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Unraveling the environmental impacts of bioactive compounds and organic

2 amendment from grape marc

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- 12 Abstract

- In a society that produces large amounts of solid waste, the search for new methods of valorisation
- has led to the development of techniques that make it possible to obtain new products from waste.
- 15 In the case of bio-waste, biological treatment such as anaerobic digestion or composting appear
- to be suitable options for producing bio-energy or bio-fertilizers respectively. Vermicomposting
- 17 is a method of converting solid organic waste into resources through bio-oxidation and
- stabilization of the organic waste by earthworms. The purpose of this study is to establish the
- 19 environmental impacts of a complete route for the valorisation of grape pomace in order to
- 20 identify environmental hotspots. In this valorisation route, different value-added products are
- 21 produced with potential application in the cosmetic, food and pharmaceutical sectors. Priority was
- 22 given to the use of primary data in the elaboration of the data inventories needed to perform the
- 23 life cycle assessment (LCA). The main findings from this study reported that the energy
- 24 requirement of the distillation process is an important hot spot of the process. Although the
- valorisation route has some poor results in terms of the two environmental indicators (carbon
- 26 footprint and normalized impact index), when economic revenues were included in this analysis,
- 27 its environmental performance was better than that of other alternatives for bio-waste recovery.

29 **Keywords**

- 30 Vermicomposting; Grape marc; Life Cycle Assessment; Value-added products; Biorefinery;
- 31 Valorisation.

1. Introduction

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Nowadays, food waste is an environmental and social problem with long-term consequences, which are not correctly characterised by current frameworks (Kibler et al., 2018). Municipal Solid Waste (MSW) management has become a matter of global concern due to its environmental implications and the high costs associated with waste management (Marshall and Farahbakhsh, 2013). MSW generation has increased considerably in recent years due to rapid urban population growth (Goorhuis, 2014). In fact, in 2016, the total waste generated in the EU-28 by all economic activities and households amounted to more than 2,500 million tonnes (Eurostat, 2019). Data published in this database indicates an increase in the quantity of waste recovered, used for backfilling or incinerated with energy recovery from 960 million tonnes in 2004 to 1231 million tonnes in 2016. However, the quantity of waste subject to disposal only decreased 6.3%, from 1154 million tonnes in 2004 to 1081 million tonnes un 2016 (Eurostat, 2019). This problem requires research on new processes to achieve the complete valorisation of food waste and public initiatives to change consumer consumption patterns and disposal behaviours (Kibler et al., 2018). It is demonstrated that reducing landfilling in favour of increased recycling of some types of materials such as glass, paper, plastic and metals leads to lower energy demand and environmental impacts (Eriksson et al., 2005). In the case of biowaste, biologic treatment such as composting or anaerobic digestion appear to be suitable options (European Comission, 2008). Poor waste management involves not only altering the different environmental compartments, but also contributing to problems of global impact. In relative terms, the management of the agricultural sector's organic fraction contributes greatly to global environmental challenges such as climate change, freshwater pollution and nutrient accumulation (Weidner et al., 2019). On the contrary, the adequate treatment of the organic waste fraction can reduce the environmental impact provided that the organic fraction of the waste stream is recovered in order to produce substances such as biogas that can be used as fuel or biofertilizers to replace those of chemical origin (Komakech et al., 2015).

The wine industry is one of the most important sectors in terms of raw material treatment and economic production in the food processing industry. According to data provided by the International Organization of Vine and Wine, world wine production in 2015 was approximately 280 million hectolitres of 78 million tonnes of grapes (Guerini Filho et al., 2018). In Galicia, the Atlantic region of NW Spain, the wine sector has a long tradition with different varieties of high oenological quality, as evidenced by mentions of excellence and awards (Vázquez-Rowe et al., 2012). Winemaking process comprises a complex sequence of activities (Escribano-Viana et al., 2018), from grape growing, harvesting, fermentation and maturation in the winery to the handling of waste generated at each stage of the process. The main solid organic residue from winemaking is grape marc, also known as grape bagasse or grape pomace, which consists of the seeds, pulp and stalks that remain after pressing the grapes. In general, the total volume of waste generated is around 20-30% of total wine production, which represents a more than meaningful percentage (Zabaniotou et al., 2018). However, this value is lower than that of other food industries, where the produced waste can account for up to 60% of the initial products (Notarnicola et al., 2017). The most common alternative for the valorisation of the grape marc in the winery is the production of brandy spirits, although there is room for innovation when it comes to the processing of this stream. However, this fraction of the grape can be considered a valuable source of polyphenols since it contains around 70% of the phenolic compounds of the grape, which could be extracted in a safe and sustainable way (Poveda et al., 2018) since only a small part of the phytochemicals applied during cultivation is transferred from the grape to the wine (Mazza, 1995). The interest in extracting and exploiting the polyphenols present in this type of waste lies in their potential use and application in a wide range of sectors, such as cosmetics, food and pharmaceuticals (Fontana et al., 2013). The current management of wine residues is still in the early stages of development, so it has focused on its application as an organic soil amendment (Domínguez et al., 2017). In small geographic areas with a high burden of agricultural activities, the inappropriate disposal of

