



Turning wine waste into value: A techno-economic and environmental study of phenolics, syngas and biochar production

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ABSTRACT

Grapes are one of the most important crops globally, but 30 % of their weight becomes waste in the wine industry. This work aims to valorise two of the most important wastes in this industry, grape marc and grape stalks, by extracting the total phenolic compounds (TPC) as well as biochar and syngas, through a pyrolysis process of the remaining organic biomass. From grape marc, 5.99 tonnes of phenolic compounds and 46.91 kg of biochar were obtained per batch, whereas for grape stalks, the TPC yield increased to 8.06 tonnes, while biochar production decreased to 27.89 tonnes per batch. To assess the environmental impacts of this biorefinery, the Life Cycle Assessment methodology was applied, revealing global warming impacts of 80.30 kg CO₂ eq and 102.07 kg CO₂ eq per kilogram of TPC for grape stalk (GS) and grape marc (GM), respectively, with steam production identified as the system's main hotspot. The initial design results are not profitable, primarily due to high equipment costs, which significantly exceed the revenues from product sales and also lead to elevated annual manufacturing costs. However, the sensitivity analysis shows that adjusting the plant's construction and operating costs to values more in line with the literature leads to a significant increase in the internal rate of return, reaching up to 36.16 % in certain scenarios. Potential improvements to the plant should focus on changing the source of heat generation to cleaner energy sources, aiming for a transition towards more sustainable production.

1. Introduction

Agriculture is a major driver of water consumption, accounting for approximately 70 % of global freshwater use and significantly contributing to biodiversity loss and land use for cultivation activities, which account for nearly 90 % of global deforestation (FAO, 2021; UNESCO, 2024). Within this sector, grapes play a relevant role with a global production of about 28.4 million metric tons in 2023, covering approximately 7.2 million hectares (International Organisation of Vine and Wine, 2024; Statista, 2024). The cultivation of grapes is responsible of around 2 % of annual agricultural greenhouse gas (GHG) emissions and around 0.3 % of global carbon emissions (Trioli et al., 2015). In 2023, about 70 % of the total production was destined for the wine industry, producing 237 mHl of this beverage worldwide (Genisheva et al., 2023; International Organisation of Vine and Wine, 2024).

The environmental impacts of this crop are not only related to the agricultural stage, as a large amount of waste is also generated in the subsequent wine production stage (Abbate et al., 2024). This directly contradicts Sustainable Development Goal 12 (SDG12), which advocates

for ensuring responsible production and consumption systems, aiming to reduce food waste and promote proper management of resources (United Nations, 2015). In this context, the adoption of circular economy principles becomes essential to minimise environmental impacts and maximise waste valorisation. Following the circular economy concept, it is a priority to reduce the depletion of natural and scarce resources (European Parliament, 2023) by fostering the recovery of materials in production process to extend the end-of-life of products (Kirchherr et al., 2017).

In the agricultural stage, the most significant grape waste is pruning residues (estimated at 5 t/ha) (Genisheva et al., 2023). In the wine industry, various types of waste such as grape stems, lees and marc are generated, representing about 30 % of the crop's total weight (Genisheva et al., 2023). During the processing stage, grape marc, the residue from crushing and juice extraction process, and grapevine stems, which result from the grape destemming process, account for 25–45 % and 2.5–7.5 % of the grape's weight, respectively (Genisheva et al., 2023). On the other hand, lees, the residual mass that settles at the bottom of fermentation tanks, represents around 3.5–8.5 % of the total

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wine residues and is composed of exhausted or dead yeasts, skins, pips and stems (Ioannidou et al., 2022).

Grape marc is mainly composed of skins, stalks, seeds and moisture, and are rich in polyphenols or certain organic acids (Muhlack et al., 2018). There are three main routes for the valorisation of this by-product: i) by chemical treatment to extract the phenolic compounds or antioxidants of interest it contains (Rivera et al., 2007); ii) by thermal treatment to obtain bioenergy or biochar (Demiral and Ayan, 2011); or iii) by biological treatment to produce biofuels and compost (Corbin et al., 2015). Additionally, grape stalk is the skeleton of the grape bunch, which is a rich source of lignocellulose compounds (i.e., cellulose, hemicellulose and lignin) and contains a significant amount of polyphenols. Several viable technologies have been proposed for the extraction of these lignocellulosic materials, such as steam explosion, ammonia fibre explosion microwave digestion (Ping et al., 2011). If the goal is to obtain phenolic compounds, the most developed method is extraction, with the success of the process depending on the type of solvent, temperature and duration of the process selected (Sette et al., 2020). In recent years, numerous studies have been published focusing on the valorisation of these by-products for the production of value-added products: kombucha from grape marc (Balmaseda et al., 2024); titania nanoparticles from grape marc (Abduraman et al., 2024); phenolics (de Freitas et al., 2024; Zemni et al., 2024); vermicompost (Cortés et al., 2020; Gómez-Brandón et al., 2023; Nascimento-Gonçalves et al., 2024) or biochar (di Bitonto et al., 2024; Frikha et al., 2021) from marc and stalks; lignocellulosic compounds or fermentable sugars from stalks (Atatoprak et al., 2022; Salgado-Ramos et al., 2022), among other valuable compounds (Baldán et al., 2023; Da Porto and Natolino, 2024; D'ambrosio et al., 2023; Filippi et al., 2023).

Using grape waste as feedstock is motivated to develop new circular business models under the biorefinery concept, which aims to convert renewable biomass into value-added products or bioenergy; however, this may not always provide environmental benefits. To determine the potential environmental advantages or drawbacks of biorefinery designs, Life Cycle Assessment (LCA) is a well-known and helpful methodology (Lago-Oliveira et al., 2023; Rebolledo-Leiva et al., 2024b), as it allows identifying the critical points that may limit new biorefinery developments. Although the valorisation of these compounds has been explored, most studies primarily focus on laboratory development, with few incorporating a techno-economic (TEA) or environmental assessment. For instance, Cortés et al. (2020) investigated the extraction of oil, polyphenols and vermicompost from grape marc, while Ioannidou et al. (2022) examined the production of succinic acid and grape seed oil from these by-products. Broadening the scope to include the valorisation of grape pomace, some additional studies incorporate environmental and techno-economic analysis (Ahmad et al., 2020; Jin et al., 2021; Zalazar-García et al., 2020).

