Production of flavonol quercetin and fructooligosaccharides from onion (*Allium cepa* L.) waste: An environmental life cycle approach

Beatriz Santiago*, Ana Arias Calvo, Beatriz Gullón, Gumersindo Feijoo, Maria Teresa Moreira and Sara González-García

Department of Chemical Engineering, CRETUS Institute, Universidade de Santiago de Compostela. 15782- Santiago de Compostela, Spain.

* Corresponding author: E-mail address: beatriz.barahona@usc.es

DOI: 10.1016/j.cej.2019.123772

Abstract

Onion (*Allium cepa* L.) is a worldwide culinary ingredient and the second most important vegetable crop. Hence, the amount of onion solid waste (OSW) is really abundant and constitutes an environmental problem due to its pungent odour and the proliferated growth of phytopathogens. However, the content of flavonol quercetin and fructooligosaccharides (FOS) makes it a potentially recoverable residue. The aim of this study is to incorporate a biorefinery approach, developing a full-scale plant for the valorization of OSW into quercetin and FOS, under a circular economy perspective and, in parallel, to evaluate the environmental profile of this alternative according to a Life Cycle Assessment perspective. To do so, inventory data are obtained from modelled processes at large scale. A mass-based allocation approach is established as baseline, although a sensitivity assessment is further developed considering the influence of the different variables on the results obtained. The results identify that the sections responsible for the extraction of quercetin and FOS, based on the use of ethanol as an extractive agent, have significant environmental burdens. Consequently, the use of this solvent is responsible for a high environmental load due to its background production processes, reaching contributing ratios of up to 30% and 50% in some categories for the extraction of quercetin and FOS, respectively. In addition, the consumption of electricity in the different stages of the process is also responsible for high environmental loads (up to 93% for flavonol quercetin and 86% for FOS) due to its dependence on fossil fuels. Therefore, improvement alternatives should be studied (e.g. microwave and ultrasound-assisted extractions) to significantly reduce impacts on the environmental profile.

Keywords: Biorefinery; Quercetin; Fructooligosaccharides; Life Cycle Assessment; Onion waste.

1. Introduction

Agro-industrial waste is an available, diverse and recyclable resource. Traditionally, these agro-industrial by-products have been used for low value-added activities such as fertilizers and animal feed or landfilled with other wastes [1–3]. However, deepening in the composition of agricultural residues, a broad range of bioactive compounds such as pigments, oligosaccharides, lipids, flavours and phytochemicals are present. These bioactive compounds have applications in the food, nutraceutical and pharmaceutical sectors. However, the valorization of agrowaste requires a change of paradigm. Beyond waste management, the approach of biorefinery emerges as a new and promising initiative: the use of agro-industrial by-products as raw material. The inherent and diverse chemical content of agro-food waste, together with the growing demand for environmental protection and resources preservation, are encouraging more efficient valorisation of these wastes for the production of value-added food ingredients, chemicals and biofuels. In this sense, progress can be expected in the coming years for integrated biorefineries, developed on the basis of waste recovery and avoiding the risk of land, feed and food competition [4,5]. Moreover, among the Sustainable Development Goals (SDG) [6] defined by the United Nations for 2030, this valorization proposal is framed within SDG 12 "Responsible consumption and production", which aims to achieve sustainable management and efficient use of natural resources, substantially reducing the generation of waste through prevention, reduction, recycling and reuse.

Onion (*Allium cepa* L.) is a biennial plant, the second most important horticultural crop after tomato, with a world production of 66 million tons [7–9]. This plant is included in the Liliaceae family and its medicinal properties are well known, mainly associated with its composition in carbohydrates, sulphur and phenolic compounds [10]. This crop is very relevant in Spain, a versatile vegetable used as ingredient in many dishes and as source of nutrients, spicy garnish and non-nutrative health promoting compounds [11].

Onion bulbs are the edible part and are classified according to their colour in yellow, red and white or on their taste as sweet and non-sweet [8]. The consumption of bulbs implies the production of agricultural residues that are the dried skin, the outer two fleshy leaves, the upper and lower bulbs, as well as undersized or damaged bulbs [12]. Its cultivation grows every year, with Spain being one of the main onion producing countries in the world [13] and around 25,000 ha are dedicated to onion cultivation, which represents 6.50% of the total Spanish horticultural area [14]. Onion processing generates a significant fraction of waste [7,9]; around 0.5 million tonnes of onion solid wastes (OSW) are produced annually in Europe, with Spain, the United Kingdom and The Netherlands being the most important producing countries.

The composition of the onion (although it varies according to the variety) presents phenolic compounds such as flavonoids, especially flavonol quercetin and quercetin derivatives (the onion is the vegetable with the highest quercetin content). Quercetin presents antimicrobial, anti-inflammatory, anti-cancer, antiviral, anti-cholesterol and antioxidant activities, among others [9]. As for the amount of quercetin, it is found in the skin and outer layers 48-fold more than the edible portion [8,9,15]. Onion residues are not suitable for the production of animal feed or organic fertilizers due to their pungent odor and proliferation of phytopathogens [9,13]. In addition, incineration is not recommended because of its high water content. Therefore, onion residues are considered a real problem for industry [12] and hence the interest in valorising this agricultural residue instead of conventional management practices as food waste [1].