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this material has led to the release of excessive amounts of polyphenols to soils. Phenolic compounds are responsible for the phytotoxic activity of grape marc, so this problem need to be monitored as it can cause inhibition problems for plant growth (Barbera et al., 2013). These agronomic problems associated with the application of grapes to soil could be minimized by stabilizing them through different organic decomposition processes as composting or vermicomposting (Gómez-Brandón et al., 2011). In the present study, vermicomposting was evaluated as a sustainable alternative for the stabilization of wine waste and for obtaining different value-added products. Vermicomposting is a natural process based on the interactions of earthworms (mainly of the species Eisenia foetida or Eisenia andrei) with the endogenous microorganisms present in the waste as a result of the decomposition of organic matter (Lleó et al., 2013). By varying the operational conditions of the process, it is possible to modify the physical and biochemical properties of the final product (Domínguez et al., 2010). Beyond the enzymatic transformations attributed to earthworms, there is a significant improvement in oxygen concentration, which favors aerobic composting of the waste under conditions of low greenhouse gas emissions (Nigussie et al., 2016). The final product obtained is vermicompost or earthworm humus, which has a stable, homogeneous, and fine particle size appearance. Vermicompost is also a nutrientrich, peat-like material characterised by high porosity, high water-holding capacity, and low C:N ratio (Domínguez et al., 2014). Residual organic matter tends to humidify, polymerize and polycondense. As a result, the levels of humic acids and, to a lesser extent, fulvic acids increase (by 20-60% compared to those present in the starting materials), affecting the chemical and structural characteristics of the organic matter (Gómez-Brandón et al., 2019). This is why the final product has high water retention capacity and nutrient content (Chen et al., 2018). Vermicomposting is considered a green and clean technology (Karmegam et al., 2019) with moderately low investment and maintenance costs and low energy consumption. According to a quantitative perspective of impact assessment, the Life Cycle Assessment (LCA) methodology has been used to assess and compare the impact of different

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waste disposal scenarios, including composting, landfilling and incineration. The LCA methodology allows the quantification and comparison of environmental impacts between the stages of a product or service throughout its life cycle, from raw materials acquisition to end-oflife. Several researches have used LCA to analyse the environmental implications of organic waste composting (Saer et al., 2013; ten Hoeve et al., 2019), incineration (Abuşoğlu et al., 2017; Dong et al., 2018; Tong et al., 2018) or landfilling (Buratti et al., 2015; Henriksen et al., 2018). However, only a few LCA studies have analysed the environmental implications of vermicomposting food waste. Within these studies, 2 research works have been published that can be considered as references of great interest for this study. Komakech et al. (2015) and Komakech et al. (2016) compared the environmental performance of different management alternatives based on anaerobic digestion, composting and vermicomposting for food waste and animal manure, but only the categories of global warming potential and eutrophication potential categories were considered in both studies. Tedesco et al. (2019) evaluated the life cycle impact of the bioconversion of fruit and vegetable waste into earthworm meal from a "cradle-to-gate" perspective. The main product obtained from vermicomposting are the worms themselves, while in the present study, the worms are mere tools which are used to valorize agricultural waste into some value-added products. The objective of this research is to evaluate the environmental impacts associated with the valorisation of grape marc through vermicomposting using an LCA approach, identifying the stages and the processes that make the greatest contribution to the environmental burdens. Therefore, the system under study converts wastes into usable materials following a circular economy approach. The function of the system is to achieve short-term stabilization of grape marc, obtaining four main outputs: a nutrients-rich biofertilizer, marketable brandy spirit, and a mixed fraction composed mainly of seeds, from which an extract rich in polyphenols and oil rich in fatty acids can be obtained.

2. Materials and methods

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The LCA methodology is based on the recommendations established in the ISO standards (ISO 14040;14044) and aims to be a comparative study in the evaluation of the environmental profile of the vermicomposting technology together with other alternatives for the final disposal of grape marc.

2.1. Definition of goal and scope

The main goal of this study was to evaluate vermicomposting as an environmentally friendly way of achieving the valorisation of grape marc waste using the LCA methodology. There are three possible options in the selection of the Functional Unit (FU), that is, based on the quantification of a single target product, the total flow of raw materials or the combination of different products (Khoshnevisan et al., 2018). In order to represent the function of the system and to be consistent with the multiple-output nature of the process, it seems correct to select a feedstock-based FU. The FU considered was the treatment of 1 tonne of grape marc.

2.2. Description of the overall system and system boundaries

The study was performed through a "cradle-to-gate" perspective, from the extraction of raw materials up to the point when the different products are ready to leave the facilities. The feedstock for the process, as already mentioned, is residual grape marc supplied by different warehouses located at a maximum distance of 130 km from the location of the vermicomposting facilities. The production plan was evaluated considering all the processes from the production of raw materials to the final products obtained from grape marc. Specifically, the system under study us divided into three subsystems (SS), which are detailed below in Figure 1: SS1. Distillation, SS2. Seed oil extraction and SS3. Vermicomposting. It is considered that the production of grape marc as co-product associated with the winemaking process and capital goods are outside the system boundaries.