Therefore, although both resources have been studied for the production of a wide range of value-added products, the majority of these studies remain at the experimental scale, and very few incorporate LCA and TEA approaches in the context of biorefinery designs. This represents a clear gap in literature where further research is needed. Accordingly, this manuscript presents a process modelling at industrial scale with the first comprehensive assessment of the environmental and economic dimensions of grape stalk and grape marc valorisation, focusing on the recovery of phenolic compounds, and the co-production of biochar and syngas, following a multiproduct system for the complete valorisation of the biomass. This valorisation route was selected due to the high industrial interest and market value of phenolic compounds, compared to other products such as oil or tannins (Taifouris et al., 2023). The proposed biorefinery consists of two main sections: (i) the extraction of phenolic compounds, and (ii) the production of biochar and syngas from the remaining biomass fraction. In addition, a sensitivity analysis has been conducted to identify the key factors that may drive or limit the economic viability of the proposed process.

2. Materials and methods

2.1. Biorefinery modelling

The plant model was designed to treat 500 tonnes per batch of each by-product, resulting in a total of 125 batches per year. In other words, the biorefinery would be capable of valorising 62.5 thousand tonnes of raw material annually. The platform consists of two main subsystems: one where the phenolic compounds are extracted (SS1), and another where the remaining biomass undergoes thermal treatment to produce biochar (SS2) (see Fig. 1).

2.1.1. SS1: Total phenolic compound extraction

The composition of grape marc and grape stalks differs, with the former having a moisture content of 61.6 %, while the latter has a slightly lower moisture content of 59.2 %. Additionally, the amount of TPC in grape marc is lower than in grape stalks, with values (on a dry basis) of 1.14 g/100 kg and 1.54 g/100 kg, respectively (Sette et al., 2020). The process starts with a size reduction by grinding the raw materials, which facilitates the extraction process. Then, the extraction is carried out with a solvent-to-raw material ratio of 2:1 (w/w) at a temperature of 348 K for 1.25 hours, using distilled water as the solvent (Garrido Makinistian et al., 2019). Once this operation has finished, centrifugation and filtration are performed, resulting in two very different products: i) a liquid stream rich in TPCs and ii) a solid fraction rich in lignocellulosic compounds, which is the starting point of SS2 (Sette et al., 2020). The TPC rich stream is purified by air drying to remove excess water at a temperature of 130 °C, obtaining a final stream with a purity of 95.1 % in both cases (i.e., marc and stalks) (Garrido Makinistian et al., 2019).

2.1.2. Subsystem 2: Biochar production

The remaining solid fraction, obtained after the filtration step in SS1, has a moisture content of 3.35 % and 4.93 % for the grape marc and grape stalks, respectively. Once these moisture contents are reached, the fraction is ground to reduce its particle size, and slow pyrolysis is carried out. Slow pyrolysis is considered the most suitable process for producing high-quality biochar, as it operates under inert or limited-oxygen atmospheres with slow heating rates, typically ranging from 1 to 30 K/min (Ronse et al., 2013). The selected heating rate in the pyrolysis was 20 K/min, as this resulted in the best yields (Sette et al., 2020), and the process occurs in three stages depending on the temperature, using natural gas as heating agent in this process: i) water evaporation and sugar volatilisation, which takes place between 300–520 K for GM and up to 540 K for GS, ii) degradation of low molecular weight components such as hemicellulose and cellulose, where the highest weight loss is observed (up to 750 K for GM and 830 K for GS), and iii) decomposition of substances with complex structures, reaching temperatures of 1173 K (Sette et al., 2020). Finally, the solid product (biochar) is separated from the gas stream (syngas) by a cyclone (Zhao et al., 2017).

2.2. Life Cycle Assessment Methodology

To determine the potential environmental impacts of the biorefinery design analysed, the four phases defined in the LCA methodology by ISO 14040–14044 were followed (ISO, 2006a, 2006b): i) goal and scope definition, ii) life cycle inventory, iii) life cycle impact assessment and iv) interpretation.

2.2.1. Definition of goal and scope

This manuscript explores the potential environmental impacts of the valorisation of two major by-products of the winery industry: marc and stalks. The research focuses on extracting valuable phenolic compounds from these by-products and utilising the remaining solid fraction to produce biochar and syngas, through a slow pyrolysis process.