Therefore, the extraction or isolation of quercetin from onion residues is the subject of several studies [1,7,16,17], in which extraction techniques such as conventional solvent extraction (using methanol, ethanol, ethyl acetate or acetone), subcritical water extraction (SWE), supercritical fluid extraction (SFE), ultrasound-assisted extraction (UAE), microwave assisted extraction (MAE) or accelerated solvent extraction (ASE) have been evaluated. In each case, advantages and disadvantages associated with each alternative have been identified, taking into account the diversity of solvents in order to increase yield and improve efficiency as a function of process costs (in terms of solvent requirement or energy consumption).

In relation to the content of fructooligosaccharides (FOS), the presence of these compounds has been verified in onion residues with pharmaceutical, food and cosmetic applications [12,18,19]. FOS have interesting prebiotic properties as immunomodulators and can be considered a source of dietary fibre as they are not hydrolysed by human digestive enzymes. Therefore, they can be used as functional additives in the food industry [20].

Consequently, this study aims to assess the environmental profile of the valorisation of OSW from the onion-based industry into flavonol quercetin and FOS by means of ethanol extraction, fulfilling the Sustainable Development Objectives. An attempt will be made to assess not only the overall environmental profile following the Life Cycle Assessment (LCA) methodology, but also to identify the main responsible processing activities from a "cradle to factory gate" approach, as has been done in other studies, for example in González-García et al. (2018) [21]. To this end, a valorisation scenario has been proposed for the production of quercetin and FOS as an alternative to one of the most widespread management practices of this type of waste, namely anaerobic digestion [22]. As far as the authors are aware, no other peer-review LCA studies of quercetin and FOS production regardless the raw material used have been reported in the literature.

2. Materials and methods

2.1. Life Cycle Assessment methodology

Life Cycle Analysis (LCA) is considered one of the most developed tools for holistically quantifying the environmental consequences linked to the life cycle of production processes, products or services [23]. Although the initial applications of LCA referred to consumer products, this tool has been used in the environmental analysis of industrial processes and waste management at various scales in recent years following the ISO 14040 guidelines [24–27] . In addition, several authors have explored the implementation of LCA methodology in biorefinery environmental studies [21, 28–31]. Its applicability in this area is therefore justified.

2.2. Goal and scope

Once the current literature on the production of quercetin and FOS from onion has been evaluated, it is possible to propose a valorization scheme under a biorefinery perspective that allows obtaining information on the associated environmental impacts. To achieve this, a real scale system based on lab-scale data is modeled [1] using Aspen Plus® software [32]. The scale-up of chemical processes requires the understanding of all the stages involved in the valorisation sequence, as laboratory processes are often far from being optimised, either in terms of resource consumption or energy efficiency [33,34]. Consequently, the environmental profiles are estimated by considering the mass and energy balances for each stage of production. As mentioned above, OSW is not suitable for animal feed production [9,13] and is therefore considered to be managed by anaerobic digestion [35].

In order to develop a biorefinery approach, the modelled plant should be located close to onion-based industries to manage the solid waste produced. In the case of Spain, the region of Castilla-La Mancha [36] must present optimum conditions as in recent years it has become the reference point for the culture of this crop not only in Spain but also in Europe.

An attributional cradle-to-gate approach is considered in this case study, using the OSW as main raw material. In previous works the functional unit used to report the environmental profile was based on the amount of raw material valued per batch [29,37]. In this case, the analysis will be based on the kilogram of product obtained (quercetin or FOS), which have a wide variety of uses and can be obtained from alternative raw materials or production sequences [35]. It is therefore possible to obtain the necessary information on both products for future comparisons with alternative production routes.

Allocation is required when a single production system produces more than one product to distribute the environmental impacts between them. In this study, a mass-based approach has been considered as baseline for distributing the impacts of common sections between the two co-products (Sections 1-3). For this purpose, the quantity produced of each co-product (quercetin and FOS) has been taken into account, based on allocation factors of 83% and 17% for quercetin and FOS, respectively, which allow the impacts to be distributed between the co-products. Economic allocation is not used as base case because prices are often confidential and vary over time. Nevertheless, and in order to discuss the effect of the allocation choice on the environmental profiles and findings, a sensitivity analysis will be carried out considering alternative allocation procedures.