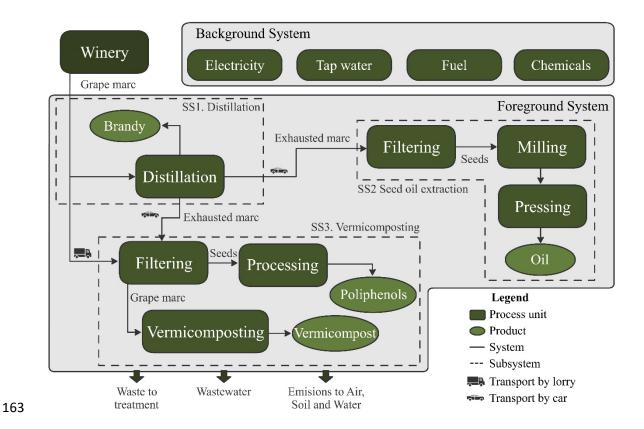


Figure 1. Valorisation scheme of grape marc targeting oil, brandy, vermicompost and a polyphenol-rich extract.

Subsystem SS1 - Distillation

Distillation of grape marc distillation to obtain different spirits is an activity traditionally used in local wineries that seek to obtain value-added products from waste. Grape marc is the perfect feedstock to produce brandy spirits named as "orujo" by simple distillation. In this study, steam distillation has been considered because it is widely used in large facilities. The use of steam and cooling water to heat and cool the grape marc and the brandy, respectively, have been considered. In addition, the production of wastewater during the distillation process has been taking into account. In this case the distillation efficiency is relatively high, obtaining 25 L of Brandy per every 200 kg of processed marc. In this subsystem, a large part of the exhausted marc that is obtained as co-product is directed to a grape seed oil extraction process (Subsystem 2), while the rest of the exhausted marc is mixed with fresh marc and is transported by lorry to subsystem 3, in which further operations that allow obtaining an extract rich in polyphenols and an organic fertilizer called vermicompost are carried out. It is important to note that no consideration has

been given to transporting these fractions from winery to distillation unit since this type of operation is usually carried out in the same place. However, transportation by lorry and car of the outputs of the distillation unit to the rest of subsystems have been considered.

Subsystem SS2 - Seed oil extraction

The exhausted marc is subjected to a filtering treatment, in which seeds are separated from the rest of the material. This exhausted marc without seeds is a waste and is sent to landfill for disposal, although it could be considered as a co-product of oil extraction and used to obtain other value-added products, as for energetic or feed purposes. Nevertheless, the main objective of this subsystem is to obtain grape seeds oil, so seeds are the principal target. These seeds are feed into a disk crusher, where a fine seed paste is obtained. The paste is pumped into a press, where the grape seed oil is obtained by crushing the seeds. This oil has a good market value due to its high content in vitamin E and linolenic acid. This process is especially interesting since the operations carried out at this subsystem are physical and the consumption of chemicals is hardly necessary, only cleaning agents.

Subsystem SS3 - Vermicomposting

The mixture of fresh and exhausted grape marc from SS1 is taken to a filter similar to the used in subsystem 2, in which seeds are separated from the grape marc. The quantity of seeds that can be separated has been assumed as 15% of the total grape marc weight. These seeds are led to a pressurized solvent extraction that allows the obtention of an polyphenols-rich extract. The use of sand as dispersant and methanol (65%) in water as solvent have been considered (Álvarez-Casas et al., 2014). In the other route, grape marc separated from the seeds was stored at 4°C until use. The grape marc was processed in pilot-scale vermireactors with a surface area of 3 m² held in a greenhouse in the University of Vigo with no temperature control and the earthworm species *Eisenia andrei* (commonly known as red worm) was used. Vermicomposting system described by Domínguez et al. (2017) was considered.. At the beginning of the trial, the vermireactor contained a layer of 12 cm of vermicompost as a bed for the earthworms. Then, successive layers of grape marc were placed through time, for processing by the earthworms. In this way,

earthworms are always located in superficial layers of the reactor, while vermicompost is deposited in the lower layers of the reactor. Thus, the reactor was filled in successive layers until a batch is completed in about 12 weeks. At this time, the vermireactor allows the treatment of 600 kg grape marc to obtain over 240 kg vermicompost ready to be used as a high-quality organic fertilizer. During the duration of the trial it is not necessary the use of additional chemicals or materials. In order to prevent desiccation, the vermireactor was watered daily and leachate was collected and sent to treatment, collecting about 10-12 L leachate per batch. The use of electric sieve and grinder to reduce the particle size of the vermicomposting is also necessary. The electric consumption was estimated considering the average use time and the power of the equipment. Polyphenols extraction was carried out before vermicomposting since, as reported in Domínguez et al. (2016), the amount of polyphenols is reduced by almost one half in a period of only 14 days and by the time period of 42 days, the decrease is about 98% of the initial amount. In the end, two main products are obtained from this subsystem, a nutrient-rich, microbiologically active organic amendment known as vermicompost and a polyphenols-rich extract.