In a multiproduct biorefinery, selecting an appropriate functional

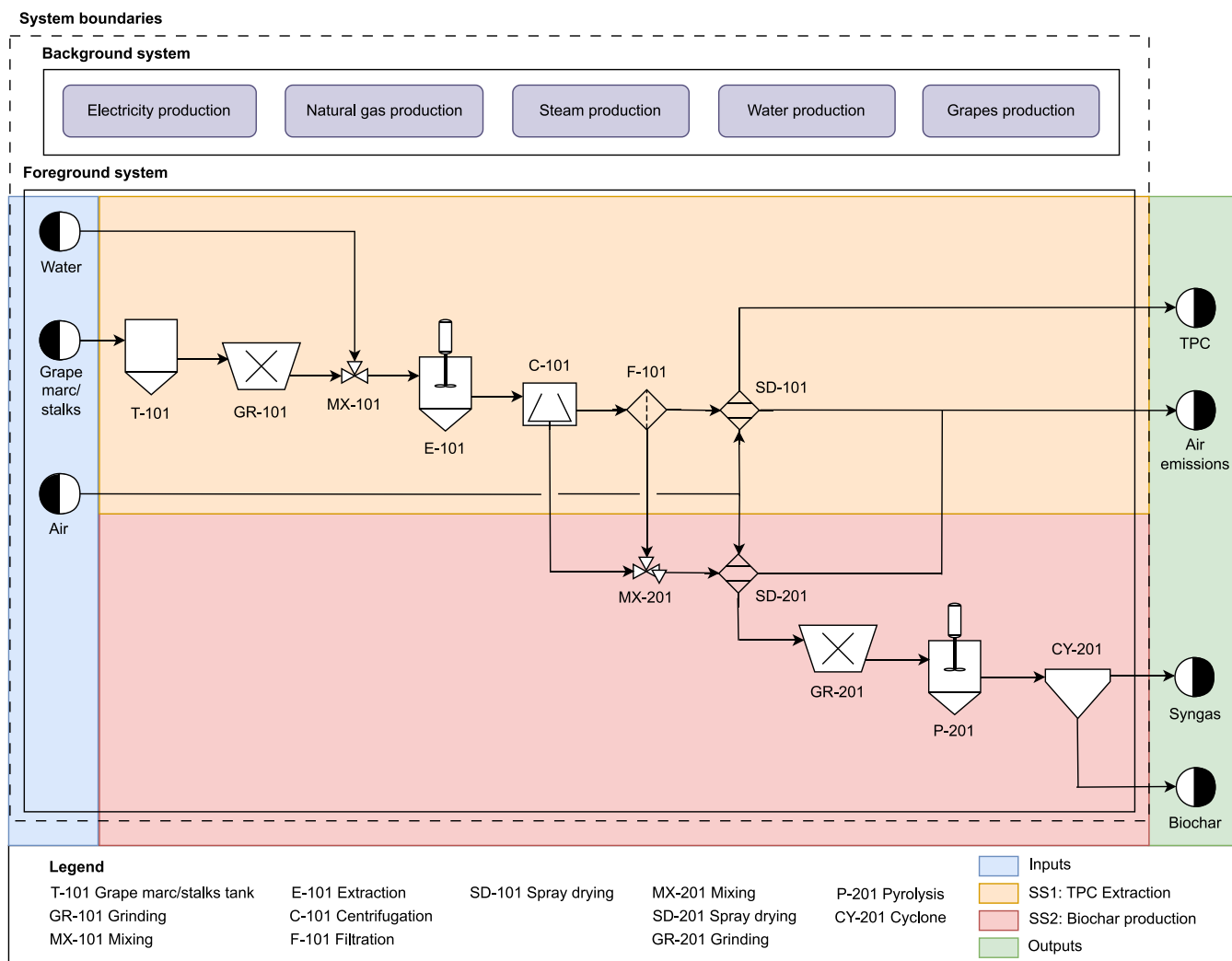


Fig. 1. Flowchart of the biorefinery with system boundaries (background and foreground system). TPC: Total Phenolic Compounds.

unit is a complex task that demands careful consideration to accurately reflect the study's objectives (Gaffey et al., 2024). Considering that the function of the platform is to obtain high value-added products, a mass-based functional unit (FU) was selected, specifically 1 kg of each product (TPC, biochar and syngas). Although the selection of a feedstock-based functional unit could also offer an interesting perspective, the aim of this study is not to compare different valorisation routes to determine which is the most feasible for processing the feedstock. Rather, it is to assess the environmental impacts of a multi-product system and compare the bioproducts obtained with those in the literature, even if they use different feedstocks. Additionally, the attributional LCA was carried out by following a 'cradle-to-gate' approach, which is commonly used in biorefinery designs and consider all environmental impacts associated with a product's life cycle, from the extraction of raw materials ("cradle") to the point where the product leaves the manufacturing facility ("gate") (see Fig. 1).

Economic allocation was performed also to distribute the loads between the three products of the biorefinery: phenolic compounds, biochar and syngas. A market price of 50 USD/kg for phenolic compounds was assumed according to Viganó et al. (2022), which established a price range between 25 and 230 USD/kg for extracts with different gallic acid contents. Selling prices for biochar and syngas were set at 2.47 USD/kg and 0.52 USD/kg, respectively (Jin et al., 2021; Sharma and Nath, 2023). Thus, TPC was assigned an allocation of 74.79 % and 66.50 % for GS and GM, respectively. Allocation factors for biochar and

syngas, when using GS, were 7.96 % and 17.25 %, and 16.66 % and 16.84 % when using GM, respectively.

2.2.2. Life cycle inventory

The life cycle inventory collects all input and output data of the proposed biorefinery. Energy requirements for equipment, as well as chemical and process water consumption, were simulated using SuperPro designer® software version 13.0 (Intelligen Inc., 2021), based on published experimental data (Garrido Makinistian et al., 2019; Sette et al., 2020). These simulation results are part of the life cycle inventory presented in Table 1. The two feedstocks are subjected to the same equipment and operational conditions. In addition, the transport of feedstock to the biorefinery was omitted, assuming that the facility is located adjacent to the processing factory (Rebolledo-Leiva et al., 2024a).

In the environmental analysis, background processes for chemicals, process water and heating agents were taken from the Ecoinvent® database version 3.9.1 (Ecoinvent, 2024), while the inventory process of the electricity generation was taken from the Ecoinvent® database, but updated considering the Spanish electricity mix during 2023 (Electricity Network, 2024). The computational implementation of the life cycle inventory data was carried out using the SimaPro v9.6.0.1 software (PRÉ Sustainability, 2024). Environmental loads of the feedstocks (i.e., marc and stalks) were taken from the research conducted by Vázquez-Rowe et al. (2012), where both are generated during Ribeiro's wine

Table 1

Inventory data of each subsystem considering both feedstocks per batch (500 t GM/GS).

| Grape marc (GM) | | | Grape stalks (GS) | | |
|-----------------|--------|------|-------------------|--------|------|
| Inputs | | | | | |
| | Value | Unit | | Value | Unit |
| GM | 500 | t | GS | 500 | t |
| Water | 1000 | t | Water | 1000 | t |
| Natural Gas | 86.46 | t | Natural Gas | 19.92 | t |
| Chilled water | 17.38 | kt | Chilled water | 17.39 | kt |
| Steam | 2.74 | kt | Steam | 2.71 | kt |
| Energy | 87,097 | kWh | Energy | 86,256 | kWh |
| Outputs | | | | | |
| TPC | 5.99 | t | TPC | 8.06 | t |
| Biochar | 46.91 | t | Biochar | 27.80 | t |
| Syngas | 145.9 | t | Syngas | 178.7 | t |
| Air emissions | | | | | |
| Water | 1301 | t | Water | 1285 | t |

Acronyms: Total Phenolic Compounds (TPC).

production, using the grape cultivation inventory from the Ecoinvent® database. To this end, the selling price for grape marc/stalk were assimilated to grape pomace and set to 32 USD/t (Jin et al., 2021), while for this wine was set in 8.50 €/0.75 L according to market prices (Viña Costeira Winery, 2024). Moreover, as the scope of the environmental assessment is cradle-to-biorefinery-gate, carbon credits related to the application of biochar are considered.

2.2.3. Life cycle impact assessment

To estimate the environmental profile of the products obtained by the integrated biorefinery design, the ReCiPe 2016 (H) V1.07/World (2010) (H) method (Huijbregts et al., 2017) was applied. This method was selected due to increased transparency, less uncertainty and increased comparability (Huijbregts et al., 2020). The characterisation factors provided were utilised to assess environmental impacts across the five categories namely: Global Warming (GW), Ionizing Radiation (IR), Terrestrial Ecotoxicity (TE), Fossil Resource Scarcity (FRS) and Human Non-Carcinogenic Toxicity (HNCT). GW was selected due to its relevance in environmental analysis of systems and products, as well as its significance in sustainability assessments of biorefineries (Murphy et al., 2013). Nuclear energy-based systems have been associated with radiation emissions, contributing to impacts related to IR and TE (Pucciarelli et al., 2023). Given that nuclear energy constitutes 20 % of the Spanish electricity mix (IEA, 2023), evaluating these impact categories is essential. FRS was included as decarbonization efforts necessitate reducing fossil fuel consumption (Ling et al., 2023), and this impact category quantifies fossil fuel usage, making it relevant to this study. Furthermore, Accardi et al. (2013) reported adverse health effects linked to biorefineries, justifying the inclusion of HNCT impacts in this analysis.