2.3. Description of the full-scale production facilities for flavonol quercetin and FOS

According to the literature, several approaches have been proposed regarding the extraction method of quercetin and other valuable compounds from onion residues. Most of these studies use simple liquid/solid extraction techniques combined with chemically-catalysed hydrolysis reaction followed by liquid/liquid extraction of quercetin. Within the solvents used in the extraction, ethyl acetate is commonly used [38]. These solvents should be recovered at the end of the extraction sequence rather than disposed of as waste. In this regard, water could also be used as a solvent for quercetin extraction, but only under subcritical conditions, i.e. at temperatures above 100°C [17], otherwise the water is too polar to be a good solvent for quercetin. Methanol and ethanol are also used to extract the highest yield of flavonol quercetin, being methanol the organic solvent that shows the best extraction results [39]. However, the ingestion or consumption of large quantities of this solvent may have an intoxicating effect on the human body. The use of solvents could be avoided with other extraction techniques such as MAE and UAE. In our modelled system, ethanol has been considered as solvent since it meets the requirements when quercetin is aimed to be used in food applications [1,40]. The proposed valorisation scenario yields two co-products, namely flavonol quercetin and FOS, as target products. Figure 1 displays the simplified system boundaries of the valorisation scheme with the corresponding sections proposed for analysis. Within each section, the different activities involved have been identified in line with the operations performed at lab-scale and designed in detail at large-scale.

<Figure 1 around here>

Therefore, the appropriate equipment required in biorefinery systems (e.g. dryer, extractor, ultrafiltration unit, flash units) as well as other secondary machinery (e.g. pumps, heat exchangers and mixers) has been chosen and designed.

Figure 2 shows the flow diagram of the plant corresponding to the valorisation sequence for quercetin and FOS production in which the different equipment designed can be identified. The valorisation sequence has been divided into ten sections or steps. Sections 1-3 are shared by both production lines (quercetin and FOS). Sections 4 and 5 focus on the production of flavonol quercetin from the permeate obtained in Section 3. The other five sections (Sections 6 to 10) focus on obtaining FOS from the solid stream obtained in Section 3. A detailed description of each section and corresponding involved operations is detailed below.

<Figure 2 around here>

Section 1: Pre-treatment of onion solid waste. In this step, the raw material is received directly from the surrounding onion industries and stored in hoppers. Secondly, the OSW is transported to the tray dryer by means of a conveyor. This treatment is necessary to reduce the moisture

content from 90% to 40%. The drying phase takes place for 120 min at 55ºC (70ºC maximum) since higher temperatures should result in the destruction of the active ingredients. It is then necessary to reduce the size of the dry raw material to obtain the optimum extraction size, i.e. around 5 mm. For this, an industrial crusher is required. Finally, the OSW at an optimum size is cooled to 10ºC and warehoused in silos and at atmospheric pressure, in order to guarantee the conservation of the raw material and avoid the proliferation of plagues since OSW needs to be processed in a maximum of 24 hours.

Section 2: Conventional solvent extraction stage. Extraction is the key step in extracting the flavonol quercetin. Conventional extraction has been preferred over others for different reasons such as economic cost, ease of implementation on an industrial scale and subsequent use in food preparation [41]. In this case, ethanol has been considered as a solvent since it is accepted by EFSA (2011) [42] in food sector. Considering the results of the literature [1], the optimal ethanol concentration for quercetin extraction to reach maximum yield should range between 50% and 80%. If the ethanol concentration increases, the extraction yield also increases. However, at concentrations above 80%, yield begins to decrease. Therefore, it has been established at 70% ethanol to obtain the highest possible extraction yield. As for the solute-solvent ratio proposed for the design, it was considered 1:100 following the recommendations of Machavarapu et al. (2013) [39]. Moreover, and with the aim of achieving a high concentration of the target compound, the liquid-to-solid ratio has been set at 10 L per kg. The extraction step was carried out at 70ºC for 3 hours.

Section 3: Centrifugation stage. After the extraction stage, the output stream is a solid-liquid suspension. Therefore, it is necessary to separate both phases in a centrifuge. The solid fraction is recovered as a residue and will be further processed as raw material in the management strategy focused on FOS production (Sections 6-10). The liquid fraction (rich on ethanol and bioactive compounds) is derived to the ultrafiltration membrane unit. This unit is required to obtain a more purified permeate without low-weight compounds (derived from OSW) that could cause technical problems in the solvent recovery step.

Section 4: Solvent recovery stage. The permeate from Section 3 includes ethanol, water and quercetin as the main compounds. Ethanol is the solvent used in the extraction and, with the aim of incorporating a “closing the loop” strategy, whether environmentally or economically, it must be recovered and recycled for later use. Thus, the permeate is sent to a flash evaporation to recover the ethanol. This step is performed at 70ºC and 30 kPa. After flash separation, there are two products: pure condensed ethanol and a mixture of water and quercetin (see Figure 2). The recovered ethanol stream is recycled to Section 2, reducing the requirements of solvent (88% of the total is recovered)

Section 5: Drying and storage. The stream rich in water and quercetin needs to be managed in order to reduce water content. To do so, it is sent to an evaporator and the final product is quercetin with 8% of moisture content. The separation is carried out at 90ºC and 30 kPa and the output steam stream is recycled to Section 2 (only 14% of the water content of the input stream is recovered because the first evaporator allowed the highest recovery yield). A spray dryer could be considered as an alternative drying operation. However, close attention should be paid to the operating temperature, as quercetin is heat sensitive. In this case, the airflow inlet temperature in the dryer should not exceed 400°C. Finally, the flow of flavonol quercetin is stored in silos at atmospheric temperature and pressure for further distribution.