2.3. Inventory analysis, data acquisition and allocation approach

The quality of the data handled in the elaboration of the life cycle inventory is especially relevant in order to ensure the reliability of the study. Therefore, the collection of inventory data requires primary data (typical of real systems under study) or secondary data (those complementary to the main process such as electricity, raw materials, water and fuel). In this study, most of the data related to the system correspond to primary data, while those relating to the background system (water, electricity, fuel and chemicals) were taken from the Ecoinvent® v3.5 database.

Regarding the distillation system, the data published in Dimou et al. (2016) has been used. In this study, a techno-economic analysis of the complete valorisation of wine lees is carried out. From this work, the data on cooling water consumption, low pressure steam and wastewater generation have been adapted to the characteristics of this study. As for the seed oil extraction subsystem, material and energy consumption has been obtained from Rinaldi et al. (2014), where the evaluation of the life cycle of the production of extra virgin olive oil in Italy is carried out. The

total amount of oil obtained from the grape seeds has been estimated based on the study of Fiori et al. (2014). In this paper, it was considered that grape seeds contain oil in the range of 8-16% depending on the crop and the harvest year. In the present study, 10% kg-oil per kg-seeds is considered. With respect to vermicomposting, primary data were obtained from the pilot-scale vermireactors held in a greenhouse in the University of Vigo. The managed data covered the identification of operational aspects of the inventoried reactor, such as the consumption of resources (water, energy, fuel...), waste management or the use of machinery. Direct emissions related to vermicomposting were estimated based on the emission factors taken from different secondary sources. Emissions of methane (CH₄), ammonia (NH₃) and dinitrogen monoxide (N₂O) due to earthworm activity were adapted from Komakech et al. (2015) considering the characteristics of the vermireactor. Non-methane volatile organic compounds (NMVOCs) emissions were adapted from Lleó et al. (2013). Products and residues of the grapevine cultivation contain biogenic carbon from captured carbon dioxide (CO₂) during crop growth. Although CO₂ emissions were calculated, these emissions were not included as they were considered as biogenic CO₂. The data necessary to model the extraction of polyphenols from the seeds obtained from the vermicompost were obtained from primary sources. A Pressure Solvent Extraction (PSE) has been considered (Álvarez-Casas et al., 2014) and material consumption of this stage was established based on the extrapolation of laboratory data to a pilot scale trial considering the primary experimental results as the basis for the analysis. Marine sand was considered as dispersant and the amount of sand was estimated considering a ratio seeds/solvent of 2/1 (w/w). Methanol 65% was considered as extracting solvent considering a solid/liquid ratio of 1/40 (w/v), as detailed in Dimitrov et al. (2019). Total electricity consumption was estimated from Pradal et al. (2016), taking into account that the methanol content in the solvent (% vol.) and the extraction duration are similar to those selected for the extraction of polyphenols from seeds. Though there may be other ways of polyphenol extraction from grape seeds, this system has been chosen due to its applicability was demonstrated by the analysis of bagasse samples from wineries in Galicia.

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(Álvarez-Casas et al., 2014). A summary of data managed for the complete valorisation of grape marc is displayed in Table 1.

Table 1. Inventory data of the valorisation scheme for grape marc

Inputs from Tech	nosphere	Outputs to Environment		
Materials	kg	Emissions to air	kg	
Grape marc	1000	NH_3	0.26	
Low pressure steam	1036.60	N_2O	$7.43 \cdot 10^{-3}$	
Sand	52.94	CH_4	$2.73 \cdot 10^{-2}$	
Methanol	2	NMVOC	$1.24 \cdot 10^{-2}$	
Vinyl polychloride	0.12	Outputs to Technosphere		
Polyethylene	0.14	Products	kg	
Cleaning product	$1.65 \cdot 10^{-3}$	Vermicompost	240	
	m^3	Polyphenols-rich extract	2.43	
Water	1.46	Seed oil	4.79	
Cooling water	10.54	Brandy	58.82	
Transport	t·km	Waste	kg	
Lorry	50.59	Exhausted marc	289.71	
Car	22.94		${f L}$	
Energy	kWh	Wastewater	441.35	
Electricity	123.66			

The system under assessment is a multi-outputs system where more than one product is obtained.

No allocation criteria were considered since a feedstock-based FU was selected, however, if it

were necessary to identify the impacts for each product, it is advisable to apply the economic allocation criterion, since the outputs are produced in very different amounts in order to avoid

attributing an unbalanced impact. Table 2 reports the market price considered for the different

added value products as well as the mass and economic allocation factors.

Table 2. Computation of allocation factors based on economic and mass allocation approach.

Product	Production (kg)	Market price (€kg)	Mass allocation	Economic allocation
Vermicompost	240	1.2 ^a	78%	11%
Polyphenols- rich extract	2.43	147.67 ^b	1%	14%
Seed oil	4.79	300^{c}	2%	56%
Brandy	58.82	8.57 ^d	19%	19%

- 271 ^a Ecocelta (2019)
- b Vieira et al. (2013)
- ^cLe petit jardin (2019)
- 274 d MAPA (2018)

(FRS).