2.3. Techno-economic analysis

2.3.1. Total capital investment

Mass and energy balances were obtained considering all the necessary process units and operational conditions (i.e., mass flow rates, composition, pressure, temperature and operating time). Subsequently, the Fixed Capital Investment (FCI) requirements have been determined by multiplied the sum of purchased equipment costs (Ceq) with a Lang factor of 5 (Dheskali et al., 2020), as the biorefinery needs to be constructed with new, high-risk technology and costly construction materials for the process. Working Capital (WC) has been estimated as 5 % of FCI (Ladakis et al., 2022) and Total Capital Investment (TCI) is the sum of FCI and WC values.

All financial estimates have been denominated in US dollars, with cost indices of the purchased equipments updated to the fiscal year 2024, based on the software's internal economic database. This ensures

that the economic evaluation reflects current market conditions, enhancing the reliability and applicability of the investment analysis.

2.3.2. Manufacturing costs

The manufacturing costs (COM) were estimated following the Eq. (1) proposed by Turton et al. (2018):

$$COM = 0.18 \times FCI + 2.73 \times C_{OL} + 1.23 \times (C_{UT} + C_{RM} + C_{WT}) \quad (1)$$

where C_{OL} means the operating labour costs, C_{UT} correspond to utility expenses, C_{RM} is the raw material expenses and C_{WT} represents the waste treatment costs. C_{OL} was determined applying the Eq. (2) (Alkayat and Gerrard, 1984), which estimates the number of operators per shift (N_{OL}). This value was rounded up to the nearest integer and then multiplied by the annual salary per operator to obtain the total labour cost.

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad (2)$$

where P is the number of process steps involving handling solids and N_{np} is the number of process steps not involving handling solids. The salary per employee has been assumed to be 50,000 USD/year for a working time of 49 weeks per year, 5 days per week and 8 hours per day (Huang et al., 2016). Additionally, the C_{RM} and C_{UT} were estimated by multiplying the unit cost by the amount of each one needed. Finally, the C_{WT} was assumed to be 0, as there are no streams requiring treatment, since the remaining waste is subjected to pyrolysis.

2.3.3. Revenues and profitability analysis

Revenues from the sale of products are estimated based on the plant's material balances and selling price of each one. For the calculation of the depreciation, seven years were assumed on the Modified Accelerated Cost Recovery System (MACRS). The most important working parameters and assumptions done in the biorefinery are included in Table 2, mostly reported by (Davis et al., 2013). The Consumer Price Index (CPI) was calculated as a mean value in Europe from 1997 to 2024 (CPI Inflation Calculator, 2024) to account for annual variations in revenues and expenses due to inflation.

The economic performance of the process is assessed using three standard indicators: net present value (NPV), internal rate of return (IRR) and minimum selling price (MSP). NPV is defined as the sum of the present values of future cash flows over a specified period (Towler and Sinnott, 2021), IRR represents the discount rate at which the NPV equals zero after taxes (Humbird et al., 2011) and MSP is the price per kg of product at which the NPV reach 0 at the end of the plant lifetime (Rebolledo-Leiva et al., 2024a).

2.4. Sensitivity and uncertainty analysis

Potential variations were considered in both the environmental and techno-economic analysis based on the critical points identified. For this, the focus was on changes related to the steam production source and equipment purchase costs. These aspects are further discussed in the results section.

Table 2

Main parameters of the techno-economic analysis.

| Parameters | Value |
|---|-----------------|
| Discount rate | 10 % |
| Plant lifetime | 30 years |
| Equity financing | 100 % |
| Plant construction duration | 3 years |
| % of project cost (1st, 2nd and 3rd year) | 8 %, 60 %, 32 % |
| CPI incomes/costs | 2.12 % |
| Land costs | 0 |
| Phenolic compounds price | 50 USD/kg |
| Biochar price | 2.47 USD/kg |
| Syngas price | 0.52 USD/kg |

The uncertainty analysis was conducted by applying the Monte Carlo method (Rubinstein and Kroese, 2016) to the secondary inventory data sourced from the Ecoinvent® database to assess how input data uncertainty affects the final results and to determine whether statistically significant differences occur (Krotov et al., 2024). This analysis was performed for both raw materials using 2000 iterations and a 95 % confidence interval, following a lognormal distribution. The results are presented in Table S1 of the Supplementary Material (SM).

3. Results and discussion

3.1. Environmental impact analysis

The environmental impact assessment results of the biorefinery, presented in Table 3, indicate that the GM process exhibits greater environmental burdens across all evaluated impact categories compared to GS. Steam generation is identified as the primary environmental hotspot, contributing significantly to the overall impact. In the IR category, electricity production is recognized as an additional critical contributor alongside GM and GS processes. Furthermore, in FRS, the consumption of natural gas demonstrates a substantial environmental footprint due to the reliance on fossil fuel resources in biorefinery operations. Steam production and GS/GM processing are observed to be the main hotspots in HNCT. The hotspots share in three products is observed to be similar as depicted in Fig. 2.

3.1.1. Global warming (GW)

Using GM for TPC extraction exhibits a 27 % higher GW impact than GS, with respective values of 102.07 and 80.30 kg CO₂ eq per kg of TPC. For biochar and syngas from GM, similar trend has been observed with an increased impact of 31.85 % and 26.95 % in comparison to GS. For biochar the GW is observed to be 2.48 and 3.27 kg CO₂ eq/FU for GS and GM respectively, while for syngas the values are observed to be 0.83 and 1.06 kg CO₂ eq/FU. Zalazar-García et al. (2020) reported emissions ranging from 45 to 420 kg CO₂ eq for total phenolic compound (TPC) extraction, depending on the extraction method used, which aligns well with the findings of our study. In contrast, while Jin et al. (2021) included biochar production as part of the valorisation process, they did not allocate specific environmental impacts to the biochar. In our analysis, however, biochar is treated as a byproduct, and its associated impacts are accordingly allocated. Steam production is identified as the predominant environmental hotspot in both processes, contributing approximately 90 % of the total impact. The processing of GM and GS is highly energy-intensive due to the requirement of substantial energy input to break their complex chemical bonds (Cancelli et al., 2020). This inherent energy demand results in higher environmental impacts, primarily driven by increased electricity and steam consumption, as outlined in Table 1. Steam production impacts are majorly derived from fossil fuel consumption which is the main cause of GHG emissions in this process followed by the fossil fuel supply chain also contributing to GW

Table 3

Environmental impacts of grape stalk and grape marc to produce 1 kg of Total Phenolic Compounds.