As previously reported, side-waste streams are produced in the quercetin-based valorisation scheme. The solid stream produced in Section 3 and Section 1 (in case of receiving OSW in poor conditions) needs to be managed and possible options could be proposed for analysis. The solid stream could be sent to an anaerobic digestion unit since other management strategies such as fodder production, organic fertilization or incineration are not recommended [9,13,22]. However, as justified in the Introduction section, the valorisation into FOS could be considered as more attractive sequence from a circular economy approach, also achieving one of the SDG12 targets proposed by the UN [6]. Therefore, the extraction of FOS from the side streams is considered as case study in this biorefinery, as displayed in Figure 1. The designed strategy based on lab-scale data from Paredes et al. (2018) [20] is up-scaled and classified in five stages as detailed below:

Section 6: Aqueous hydrolysis. The solid stream from Section 3 is rich in water, ethanol and FOS. The process is carried out with boiling water at 100ºC in a pressurized reactor to obtain soluble oligosaccharides in the liquid fraction.

Section 7: Conventional solvent extraction. Taking into account the extraction proposed in Section 2, 70% ethanol has been selected as the potential solvent for extracting FOS from the liquid fraction from Section 6. Similar to Section 2, this stage is performed at 70ºC.

Section 8: Centrifugation. Again, after the extraction stage, the output stream is a solid-liquid suspension that is separated in a centrifuge unit. The liquid fraction (ethanol-based supernatant) is derived to an ultrafiltration membrane unit containing FOS in the permeate solution. As in Section 3, it is proposed that this unit obtains a purified permeate that allows the solvent to be recovered at the next stage. The solid fraction is recovered from both units (centrifuge and membrane) as waste for its subsequent management (i.e. landfill), which has been excluded from analysis because it is outside the limits of the system.

Section 9: Solvent recovery. The permeate from Section 8 includes ethanol, water and FOS as main compounds. This stream is sent to a flash evaporation unit (70ºC, 20 kPa) where a pure ethanol condensate is finally obtained for recycling to Section 2, considerably reducing solvent requirements (almost 78% of the total is recovered).

Section 10: Drying and storage. A new flash evaporation unit operating at 90ºC and 20 kPa has been designed in order to separate water from pure FOS and recirculate it to Section 7, thereby reducing the water consumption required in the process. The final product obtained is FOS with 18% moisture. This percentage is large due to the ability of the compound to retain water (high solubility), being also the percentage of water recovery so low (less than 2%).

2.4. Life cycle inventory data and sources

Special attention has been paid to the preparation of the life cycle inventory needed to carry out the environmental analysis. This step is the most relevant in an LCA study, as the quality and representativeness of the environmental results depend directly on the quality of the data considered. Since the system is a large-scale biorefinery, mass and energy balances for the foreground system have been established and modelled (Figure 1).

Modelling the full-scale facility requires the background information of the laboratory production process. In the literature focusing on quercetin extraction by different extraction methods, several laboratory-scale studies can be found [1,7,16,17]. In this study, the procedures processed by Jin et al. (2011) [1] have been followed in detail as a starting point, i.e. information has been gathered on the steps required, the type of equipment, the operating conditions and the performance for the specific plant design. The engineering scale-up framework proposed by Piccinno et al. (2016) [33] has been followed, starting with the laboratory protocols, the design of the full-scale production flow diagram divided by the production stages, the engineering design of the equipment involved in each production stage, as well as the design of the infrastructure needed to connect the stages (pumps, pipelines, conveyors). All these calculations have been adapted in the context of an LCA study (Piccinno et al., 2016) [33]. The estimated energy and mass flows have been obtained as foreground inventory data. Calculation procedures, design equations [43] and simulations using Aspen Plus® software were used in the specific design of the equipment. The simulations for the mass and energy balances have been performed with experimental results identified in the literature [1]. Table 1 summarizes the most relevant life cycle inventory data of the foreground system, data obtained from simulations performed with Aspen Plus® software, taking into account the procedure reported by Braz de Oliveira et al. (2011) [44] and Paredes et al. (2018) [20].

<Table 1 around here>

Regarding the recovery of ethanol used as solvent in the two extraction stages (i.e., the 4th and 9th), it is recovered, reaching an overall recycling rate of almost 72% from simulations carried out in Aspen Plus®. However, the overall ethanol losses are around 10%, as it is embedded in the solid streams of Section 8, which are sent for treatment, but the possibility of revaluation of these streams is contemplated.