- 2.4. Life cycle impact analysis: methodology
- The software SimaPro 9.0 (PRé Consultants, 2017) was used for the computational implementation of the inventories. The methodology considered to express the environmental impacts was ReCiPe 2016 v1.1. in a hierarchist perspective with the following impact categories at midpoint level (Huijbregts et al., 2017): Global Warming (GW), Stratospheric Ozone Layer Depletion (SOD), Ozone Formation (OF), Terrestrial Acidification (TA), Freshwater Eutrophication (FE), Marine Eutrophication (ME), Human Toxicity (HT), Terrestrial Ecotoxicity (TET), Freshwater Ecotoxicity (FET), Marine Ecotoxicity (MET) and Fossil Resource Scarcity

3. Results and discussion

- 3.1. Environmental performance of the overall process
- The environmental assessment was carried out from a cradle-to-gate, excluding from the analysis the production of the raw material (grape marc) since it was considered as a waste from wineries and environmental impacts were totally allocated to the main product of these production systems e.g. bottled wine as the main product. The environmental impacts according to the characterisation phase are reported in Table 3. Most environmental burdens are allocated to oil, as the price is very high and, therefore, the economic allocation factor is also high. However, environmental impacts assigned to vermicompost production are much lower. For example, in the case of GW category, the production of 1 kg vermicompost only involves the emission of approximately 200 g CO_2 eq.
- It is important to highlight other benefits derived from the use of vermicompost as organic fertilizer in substitution of other more consolidated alternatives such as the use of peat or compost as a soil amendment. The vermicompost produced during the process can be used in vineyards as an organic fertilizer. In fact, due to the chemical characteristics of vermicompost $(20.2 \pm 1.3 \text{ g/kg})$

Nitrogen and 2.1 ± 0.1 g/kg Phosphorous, among other nutrients), the 240 kg produced per batch can provide the amount of nitrogen to the soil as 346.3 kg peat. If vermicompost use as organic fertilizer is taking into account, environmental benefits can be calculated by determining the avoided life cycle impacts of peat mining processes and subtracting them from each impact category. When the use of peat is avoided by utilizing vermicompost, all its environmental impacts are also prevented, and the life cycle inventory of peat can be considered a credit to the life cycle burdens of vermicompost production.

Beyond the comparative performance as soil amendment, it is relevant to identify other benefits associated to preservation of biodiversity and improved resilience of the crops against pests. This enriched-microbial environment provides macro and micro-nutrients to the soil and avoids the extensive use of pesticides, two major consequences that should not be ignored. Direct consequences of the use of vermicompost as a soil amendment are attributed to improved germination, growth, flowering and fruit production for a wide range of plant species, such as trees, horticultural crops and aromatic, medicinal and ornamental plants (Lazcano and Domínguez, 2011).

Table 3. Impact assessment results associated with the different products obtained in the process per functional unit (1 tonne of grape marc)

	Unit	Vermicompost	Polyphenols-rich extract	Seeds oil	Brandy	Total
GW	kg CO ₂ eq	48.9	61.0	244.2	85.7	439.7
SOD	kg CFC11 eq	$2.18 \cdot 10^{-5}$	$2.72 \cdot 10^{-5}$	$1.09 \cdot 10^{-4}$	$3.82 \cdot 10^{-5}$	1.96 · 10-4
OF	$kg NO_X eq$	0.1	0.1	0.4	0.1	0.7
TA	kg SO ₂ eq	0.2	0.2	1.0	0.3	1.8
FE	kg P eq	$7.81 \cdot 10^{-3}$	$9.73 \cdot 10^{-3}$	$3.90 \cdot 10^{-2}$	$1.37 \cdot 10^{-2}$	7.02 · 10-2
ME	kg N eq	$8.38 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$	$4.18 \cdot 10^{-3}$	$1.47 \cdot 10^{-3}$	$7.53 \cdot 10^{-3}$
HT	kg 1,4-DCB	0.9	1.1	4.6	1.6	8.2
TET	kg 1,4-DCB	136.8	170.4	682.5	239.4	1229.1
FET	kg 1,4-DCB	1.3	1.6	6.4	2.2	11.5
MET	kg 1,4-DCB	1.8	2.2	9.0	3.1	16.2
FRS	kg oil eq	14.8	18.5	74.0	26.0	133.3

According to the results obtained, most of the environmental burdens derived from the valorisation strategy are related to the distillation unit (SS1), as displayed in Figure 2. This subsystem, along with subsystem 3, are responsible for more than 80% of the environmental burdens in all impact categories, except for FET and MET. Subsystem 1 can be highlighted in categories GW (74.7%), TET (74.7%) and FRS (73.7%). In relation to subsystem 2, it is the main contributor in MET and FET categories, which are highly sensitive to both waste and wastewater treatment. On the contrary, in GW, TA and ME the environmental burdens related with this subsystem are minimal, with an average of 2.6%.