| Impact category | Units | TPC | | BC | | SG | |
|-----------------|-----------------------|--------|--------|------|------|------|------|
| | | GS | GM | GS | GM | GS | GM |
| GW | kg CO ₂ eq | 80.30 | 102.07 | 2.48 | 3.27 | 0.84 | 1.06 |
| IR | kBq Co-60 eq | 4.21 | 5.15 | 0.13 | 0.17 | 0.04 | 0.05 |
| TE | kg 1,4-DCB | 128.09 | 156.43 | 3.95 | 5.00 | 1.33 | 1.63 |
| HNCT | kg 1,4-DCB | 20.50 | 25.21 | 0.63 | 0.81 | 0.21 | 0.26 |
| FRS | kg oil-eq | 29.63 | 49.69 | 0.91 | 1.49 | 0.31 | 0.49 |

Acronyms: Grape Stalk (GS), Grape Marc (GM), Total phenolic contents (TPC), Biochar (BC), Syngas (SG), Global warming (GW), Ionizing radiation (IR), Terrestrial eco-toxicity (TE), Fossil resource scarcity (FRS), Human non-carcinogenic toxicity (HNCT).

(Ecoinvent, 2024). The elevated GW profile of GM, compared to GS, can be attributed to its distinct composition. While GS is composed of three main biopolymers, namely cellulose, hemicellulose and lignin (Cancelli et al., 2020), GM comprises approximately 19 % protein by weight, along with fructose and glucose (Muhlack et al., 2018). The higher energy requirement for GM processing is due to the greater difficulty in breaking protein bonds compared to biopolymers, making its conversion more energy-intensive than that of GS (Mattaini, 2020). Environmental impacts and hotspots of the process has been depicted in Fig. 2.

3.1.2. Ionizing radiation

IR impacts are often omitted in LCA studies due to the absence of standardized methodologies for their integration with other impact categories (Paulillo et al., 2019). However, when nuclear energy is included in the energy mix, evaluating IR impacts becomes essential (Le-Boulch et al., 2024). Since the Spanish electricity mix consists of 20 % nuclear energy and the biorefinery exhibits a high electricity consumption per FU (refer to Table 1), IR impacts are considered in this assessment. In the case of TPC, IR impact for GM is 5.15 kBq Co-60 eq, which is 23 % higher than GS, valued at 4.21 kBq Co-60 eq per FU. For biochar, GM and GS impacts are observed to be 0.17 and 0.13 kBq Co-60 eq, whereas for syngas the values are observed to be 0.05 and 0.14 kBq Co-60 eq respectively. Steam production is identified as the primary hotspot, contributing approximately 42 % of the total impact, followed by electricity consumption, which accounts for 20 %. The IR impacts from steam production stem from the energy demand associated with industrial processes, which are modelled using the average European dataset, incorporating nuclear energy (Ecoinvent, 2024). The higher IR impact of GM is attributed to its greater energy requirement for processing compared to GS.

3.1.3. Fossil resource scarcity

In both subsystems, steam production is identified as the primary environmental hotspot, followed by natural gas consumption. In this study, the natural gas data is sourced from the Spanish market, while steam production is modelled using the average European dataset, as specific data for steam production with Spain as the provider is unavailable (Ecoinvent, 2024). For the GS feedstock, steam production accounts for approximately 85 % of the total environmental impact, followed by natural gas, which contributes around 9 % of total emissions. In the case of GM, the contributions of steam production and natural gas are 67 % and 31 %, respectively. The higher reliance on natural gas in the GM process is attributed to its greater energy demand, which arises due to its chemical structure (Muhlack et al., 2018). Natural gas is the main fuel consumed to produce steam resulting in contribution in FRS. For TPC, the FRS impacts using GM and GS are 46.69 kg oil-eq and 29.63 kg oil-eq/FU, respectively. For biochar, it is valued at 1.49 and 0.91 kg oil-eq/FU whereas for syngas the values are recorded at 0.49 and 0.31 kg oil-eq/FU respectively. These values, along with the identified hotspots, are illustrated in Fig. 2.

3.1.4. Terrestrial ecotoxicity

For TPC output, the TE impact is 156.43 and 128.09 kg 1,4-DCB per kg of product using GM and GS, respectively, indicating that the former exhibits 22 % higher impacts than GS. Similar trend has been observed for byproducts as GM impacts are observed to be 26.58 % and 22.5 % higher than GS for biochar and syngas respectively. Valorisation processes have been observed to be energy intensive, and the outputs of our system (GS and GM) are reported in literature to exhibit medium to high toxicity impacts (Metcheva et al., 2022; Sousa et al., 2019). These trends are also observed in our study as steam production is the primary environmental hotspot followed by the GM and GS cultivation and processing. Furthermore, in this study, the Spain electricity mix is utilised, comprising approximately 44.5 % nuclear and wind energy, both of which have been documented in the literature as having high TE impacts (IEA, 2023; Marques et al., 2021; Le-Boulch et al., 2024).