Although the use of primary data is recommended, it is sometimes necessary to use secondary data mainly for background processes. This is the case for inventory data for the background system, which includes upstream activities associated with the production of utilities (electricity and liquefied petroleum gas) and other inputs to the foreground system (e.g., ethanol and tap water). The Ecoinvent® database version 3.5 has been used as the main source of secondary data [45].

The OSW based biorefining is planned in Spain, as it is one of the most important onion-producing countries in Europe. Transport activities in the production of quercetin and FOS have not been considered since both processes are carried out in the same plant. The processes of infrastructure, construction, installation or closure of the production plant have not been considered, due to the useful life foreseen in this type of industrial facilities, the impact is considered insignificant. It has been considered that the operating time of the plant is 330 days per year, which is common in industrial processes. Accordingly, the electricity mix used in the environmental analysis considers updating the database of Dones et al. (2007) [46] taking into account current data on average electricity generation and import/export data from Spain from 2017 [47], which derive 66.7% from non-renewable sources – mostly nuclear and oil/coal energy, and 33.3% from renewable energies – mostly wind and hydraulic. Table 2 summarises detailed information on the data sources used for the different base processes included in this study.

<Table 2 around here>

2.5. Life cycle impact assessment methodology

The classification and characterisation steps of the standardized LCA methodology have been considered in the study avoiding normalization and weighting since there are optional in LCA studies [23,48,49]. To do so, characterisation factors reported by the Centre of Environmental Science of Leiden University -CML 2001 method v2.05 [50] have been used for the analysis. SimaPro v9.0.0 software [51] has been used for the computational implementation of life cycle inventory data.

The following impact categories were evaluated: global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), ozone layer depletion potential (ODP) and photochemical oxidation potential (POP). Moreover, the cumulative energy demand (CED), measured in MJ, was determined using methods developed by Frischknecht et al. (2007) [52]. The choice of these impact categories was made to provide a complete and complete synopsis of the environmental effects related to the production process being evaluated.

3. Results and discussion

Table 3 shows the results obtained in the present study and based on a cradle-to-factory gate perspective in terms of the functional unit, (kg of each product obtained from OSW). The contribution of each section of the process to each category is shown, which allows the critical points of the valorisation scheme to be given. Sections 1, 2 and 3 are common to produce quercetin and FOS but Sections 4 and 5 correspond only to quercetin and Sections 6-10 are specific to FOS production.

<Table 3 around here>

3.1 Overall environmental performance

Figure 3 illustrates the distribution of environmental burdens and cumulative energy demand among the valorization stages involved, whether in quercetin and FOS production. Taking into account the complete set of environmental results, it can be observed that Section 1 constitutes the environmental hotspot of quercetin with contribution ratios ranging from 45% to 63% depending on the impact category. This section is also relevant to the FOS production line, with scores ranging from 15% to 28%. The conventional solvent extraction stage, Section 2, contributes significantly to the photochemical oxidant potential (POP) category corresponding to quercetin production (almost 37%) and 12% for FOS. This is mainly due to the background production process involved in the production of the ethanol required. As previously mentioned, Section 3 is a common stage in the valorisation sequence of both target products. This section reports a negligible contribution to all categories (below 3% for quercetin and 1% for FOS) considered for analysis regardless the target product.

The rationale behind this low contribution is based on the fact that in this section there is only energy consumption (electricity) and no chemicals or other compounds are required as in other sections. Furthermore, in terms of electricity it is not as relevant, as it is not the section with the highest electricity consumption (see Table 1).

Once the common sections for both processes have been analyzed, the sections that only contribute to the environmental burdens due to quercetin and FOS production will be analysed separately.

Section 4 presents notable contributions to the environmental impacts associated with the production line focusing on quercetin production. Contributing ratios between 17% and 28% have been identified, as detailed in Figure 3a. These impacts are mainly due to the electricity used in the evaporation and heating units to recover the ethanol and re-circulate it to Section 2. The environmental profile is not significantly altered because the drying stage (Section 5), as shown in Figure 3a, i.e. the scores contributing to the different categories evaluated are less than 1%. These values are so small due to the reduced water content in the quercetin-rich stream that the equipment used in this section (focused on reducing moisture content) does not require large amounts of energy (see Table 1). Most of the water is recycled in the ethanol recovery stages.

As for FOS, Section 6 implies a slight contribution to the overall profile with the most prominent effect in three categories: AP (17%), ODP (16%) and EP (15%). The rationale behind these results is due to the electricity required in the equipment to perform aqueous hydrolysis (both in the reactors and in the heaters), which represents 13% of the total electricity needs in the entire valorizarion route. The environmental impacts derived from Section 7 are those derived from the solvent extraction. The effect of this section is truly significant in all the categories analyzed, as detailed in Figure 3b.