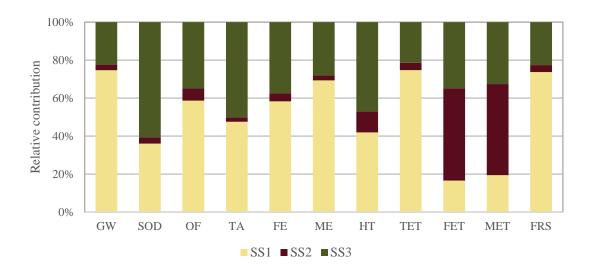


Figure 2. Contribution of the different subsystems (SS1-SS3) to the environmental impacts associated with the valorisation of grape marc

Thus, subsystem 3 presents environmental impact values lower than 40% in all impact categories, except in SOD, TA and HT categories (60.6%, 50.1% and 47.1% respectively). This is mainly due to nitrogen-based gas emissions during the vermicomposting stage, mostly ammonium and dinitrogen monoxide, which have high characterisation factors in these impact categories. Focusing on GW, the environmental burdens of this category are assigned to subsystem 1, mainly associated with the combustion of fossil fuels to obtain the steam required for the distillation of grape marc. Direct emissions into the atmosphere associated with the vermicomposting process were quantified in subsystem 3; however, most of these emissions were substances as ammonium that has no impact in this category, in addition, the production of N2O and CH4, with high

characterisation factors in this category, is minimal. Direct CO₂ emissions from vermicomposting should not be considered as fossil carbon, but as biogenic CO₂, so they were not included in the inventory analysis. Determining the environmental impacts per activity involved in the valorisation process is useful to locate the "hot spots" of the process. In this way, Figure 3 displays the distribution of environmental burdens per activity in the valorisation of grape marc.

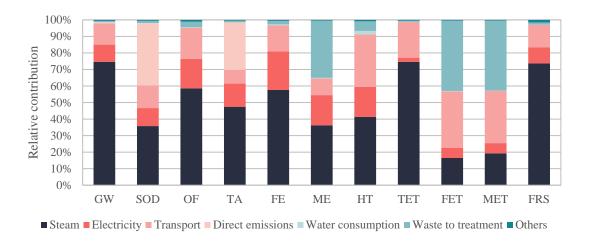


Figure 3. Relative contributions per activity to the environmental profile of the valorisation of grape marc (1 tonne grape marc as functional unit).

As for the activities associated with these impacts, steam consumption is the most impacting activity in almost all impact categories (Figure 3). Consequently, steam consumption is the main hotspot within the entire valorisation process and should have, therefore, the highest priority for process improvement from an environmental point of view. Omitting FET and MET categories, steam consumption exhibits global contributions ranging from 35.7% in SOD to 74.6% in TET and GW. Regarding GW category, steam production stands out for GHG, SO₂ and NO_x emissions associated with the combustion of fossil fuels. With respect to TET category, steam consumption is the main contributor, due to the emission of heavy metals into the air derived from the burning of fossil fuels. It seems to be consistent that steam consumption was the most contributing process also in FRS, as it is an activity with high energy requirements. In relation to ME, FET and MET categories, the high contribution of waste treatment is remarkable (34.6%, 42.6% and 42.4% respectively), corresponding to the environmental impacts arising from the landfill treatment of

waste generated during the production of seed oil in SS2. It is important to note that the information relating to the treatment of waste in landfills has been taken from the Ecoinvent® database, where a significant amount of metals is emitted to water and air. High concentrations of heavy metals, especially Cu and Zn, are behind the impacts observed in these two categories. It is especially noteworthy that electricity consumption has a low impact on almost all impact categories, which is not frequently found in LCA studies. The rationale behind this evidence is attributed to a low consumption of electricity, reaching a maximum contribution of 23.4% in FE. Most of this environmental impact comes from phosphate emissions from coal mining, which account for 10% of the Spanish profile. The contribution of transport is similar in all categories, with no substantial differences highlighted. Toxicity group was the most affected by transportation activities. Specifically, the categories of HT (31.7%), FET (34.2%), MET (31.5%) and TET (21.6%) as a consequence of emissions of heavy metals into the atmosphere such as copper or zinc derived from the consumption and combustion of gas oil. As for the environmental impacts related to water consumption, the contribution is practically insignificant, below 0.6% in all the impact categories considered, except for HT, where it reaches the maximum contribution of 2.4%. The rest of the inventoried inputs have almost no impact, so they have been unified in the "others" category, which presents an average contribution lower than 1%.

3.2. Comparative assessment with biowaste treatment practices

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It is important to note that in this section different biowaste treatment practices in the exhausted marc from SS1. Distillation have been compared with the entire foreground system of the present study. This combination of distillation and the different biowaste treatments has been decided based on the fact that grape marc distillation to produce brandy spirits is a practice widely distributed in wineries around the world. The treatment of 1 tonne of biowaste were maintained as functional unit. The chosen treatments were landfilling, anaerobic digestion, incineration, and composting, according to the datasets included in Ecoinvent®. Detailed information on the different treatments after the baseline scenario is summarized in Table 4.