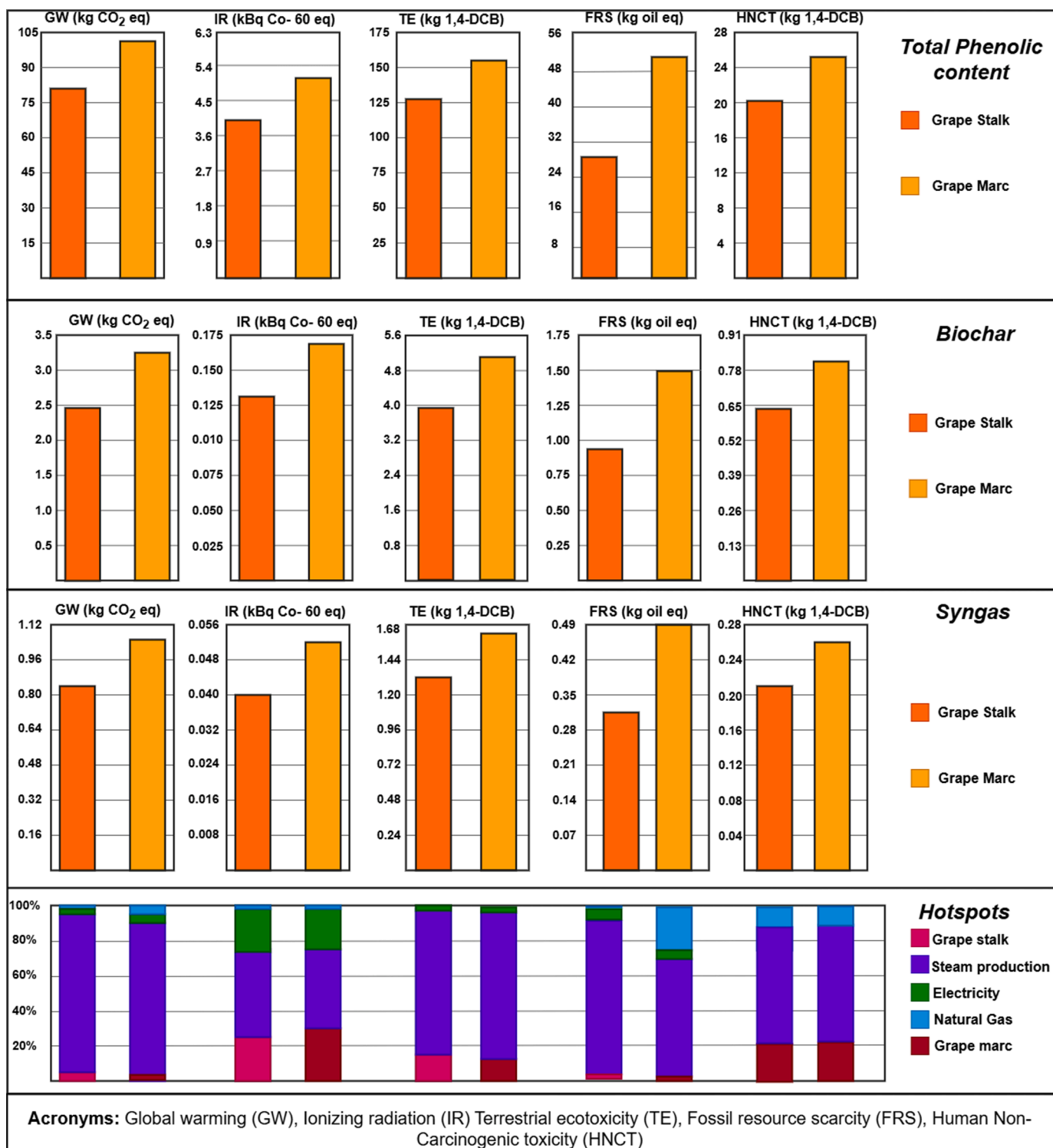


Fig. 2. Grape stalk and grape marc environmental impacts and hotspot analysis per FU.

Additionally, within steam production, electricity consumption accounts for approximately 90 % of the total impacts, making it a key contributing factor (Ecoinvent, 2024; Zeilerbauer et al., 2023).

3.1.5. Human non-carcinogenic toxicity

Biorefineries have been documented to pose risks to human health due to the emission of particulate matter into the air and soil (Accardi et al., 2013). In this study, for TPC, HNCT impacts of GM and GS are quantified at 25.2 and 20.5 kg 1,4-DCB eq, respectively. For biochar the

impacts of using GM and GS are 0.81 and 0.63 kg 1,4-DCB eq, while for syngas impacts are valued at 0.26 and 0.21 kg 1,4-DCB eq/FU, respectively. The primary environmental hotspot is steaming production, accounting for approximately 61 % of the total impact in both scenarios, followed by GM and GS processing, contributing 27 % and 28 %, respectively. The high impact of steam production is attributed to industrial process emissions, which have been linked to adverse effects on human health (Metcheva et al., 2022; Zhang et al., 2023). Russo et al. (2021) identified several environmental hotspots in apple pomace

supply chain, including fertiliser and fuel usage which are employed as the background processes in this study and contribute to the GM and GS processes. Therefore, the share in HNCT category arise from the background process involving cultivation, fertilizers and fuel consumption.

3.2. Techno-economic analysis

The detailed results regarding capital investment and working capital, the plant's annual operating costs and the revenues generated from the sale of biorefinery's products are presented in Table 4.

The analysis reveals that in both scenarios (i.e., using marc and stalks), the total capital investment is substantially high, amounting to approximately \$1.15 billion. The most expensive pieces of equipment are the cyclone, the centrifuge and the tray dryer, accounting for more than 160 million dollars, which represents approximately 75 % of the total equipment cost. Although the investment required to set up both scenarios is similar, the valorisation of grape stalks requires an initial investment of 30 million dollars less. This difference is due to slight variations in equipment costs, as the composition of the raw materials differs slightly, leading to variations in the process flows, which in turn affect equipment size and cost. The utility and raw material acquisition costs do not exceed 8 million dollars, with the high capital investment being the primary contributor to the annual manufacturing cost. Additionally, in the grape stalk scenario, annual operating costs are approximately six million dollars lower, mainly due to reduced utility expenses, as natural gas consumption varies across subsystems.

Focusing on the annual revenues from product sales, it becomes evident that they are higher when using grape stalks, as the amount of phenolic compounds extracted is greater (1.14 g/100 kg in grape marc and 1.54 g/100 kg in grape stalks). The amount of syngas produced is also higher in the case of grape stalks, while more biochar is obtained from grape marc, but the selling prices of these are significantly lower than those of the phenolic compounds, making their quantity less important, with the focus on maximising the phenolic content to increase revenues. Nevertheless, these annual revenues are not sufficient to cover the annual operating costs of either plant, being 71 % lower in the case of grape marc and 66 % lower for grape stalks. It is also important at this point to assess the influence of the variability of the selling price of phenolic compounds, as Viganó et al. (2022) report a wide range from 25 to 230 USD/kg. Assuming the maximum price value (i.e., 230 USD/kg), the NPV would still remain negative and the IRR would reach only 3.11 % for the grape stalk case. In contrast, for grape marc, annual costs would still slightly exceed revenues, due to the lower yield of phenolic compounds obtained. To deepen the analysis, in Scenario 4, the sensitivity analysis increased the selling price to 200 USD/kg and adjusted the equipment purchase costs. This price fluctuation was discussed to evaluate its impact on the overall project economics.

After examining and explaining the expenses and revenues in each scenario, calculating the economic profitability of the design using NPV

Table 4
Summary of Costs and Revenues from the Techno-Economic Analysis for each feedstock (USD).

| Parameters | Grape marc scenario | Grape stalks scenario |
|-------------------------|---------------------|-----------------------|
| Equipment purchase cost | 222,081,000 | 216,449,000 |
| FCI | 1,110,405,000 | 1,082,245,000 |
| WC | 55,520,250 | 54,112,250 |
| TCI | 1,165,925,250 | 1,136,357,250 |
| C _{oi} | 700,000 | 700,000 |
| C _{ut} | 7,823,004 | 6,496,831 |
| C _{rm} | 2,043,750 | 2,043,750 |
| COM | 213,920,007 | 207,220,015 |
| Annual revenues | 61,396,838 | 70,589,461 |

Acronyms: Fixed Capital Investment (FCI), Working Capital (WC), Total Capital Investment (TCI), Operating Labour Costs (C_{oi}), Utilities Costs (C_{ut}), Raw Materials Costs (C_{rm}), Manufacturing Costs (COM).

and IRR do not have sense, as the initial investment would never be recovered. Therefore, the next step is to calculate the MSP of the grape stalk scenario, as the revenues obtained are higher and both the manufacturing costs and capital investment are lower compared to GM. Assuming that the price of all products increases proportionally, should be multiplied per a minimum of 4.6 to reach a positive NPV with a 10 % rate of return at the end of the plant's useful life.