Nevertheless, it is quite relevant in POP (57% of total contributions) together with CED (44%) and EP (42%). The cause of these high impacts is twofold: the emissions derived from the production of ethanol required as an extractive agent (background process) in the case of POP and the production of electricity required in the involved equipment (in the remaining categories), with the extraction being the most relevant unit. The centrifugation and drying stages (Section 8 and Section 10, respectively) do not contribute much to the overall results Contributions from Sections 8 and 10 to the environmental profile are negligible (below 4% and 1%, respectively, of the total impacts) due to the small amount of energy required by the equipment involved in these stages (see Table 1). In the case of Section 10, this low energy expenditure is due to the small amount of water that is in the inlet stream of the section, since a large part of the water is recovered in the previous section. Finally, the solvent recovery stage (Section 9) contribute lighlty to the overall environmental results associated with FOS, being around 11% in terms of ODP, AP and CED. The rationale behind these results is due to the electricity employed in the equipment in this section allowing the recovery and recirculation of ethanol to Section 2.

<Figure 3 around here>

3.2 Identification of hotspots

The identification of environmental hotspots emerges in this work as a key issue in order to propose further improvement actions for the current valorisation scheme. Thus, the following identifies and details the operations involved in the OSW valorisation system, which are responsible for the highest environmental burdens and energy requirements.

Regarding the profile associated with quercetin (see Figure 4a), the production of electrical requirements is mainly responsible for the impacts. All electricity is obtained directly from the national grid, which relies heavily on fossil fuels. Thus, its production contributes to 55-93% of the impacts depending on the category being the air heater from Section 1, the extractor unit from Section 2 and the heater from Section 4 the equipment with the highest energy consumption (see Table 1). The production of ethanol required in the extraction stage (Section 2) is also relevant, involving 5-31% of global impacts (mainly in POP). Production of Liquefied Petroleum Gas (LPG) used to heat the air in the pre-treatment stage (Section 1) has a significant effect on GWP (25%), POP (14%) and CED (14%). Environmental burdens related to tap water consumption are negligible.

Regarding the environmental profile linked to FOS, electricity consumption also plays an important role, contributing 42% to 86% of the total impacts (Figure 4b), specially attributed to the heater used to reduce the amount of moisture of the OSW at the inlet of the pre-treatment stage (Section 1). Also important is the requirement of electricity in the evaporator unit to recover ethanol in Section 7 and to perform aqueous hydrolysis (reactor) in Section 6. Ethanol production contributes between 11% and 54% of the impacts; they correspond to the extraction process of Sections 2 (quercetin) and 7 (FOS). As for the production of LPG used only in Section 1, its most significant impacts are in GWP (11%) and in the rest of the categories lower than 5%. Finally, the impacts due to the production of tap water used in Sections 2 and 7 (extraction stages) and 6 (aqueous hydrolysis) are insignificant (less than 1%).

<Figure 4 around here>

3.3 Sensitivity assessment: alternative allocation procedures

As indicated above, mass allocation is used for this LCA study as a baseline; however, an economic allocation could also be considered as an alternative for allocating impacts from common stages among co-products, as fluctuations and discrepancies in outcomes could be obtained. The formulation of an economic allocation will be performed in Scenario A taking into account the market prices identified in the literature [53] for both co-products (see Table 4). In addition, an alternative mass-allocation (from now, Scenario B) has been proposed for the analysis that distributes the impacts of these common sections, although considering the outflows of Section 3 (Centrifugation), which are the permeate (the input for flavonol quercetin valorisation) and the solid flow (the input for FOS valorisation). Therefore, and in order to discuss variations in environmental performance, these two possible allocation procedures have been considered as part of the sensitivity assessment. Table 4 shows the comparative values between the identified alternative scenarios.

<Table 4 around here>

Figure 5 illustrates the comparative environmental profiles for the co-products under study taking into account alternative allocation approaches.

<Figure 5 around here>

According to the results, it is shown that the impacts report an opposite behaviour for flavonol quercetin and FOS. Thus, the profile corresponding to flavonol quercetin (Fig. 5a) increases by about 8% in all impact categories considered for evaluation when considering an economic allocation (Scenario A). On the contrary, the profile associated with FOS (Fig. 5b) improves considerably, with reductions ranging from 15% to 19%, depending on the category in which this allocation is considered. With respect to Scenario B, the results show a decrease of around 18% in all impact categories for quercetin (Fig. 5a); conversely, an increase in impacts associated with FOS production ranging from 32% to 42% can be identified.

Therefore, the selection of the allocation procedure considerably affects the results and opposing conclusions can be drawn. However, attention should be paid to economic allocation, as prices are not stable and vary according to the quantity of product to be sold.

3.4 Improvement Outlook

In the designed plant, the sections whose goal is the pre-treatment of onion solid waste to facilitate the subsequent valorisation steps (Section 1) and the recovery of the extractive agents (Sections 4 and 9) used in the extraction sections (Sections 2 and 7) are the key environmental aspects due to the large energy needs consumed in their equipment, as well as the background process involved in the production of ethanol used as extractive agent. Bearing in mind the losses of ethanol fixed in the solid stream derived from Section 8, the recovery of this solvent could be considered as a potential improvement action since around 10% of total ethanol required in the valorisations strategies is wasted. In addition, improvement actions based on the management of the steam-rich output stream of the water recovery stages (i.e., Sections 5 and 10) could be considered. These steam-based streams could be used for heating purposes to reduce the energy needs of the equipment in Sections 4 and 9 (currently 23% of the total electricity required in the plant is produced in both stages).