Table 4. List of Ecoinvent® database processes considered for end of life treatments

Treatment	Ecoinvent® database process
Landfilling	Inert waste {Europe without Switzerland} treatment of inert waste, sanitary landfill Cut-off, U
Anaerobic digestion	Biowaste {RoW} treatment of biowaste by anaerobic digestion Cut-off, U
Incineration	Biowaste {GLO} treatment of biowaste, municipal incineration Cut-off, U
Composting	Biowaste {RoW} treatment of biowaste, industrial composting Cut-off, U

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Operational costs of the different scenarios were estimated based on different scientific publications. The operating costs of landfill and composting were taken from a study focused on the optimal design of the windrow composting system (Vigneswaran et al., 2016). The estimation of costs of anaerobic digestion and incineration was performed from a model that optimizes different waste treatments (Münster et al., 2015). Finally, as far as vermicomposting is concerned, an LCA study was used as the calculation base; in this study, the environmental impacts of vermicomposting are calculated in terms of global warming and eutrophication. In addition, an economic comparison of different manure management systems was carried out. The different alternatives studied were the use of fresh manure as fertilizer, vermicomposting and the dumping of untreated waste (Komakech et al., 2016). The environmental burdens of each scenario were calculated by analysing the corresponding Ecoinvent® process while vermicomposting scenario corresponds to the present case study. The results of this comparative study have been presented in terms of two indicators: carbon footprint and the normalized impact index of the ReCiPe methodology. The normalized impact index reflects the results of environmental burdens in the form of different impact categories, offering a global view of the environmental performance of the process. In this case the same impact categories have been used as in Section 3.1. Figures 4 and 5 display the environmental impact in terms of carbon footprint (kg CO₂ eq) and normalized impact index (pts); and the operational costs (€tonne) of the different scenarios present in the study. The comparative profiles for the different treatments considered have been obtained considering the treatment of 1 tonne of biowaste (grape marc) as functional unit.

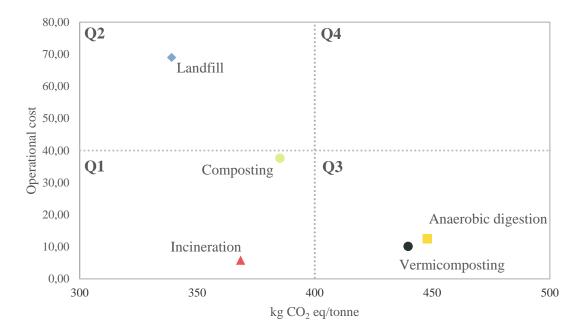


Figure 4. Comparative results related to different valorisation process considering the treatment of 1 tonne of grape marc in terms of carbon footprint.

Figure 4 presents the GW impact and the operational costs of all the alternatives considered in the study. In terms of carbon footprint, anaerobic digestion presents the worst environmental performance, due to the direct emissions of GHGs as methane. However, anaerobic digestion presents a low operational cost of about €12 per tonne of waste. On the contrary, landfilling is located in the second quadrant and presents the lowest environmental burdens of all the alternatives studied thanks to low GHG emissions when this process is compared with any of the other scenarios. However, operation costs derived from landfill are the highest of all the alternatives, since it is not possible to obtain revenues from the sale of a product with a market value that allows reducing the operation costs. Composting is located in the first quadrant, but very close to the second, mainly due to bad economic results. On the other hand, the other alternatives (incineration and vermicomposting) are situated in the first and third quadrant respectively, which correspond to low operational costs and low or medium environmental impact. It is quite relevant that biological treatments present the worst environmental results in terms of carbon footprint, mainly due to the GHGs emissions generated in the fermentation processes and anaerobic digestion. However, these processes produce value-added products

(biogas, compost, vermicompost...) which would improve the environmental profile if they were considered.

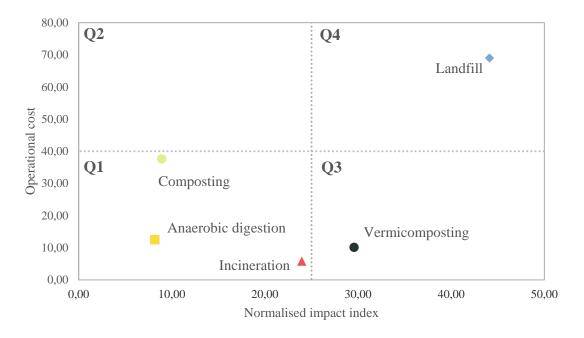


Figure 5. Comparative results related to different valorisation process considering the treatment of 1 tonne of grape marc in terms of normalised impact index of the ReCiPe methodology.

Figure 5 shows the environmental impact in terms of the normalised impact index of the ReCiPe methodology. This approach provides a global view of the impacts generated within the process in a single value that facilitates the communication of the results. Thus, the calculation of environmental performance is not limited to a single impact category. The same importance is given to other categories that are normally ignored in relation to the carbon footprint, such as ecotoxicity, acidification or eutrophication.

According to the results represented in Figure 5, landfilling and vermicomposting scenarios reported the worst environmental profiles. In contrast to using the carbon footprint as the indicator of environmental impact, the alternative with the worst environmental profile is landfill, as ecotoxicity and human toxicity categories include heavy metals pollution. As for anaerobic digestion, which presented the worst environmental profile in previous graph, it has the lowest environmental impact value in this case. Vermicomposting presents a relatively high environmental impact in both indicators (carbon footprint and normalised impact index).