Comparing with results from other similar studies in the literature, Ioannidou et al. (2022) designed a biorefinery to process 805 thousand tonnes of winery waste annually, more than 10 times the capacity selected in this study. The given parameters include an annual CRM of \$39.75 million, Cut of \$27.22 million, Col of \$6.35 million, FCI of \$254.66 million and COM of \$145.6 million, which aligns with the difference in plant scale between both designs, except for the FCI, which is four times higher in the designed plant of this study. On the other hand, Jin et al. (2021) designed a biorefinery to produce polyphenols, seed oil and biochar with a treatment capacity of 36,000 tonnes of grape pomace per year, approximately half of the selected capacity in this manuscript. The FCI is \$59.6 million, with total operating costs of \$16.3 million per year, which is lower than the results obtained in this study. Regarding methodologies, Jin et al. (2021) estimate equipment costs using a SuperPro® database along with vendor quotations and literature, with quotations updated to 2019, while Ioannidou et al. (2022) estimate the cost based solely on literature. This clearly indicates that both investment and operating costs are excessively high and should be analysed in detail, as the previously cited studies report lower costs despite using two different estimation approaches, making this a key parameter in the sensitivity analysis when determining the feasibility of a profitable design. Moreover, beyond differences in plant scale and estimation methods, other relevant factors may account for the observed discrepancies in economic performance. One key aspect is the extraction yield of value-added products. In this study, the yields obtained were approximately 12 kg of phenolic compounds and 94 kg of biochar per tonne of grape marc and 16 kg of phenolics and 56 kg of biochar per tonne of grape stalks. In comparison, Ioannidou et al. (2022) reported yields of 8 kg of phenolic compounds, 5 kg of seed oil and 38 kg of succinic acid per tonne of winery waste, while Jin et al. (2021) achieved significantly higher yields of approximately 50 kg of grape oil, 40 kg of polyphenols, and 162 kg of biochar per tonne of grape pomace. These higher yields directly improve revenue generation and thus enhance profitability. For example, in the study by Jin et al. (2021), the selling price of biochar is the same; however, the amount produced is nearly double in the case of grape marc and almost triple for stalks. Additionally, they obtained higher yields of the main compound, polyphenols, and the seed oil had a selling price nearly eight times higher than that of syngas. In addition, the biorefinery proposed in this manuscript exhibits relatively high energy requirements, particularly due to the thermal energy demand associated with both phenolic extraction and slow pyrolysis, which significantly increase utility costs.

3.3. Sensitivity analysis

3.3.1. Steam generation sources to improve environmental performance

Steam production has been identified as the primary hotspot across all impact categories in the environmental analysis. To address this, a bio-based energy source has been proposed as alternatives to fossil fuels for industrial energy production (El-Araby, 2024). Additionally, a solar thermal energy system has been suggested as a replacement for conventional fossil fuel-based systems. Thus, two alternative scenarios were modelled and compared with the baseline scenario (steam production using the European mix generation): i) Scenario A: Steam generation from wood; and ii) Scenario B: Steam generation from solar energy.

The analysis revealed that Scenario A and Scenario B led to an 87 % and 90 % reduction in global warming impact, respectively. The reduction in this category is primarily due to the change of natural gas combustion by cleaner alternatives. Zheng et al. (2022) reported that

using biomass can lead to emissions reductions of up to 90 %, while Gobio-Thomas et al. (2023) found that solar-based systems can achieve reductions of around 80 %. The findings from our sensitivity analysis align closely with these results, with variations attributable to differences in geographical context and technological configurations. Also in FRS, the 90 % impacts reduction is observed due to decrease in consumption of fossil fuels. The quantitative results of assessment have been depicted in Table 5.

3.3.2. Techno-economic

The sensitivity analysis of the techno-economic assessment is conducted by varying selected parameters in the process simulation to explore potential profitability improvements for the grape stalk scenario, as it offers better economic results, such as changes in manufacturing or equipment purchase costs, that are lower in the literature reviewed:

- Scenario 1: the equipment purchase costs are reduced by a factor of four to align the FCI values given in this manuscript with those reported by Ioannidou et al. (2022), as the other reported parameters were at least mostly consistent with the scale change between both biorefinery designs.
- Scenario 2: the equipment purchase costs are reduced by a factor of 10, as this is the approximately average difference between the results reported by Ioannidou et al. (2022) and those of this study in C_{RM} , C_{ut} and C_{ol} . Additionally, the FCI obtained with this is approximately double that reported by Jin et al. (2021) for a plant that processes roughly half the raw material.
- Scenario 3: the utility costs are decreased by 25 % to assess the influence of these prices on the manufacturing costs of the plant, and product sales revenues are increased by 25 %.
- Scenario 4: the equipment purchase costs were recalculated based on literature values to provide a close comparison of the proposed design (Seider et al., 2017; Towler and Sinnott, 2021; Turton et al., 2018; Woods, 2007). This methodology estimated the equipment costs based on key parameters such as volume or treatment capacity. Additionally, the selling price of phenolics was increased up to 200 USD/kg, following the range value reported by Viganó et al. (2022).

Fig. 3 shows the results obtained in each one of the scenarios analysed in terms of NPV and IRR. In Scenario 1, despite the drastic reduction in the initial investment required, the IRR is slightly above 0 % and the NPV is far from being positive (-\$216.59 million), but at least annual revenues now exceed expenses. In contrast, Scenario 2, based on equipment purchase costs aligned with related literature, demonstrated an improvement in the economic performance, achieving an NPV of 308.68 million dollars and an IRR of 36.16 %. This may indicate the relevance of the selected procedure to estimate the investment cost for the profitability of biorefinery designs at early stages. In Scenario 3, the annual revenues from product sales are lower than the manufacturing costs of the plant, showing that the effect of this modification is not significant in the results obtained. In the case of increasing the sales price, however, revenues increase by 18 million dollars. On the

other hand, the reduction in utility costs barely lowers the manufacturing costs by two million dollars, confirming the high influence of equipment purchase costs on the final profitability. Finally, in Scenario 4, the estimation of equipment costs results in a reduction of more than \$100 million, bringing the total capital investment down to 114.9 million dollars. The detailed equipment cost breakdown can be found in Table S2 of the Supplementary Material. Furthermore, the increase in the selling price of phenolic compounds leads to annual product revenues of 221.7 million dollars, resulting in an IRR of 19.69 % and an NPV of 607.32 million dollars. Consequently, the sensitivity analysis clearly shows that the key factor for higher profitability is the equipment acquisition costs, as they significantly influence both the initial capital investment and the annual operating costs of the plant. In addition, the extraction yield of phenolic compounds and their selling price play a decisive role, as phenolics are the most valuable product and ultimately determine the economic viability of the plant.