The search of alternative extraction techniques [12] to obtain quercetin and FOS as well as the modification of the extraction conditions could constitute an outstanding improvement since it requires about 17% of the total electricity in Sections 2 and 7, as well as the requirement for extractive agent. Microwave and ultrasound-assisted extraction techniques, whose extraction times are shorter than conventional solvent extraction, could result in lower energy and chemical requirements [54]. Different microextraction techniques could be valorized in the future taking into account their advantages such as the use of small proportions of solvent in comparison with conventional ones [55].

Finally, pre-treatment activities are among the most environmentally negative stages due to the electricity required in the equipment responsible for reducing the amount of moisture in the raw material (i.e., OSW). In addition, temperature is a very important parameter since high values cause the destruction of the active principles, with 70ºC being considered the maximum accepted value. In view of this, several novel approaches should be studied, including physico-chemical processes such as microwave and ultrasounds [56] in order to improve the energy efficiency in Section 1, thus contributing to the reduction of the environmental burdens without altering the components of the onion waste.

Conclusions

The large-scale production of flavonol quercetin and FOS from OSW has been designed and environmentally assessed to identify environmental hotspots and to propose future strategies for improvement. The pre-treatment, solvent extraction and solvent-recovery stages included in this study result in significant environmental burdens. The use of ethanol as solvent to extract the target products in their corresponding sections and the electricity consumption are behind these significant environmental burdens. Therefore, the use of alternative extraction techniques should be carried out to improve the environmental profile.

Acknowledgements

This research has been partially supported the STAR-ProBio project funded by the European Union's Horizon 2020 Program (Grant agreement No. 727740), by a project granted by Xunta de Galicia (project ref. ED431F 2016/001) and by the Spanish Government CTQ2016-75136-P. Dr. S. González-Garcia and Dr. B. Gullón would like to express their gratitude to the Spanish Ministry of Economy and Competitiveness for financial support (Grant references RYC-2014-14984, IJCI-2015-25305, respectively). B. Santiago thanks to the Spanish Ministry of Science, Innovation and Universities for financial support (Grant reference BES-2017-081715). The authors belong to the Galician Competitive Research Group GRC 2013-032 and to CRETUS Strategic Partnership (AGRUP2015/02). All these programmes are co-funded by Xunta de Galicia and FEDER (EU).

References

[1] E.Y. Jin, S. Lim, S. Kim, Y. Park, J.K. Jang, M. Chung, H. Park, Optimization of Various Extraction Methods for Quercetin from Onion Skin Using Response Surface Methodology, Food Sci. Biotechnol. 20(6) (2011) 1727–1733. doi:10.1007/s10068-011-0238-8.

[2] C.S. Ki Lin, L.A. Pfaltzgraff, L. Herrero-Davila, E.B. Mubofu, S. Abderrahim, J.H. Clark, A.A. Koutinas, N. Kopsahelis, E. Al., Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective, Energy Environ. Sci. 6 (2013) 426–464. doi:10.1039/C2EE23440H.

[3] T.P. Thuy Pham, R. Kaushik, G.K. Parshetti, R. Mahmood, R. Balasubramanian, Food waste-to-energy conversion technologies: Current status and future directions, Waste Manag. 38 (2015) 399–408. doi:10.1016/j.wasman.2014.12.004.

[4] M. Weiss, J. Haufe, M. Carus, M. Brand, S. Bringezu, B. Hermann, M.K. Patel, A Review of the Environmental Impacts of Biobased Materials, J. Ind. Ecol. 16 (2012) S169–S181. doi:10.1111/j.1530-9290.2012.00468.x.

[5] I. Spiridon, R.N. Darie-nita, G. Elena, J. Ludwiczak, I. Alexandra, C. Spiridon, M. Niculaua, New opportunities to valorize biomass wastes into green materials, J. Clean. Prod. 133 (2016) 235–242. doi:10.1016/j.jclepro.2016.05.143.

[6] United Nations, SDG, (2019). https://www.un.org/sustainabledevelopment/.

[7] I.S. Choi, E.J. Cho, J.-H. Moon, H.-J. Bae, Onion skin waste as a valorization resource for the by-products quercetin and biosugar, Food Chem. 188 (2015) 537–542. doi:10.1016/j.foodchem.2015.05.028.

[8] J. Kwak, J. Min, N. Kim, M. Valan, S. Kim, M. Kyoung, S. Kim, Variation of quercetin glycoside derivatives in three onion (Allium cepa L .) varieties, Saudi J. Biol. Sci. 24 (2017) 1387–1391. doi:10.1016/j.sjbs.2016.05.014.

