a total power of 0.77 kW/kg of product and a heat flow of 10.64 MJ/kg of product (exergy of heat flow: 8.87 MJ/kg of product). In summary, the exergy of utilities for this process corresponded to 11.64 MJ/kg of product. This outcome indicates that the heat recovery setting included in the pyrolysis reaction improves its energy efficiency. Table 5 summarizes the exergy results for the gasification and pyrolysis processes.

Table 5. Exergy analysis results for gasification and pyrolysis processes.

| Process  | EXmass | EXin | EXout | EXloss | EXwaste |
|----------|--------|------|-------|--------|---------|
| Gasification | 604.23 | 4207.65 | 127.45 | 4080.20  | 639.76  |
| Pyrolysis  | 43.21  | 54.85 | 6.09  | 48.75  | 18.14  |

The results of Table 5 show the better exergetic numbers for the pyrolysis process, compared to gasification. A critical aspect of gasification processes is the amount of exergy wasted, due to the high utility requirements. In the case of pyrolysis, this effect is much less, by a long margin. In numbers, this means that gasification consumes 85% of the total inlet exergy. Meanwhile, pyrolysis only uses 21.22% of the total exergy for heat supply requirements. Figure 4 depicts a result comparison between the simulated gasification and pyrolysis processes, based on the proposed exergy analysis.

The sustainability assessment complements the exergy analysis. Process data were used to estimate the performance indicators and their corresponding targets. Air and process water flows were supplied in both processes. These are renewable inputs, the same as biomass feedstock. The total energy consumption for the pyrolysis process was 12.93 MJ/kg of product, and for gasification, this value was 3695.78 MJ/kg of product.
The energy usage is much higher in gasification than in pyrolysis. This result somewhat explains the outcomes of the exergy analysis. Another important parameter for evaluating sustainability was the CO$_2$ emissions of each process. The gasification process generates 220.41 kg of CO$_2$/kg of product. In the case of pyrolysis, this quantity corresponds to 2.09 CO$_2$/kg. This outcome is also associated with emissions coming from energy generation, which is more significant for the gasification process. This relation might indicate a better environmental profile of the pyrolysis process. Another evaluated parameter is the energy efficiency (or net energy). This parameter measures energy balance, considering the energy consumed in the system and the energy content in the product. Ideally, it is expected that this value would be at least equal to the unity, reflecting an energy neutral design. High energy-efficient processes would show an energy efficiency $>$1, while a poor-efficient system would show otherwise [50]. In this sense, the best target (equals to unity) was set to reflect an energy-neutral system, but values higher than this (or 100%) can be expected. Tables 6 and 7 summarize the targets and current values for the evaluated sustainability indicators.

Figure 4. Exergy results of pyrolysis and gasification processes.

Table 6. Summary of targets, current value, and percent score of sustainability indicators.

| Indicator (Gasification) | Best | Worst | Current | Percent Score |
|-------------------------|------|-------|---------|---------------|
| Renewability index      | 1    | 0     | 0.984   | 98.4%         |
| Global warming potential| 0    | 3,120,980 kg CO$_2$ | 367,380 kg CO$_2$ | 88.2%         |
| Production yield        | 1    | 0     | 0.032   | 3.2%          |
| Energy efficiency       | 1    | 0     | 0.003   | 0.3%          |
| Exergy efficiency       | 1    | 0     | 3%      | 3.0%          |

Table 7. Summary of targets, current value, and percent score of sustainability indicators.

| Indicator (Gasification) | Best | Worst | Current | Percent Score |
|-------------------------|------|-------|---------|---------------|
| Renewability index      | 1    | 0     | 1       | 100.0%        |
| Global warming potential| 0    | 46,479.2 kg CO$_2$ | 8138 kg CO$_2$  | 82.5%         |
| Production yield        | 1    | 0     | 0.077   | 7.7%          |
| Energy efficiency       | 1    | 0     | 1.106   | 110.6%        |
| Exergy efficiency       | 1    | 0     | 11%     | 11.1%         |
4. Discussion