4. Conclusions

This research evaluated the environmental and economic sustainability of a multiproduct biorefinery designed to valorise wine industry waste, specifically grape marc and grape stalks, into high-value products: phenolic compounds, biochar and syngas. Grape marc processing resulted in higher environmental impacts across all categories compared to grape stalks, primarily due to its more energy-intensive degradation requirements. The environmental profile in both cases reveals that the main hotspot of the design is steam production, due to the high energy demand in the biorefinery, followed by the environmental impacts associated with raw material procurement. Nevertheless, as demonstrated by the sensitivity analysis, these impacts can be significantly reduced by switching to cleaner fuels for steam generation. The initial techno-economic suggests that the baseline design is not economically viable due to high capital and operating costs. However, a sensitivity analysis showed that adjusting key parameters could substantially improve the economic outcomes, with an internal rate of return (IRR) exceeding 30 %, aligning with values reported in the literature. Grape stalks emerged as the more economically favourable feedstock, owing to higher phenolic compound yields and lower utility demands.

Although it may be possible to make this form of valorisation profitable and generate benefits, future research could focus on improving the heat generation method, currently reliant on steam produced from fossil fuels. Shifting to cleaner energy sources, such as solar or cogeneration, could help reduce environmental impacts, particularly global warming and fossil resource scarcity. Additionally, exploring synergies with local industries, such as using biochar for soil amendment or syngas for energy generation, could enhance the circularity and economic viability of the biorefinery system.

List of abbreviations

LCA: Life Cycle Assessment
 GHG: Greenhouse Gas Emissions
 GW: Global Warming
 IR: Ionizing Radiation

Table 5
 Environmental sensitivity analysis impacts (FU: 1 kg of Total Phenolic Compounds).

| Impact category | Units | Grape Marc | | | Grape Stalk | | |
|-----------------|-----------------------|------------|------------|------------|-------------|------------|------------|
| | | Baseline | Scenario A | Scenario B | Baseline | Scenario A | Scenario B |
| GW | kg CO ₂ eq | 102.07 | 13.4 | 9.56 | 80.30 | 10.55 | 7.53 |
| IR | kBqCo-60 eq | 5.15 | 2.25 | 3.06 | 4.21 | 1.84 | 2.50 |
| TE | kg 1,4-DCB | 156.43 | 30 | 33.5 | 128.09 | 24.60 | 27.43 |
| HNCT | kg 1,4-DCB | 25.21 | 23 | 10.9 | 20.50 | 18.78 | 8.91 |
| FRS | kg oil-eq | 49.69 | 3.05 | 2.55 | 29.63 | 1.82 | 1.53 |

Acronyms: Global warming (GW), Ionizing radiation (IR), Terrestrial eco-toxicity (TE), Fossil resource scarcity (FRS), Human non-carcinogenic toxicity (HNCT).

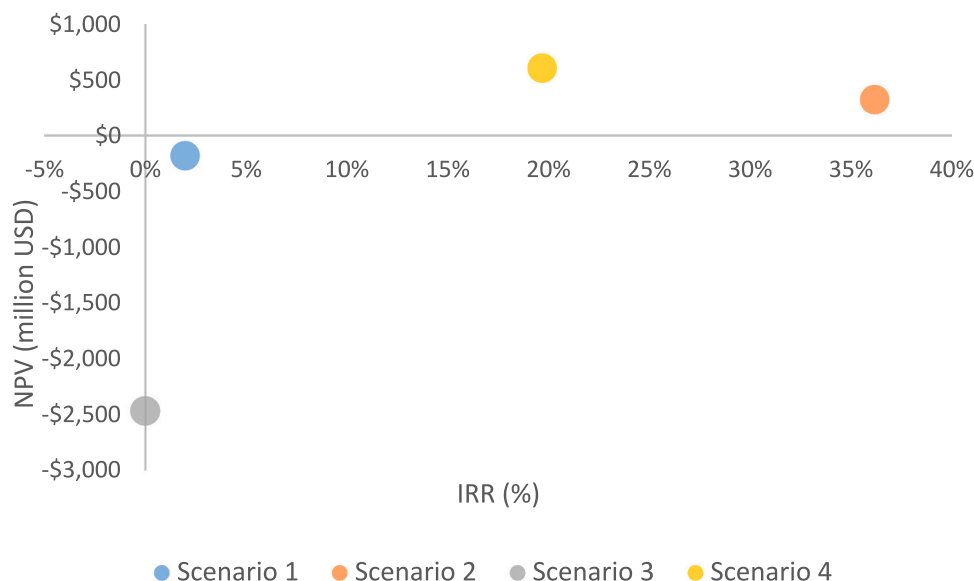


Fig. 3. NPV and IRR obtained in each one of the scenarios analysed in the sensibility analysis.

TET: Terrestrial Ecotoxicity
 FRS: Fossil Resource Scarcity
 HNCT: Human Non-Carcinogenic Toxicity
 GM: Grape Marc
 GS: Grape Stalks
 TPC: Total Phenolic Compounds
 FCI: Fixed Capital Investment
 Ceq: Purchased Equipment Costs
 WC: Working Capital
 TCI: Total Capital Investment
 COM: Manufacturing Costs
 C_{OL} : Operating Labour Costs
 C_{UT} : Utility Costs
 C_{RM} : Raw Material Costs
 C_{WT} : Waste Treatment Costs
 MARS: Modified Accelerated Cost Recovery System
 CPI: Consumer Price Index
 NPV: Net Present Value
 IRR: Internal Rate Return
 MSP: Minimum Selling Price

CRedit authorship contribution statement

Sara González-García: Writing – review & editing, Supervision, Investigation, Funding acquisition. **Ricardo Rebolledo-Leiva:** Writing – review & editing, Supervision, Software, Investigation, Conceptualization. **Arsal Tehseen:** Writing – original draft, Visualization, Software, Methodology, Investigation. **Adrián Agraso-Otero:** Writing – original draft, Visualization, Software, Methodology, Investigation.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.indcrop.2025.121290](https://doi.org/10.1016/j.indcrop.2025.121290).

Data availability

Data will be made available on request.

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