However, the multi-product nature of the vermicomposting process bust be taken into account, in the next section an additional analysis that considers the outputs of the different processes is carried out

3.3 Environmental implications of switching from mass-based FU to a benefit-based one

The results shown in section 3.2 were related to a functional unit based on the amount of biowaste treated: 1 tonne of grape marc. This functional unit is useful when analysing valorisation systems where multiple by-products are obtained as it corresponds to the amount of valorised. However, the quantity of valuable by-products, which also have different market prices, is variable and depends on the alternative. Therefore, the potential revenue obtained per alternative is different and depends on the technology used. Thus, in addition to the environmental characterisation of the process, it is important considering the production of value-added products that have certain environmental benefits. These environmental benefits come from the environmental credits produced by not manufacturing these products which consume raw materials and energy. The selection of an economic-based Functional Unit has been discussed in previous studies where different biorefinery-based system have been assessed (Budzinski and Nitzsche, 2016; González-García et al., 2018; Pérez-López et al., 2014)

To consider the market price of all outputs produced, an alternative functional unit based on the economic benefit expected in each scenario was chosen. The alternative functional unit proposed for this section is the generation of €100 of economic revenue from the sale of the different outputs. The landfill scenario was not included in this comparative analysis since no outputs with market value was considered.

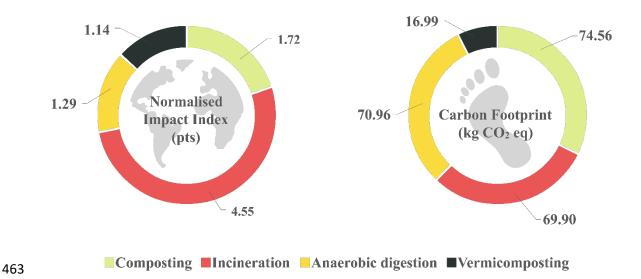


Figure 6. Comparative environmental impacts in terms of the normalised impact index (pts) and the carbon footprint (kg CO_2 eq) considering €100 of revenue as a functional unit.

Figure 6 shows the main environmental indicators in terms of Normalised Impact Index and Carbon Footprint considering €100 of economic revenue as a functional unit. Different results can be obtained if a mass-based FU or an economy-based FU is chosen. According to the results, as previously reported in Figures 4 and 5, vermicomposting involved low impact in terms of the two selected indicators. In this case, it had the lowest environmental impact in both cases (1.14 pts. and 16.99 kg CO₂ eq). This can be explained by the fact that vermicomposting can be considered as a biorefinery-based process, from which several added-value products can be obtained.

The incineration scenario maintains a performance similar to that of the previous analysis, in terms of carbon footprint presents a relatively low impact (69.90 kg CO₂ eq). However, when the rest of the impact categories considered in the study are incorporated, the impact increases, being the alternative with the worst environmental profile in terms of the normalised impact index (1.29 pts.). Anaerobic digestion presented the worst environmental profile in terms of carbon footprint (more than 450 kg CO₂ eq per tonne of biowaste) due to methane emissions, however, in this analysis, when considering the benefits provided by biogas, the carbon footprint of this alternative is almost equal to the alternatives of composting and incineration. In terms of the carbon footprint, composting shows the worst environmental behaviour (74.56 kg CO₂ eq), mainly due to the low

market price of compost and the amount of GHGs emissions during the process. It has been shown that the use of an environmental indicator which assesses the complete profile of the process (normalised impact index) and not only a specific aspect (carbon footprint) is appropriate.

In this way, not a single environmental aspect is enhanced, as shown in Figure 4, where the landfill presented the lowest environmental impact in terms of carbon footprint, but the most shocking profile when the normalised impact index was evaluated. In addition, if a global vision of the different alternatives is considered (both waste treatment and production of added-value products), vermicompost is proven as the best alternative to biowaste treatment.

4. Conclusions

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In recent years, there is a growing interest in the exploitation of the waste generated by the wine industry. This study has shown that grape pomace is a feedstock with the capacity to produce a wide range of value-added products, which represents a great opportunity for the wine sector in the future. Furthermore, it has been proven that vermicomposting is an innovative and environmentally sustainable valorisation treatment. Using the LCA method, it has been demonstrated that the energy needs of the distillation process are an important hotspot of the process. On the basis of the results obtained in this study, it would be interesting to analyse, in future research, a scenario in which most fossil energy sources would be replaced by renewable energy sources. If economic allocation factors are considered, the environmental burdens of the process can be distributed among the different products, which corresponds to 200 g CO₂ eq per kg produced vermicompost. The comparative analysis between the end-of-life treatments has shown that, although vermicomposting presents some poor results in terms of carbon footprint and normalised impact index, its environmental performance is better than the other alternatives when economic revenues are included in the analysis. This study provides relevant information in the basic design of a patent on which the process has been developed on a commercial scale and can contribute to the development of the process, not only from an environmental but also from an economic point of view.

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