The irreversibility flow of the gasification process (4080.21 MJ/kg of product) is much higher than the corresponding value for pyrolysis (48.75 MJ/kg of product). This finding means that the exergy consumption in gasification is almost 84 times higher than pyrolysis. This is a considerable difference; therefore, one can establish that the modeled pyrolysis process is more refined than gasification, from an energy distribution viewpoint. This fact is supported by the obtained exergy efficiency of both processes. However, it is worth mentioning that both processes probably need more refinement, since the obtained exergy efficiencies are rather low (11% vs. 3%).

Another exergetic performance parameter that was evaluated in this study was the resource exergy intensity, which indicates the current flow of exergy needed to complete 1 kg of product production. Gasification obtains an intensity of 4080 MJ/kg of product and pyrolysis obtains 18.64 MJ/kg of product. The results that are consistent with previous exergy outcomes confirm the better energetic profile of the pyrolysis process. Globally, the evaluated thermochemical technologies are expending too much energy to produce biofuel. The ways forward, to improve the current designs, involve including optimization strategies such as heat integration [51], mass integration [52], or combined approaches (e.g., heat-integrated water recycling networks) [53].

The sustainability evaluation delivered interesting results, in terms of a broader perspective (beyond exergy assessment). The results described in Tables 6 and 7 indicate an overall better performance of the pyrolysis process than gasification. This difference is more significant in the energy and exergy areas than the other ones, with higher performances from the pyrolysis process. Figure 5 displays a radial chart with percent score results for each indicator, to better illustrate these results.

![Radial chart of percent score for sustainability indicators.](image)

Globally, there is a parity in terms of renewability and global warming potential quantitative values. This is an expected result, since the nature of these processes is similar, and they use bio-based feedstock (second-generation). Consequently, very high percent scores for the renewability material index were obtained in both cases. Conversely, this is not the case for the energy and exergy efficiency indexes. The results reflected that the gasification process requires significant improvements to reach higher efficiencies that make this process more sustainable. An important fact is that more energy is consumed in the process than is obtained in the product. This is a clear sign that the process is not efficient enough to generate cleaner energy. From these outcomes, the need to include optimization strategies that might lead to a better performance of these technologies is evident. The addition of a water regeneration system and using internal heat streams to meet energy requirements are suitable alternatives to accomplish that goal.
5. Conclusions

This study presents a comprehensive process simulation, exergy analysis, and indicator-based sustainability evaluation to compare pyrolysis and gasification processes, to produce second-generation biofuels. This approach lets energetic and efficient-based hotspots and improvement breaks, from a thermodynamic and sustainability perspective, to be identified. The framework combined feedstock selection, process simulation, exergy analysis, and sustainability assessment to support decision making, research, and development progress, to advance the TRLs of these technologies. This approach was proposed as a straightforward tool for researchers to first screen technologies at early design stages, allowing optimization at low maturity phases. The results revealed that the gasification process is thermodynamically more inefficient than pyrolysis, with a resource exergy efficiency of 3%. Energy consumption and utility requirements seem to be significant drawbacks of the gasification process to reach high exergetic efficiencies. The pyrolysis process delivers a product with a higher energy content than is consumed during its processing, with an efficiency of 110.6%. The sustainability evaluation confirms the results given by the exergy assessment, indicating pyrolysis as a more attractive alternative. However, there is still potential in the gasification process, which can reach higher efficiency levels with some improvements. The ways forward to improve this process might involve using process optimization strategies or developing technological improvements. Regarding the pyrolysis process, even though the simulated setting is more refined than gasification, some improvements are still needed to make this process energy friendly. Future works might include intensification strategies and integration methods, such as heat, mass, or property integration, to achieve the most suitable topologies, in terms of energy and global sustainability.

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