[9] L. Campone, R. Celano, A.L. Piccinelli, I. Pagano, S. Carabetta, R. Di Sanzo, M. Russo, E. Ibañez, A. Cifuentes, L. Rastrelli, Response surface methodology to optimize supercritical carbon dioxide / co- solvent extraction of brown onion skin by-product as source of nutraceutical compounds, Food Chem. 269 (2018) 495–502. doi:10.1016/j.foodchem.2018.07.042.

[10] B. Rodríguez Galdón, E.M. Rodríguez Rodríguez, C. Díaz Romero, Flavonoids in Onion Cultivars (Allium cepa L .), J. Food Sci. 73 (2008) 599–605. doi:10.1111/j.1750-3841.2008.00903.x.

[11] T. Albishi, J.A. John, A.S. Al-khalifa, F. Shahidi, Antioxidative phenolic constituents of skins of onion varieties and their activities, J. Funct. Foods. 5 (2013) 1191–1203. doi:10.1016/j.jff.2013.04.002.

[12] K. Sharma, N. Mahato, H.S. Nile, T. Lee, Y.R. Lee, Economical and environmentally-friendly approaches for usage of onion (Allium cepa L.) waste, Food Funct. 7 (2016) 3354–3369. doi:10.1039/c6fo00251j.

[13] E. Roldán, C. Sánchez-Moreno, B. de Ancos, M.P. Cano, Characterisation of onion (Allium cepa L .) by-products as food ingredients with antioxidant and antibrowning properties, Food Chem. 108 (2008) 907–916. doi:10.1016/j.foodchem.2007.11.058.

[14] Statistical Yearbook, Ministry of Agriculture, Fisheries and Food, Gov. Spain. (2018). https://www.mapa.gob.es/es/estadistica/temas/publicaciones/anuario-de-estadistica/2018/default.aspx?parte=3&capitulo=07&grupo=6 (accessed September 20, 2009).

[15] T.N. Ly, Ch. Hazama, M. Shimoyamada, H. Ando, K. Kato, R. Yamauchi, Antioxidative Compounds from the Outer Scales of Onion, J. Agric. Food Chem. 53 (2005) 8183–8189. doi:10.1021/jf051264d.

[16] A. Wach, K. Pyrzyn, M. Biesaga, Quercetin content in some food and herbal samples, Food Chem. 100 (2007) 699–704. doi:10.1016/j.foodchem.2005.10.028.

[17] M. Ko, C. Cheigh, S. Cho, M. Chung, Subcritical water extraction of flavonol quercetin from onion skin, J. Food Eng. 102 (2011) 327–333. doi:10.1016/j.jfoodeng.2010.09.008.

[18] L. Jaime, M.A. Martín-Cabrejas, E. Mollá, F.J. López-Andréu, R.M. Esteban, Effect of Storage on Fructan and Fructooligosaccharide of Onion (Allium cepa L .), J. Agric. Food Chem. 49 (2001) 982–988. doi:10.1021/jf000921t.

[19] V. Benítez, E. Mollá, M.A. Martín-cabrejas, Y. Aguilera, Characterization of Industrial Onion Wastes (Allium cepa L .): Dietary Fibre, Plant Foods Hum. Nutr. 66 (2011) 48–57. doi:10.1007/s11130-011-0212-x.

[20] L.L.R. Paredes, F.R. Smiderle, A.P. Santana-filho, A. Kimura, M. Iacomini, G.L. Sassaki,

Yacon fructans (Smallanthus sonchifolius) extraction , characterization and activation of macrophages to phagocyte yeast cells, Int. J. Biol. Macromol. 108 (2018) 1074–1081. doi:10.1016/j.ijbiomac.2017.11.034.

[21] S. González-garcía, L. Argiz, P. Míguez, B. Gullón, Exploring the production of bio-succinic acid from apple pomace using an environmental approach, Chem. Eng. J. 350 (2018) 982–991. doi:10.1016/j.cej.2018.06.052.

[22] R.T. Romano, R. Zhang, Anaerobic digestion of onion residuals using a mesophilic Anaerobic Phased Solids Digester, Biomass and Bioenergy. 35 (2011) 4174–4179. doi:10.1016/j.biombioe.2011.06.036.

[23] ISO 14040, Environmental Management-Life Cycle Assessment- Principles and Framework, Geneve, Switzerland, 2006.

[24] W. Klopffer, G. Rippen, Life cycle analysis and ecological balance: Methodical approaches to assessment of environmental aspects of products, Environ. Int. 18 (1992) 55–61.

[25] S.M. Al-salem, S. Evangelisti, P. Lettieri, Life cycle assessment of alternative technologies for municipal solid waste and plastic solid waste management in the Greater London area, Chem. Eng. J. 244 (2014) 391–402. doi:10.1016/j.cej.2014.01.066.

[26] D. Kralisch, D. Ott, D. Gericke, Rules and benefits of Life Cycle Assessment in green chemical process and synthesis design: a tutorial review, Green Chem. 17 (2015) 123–145. doi:10.1039/c4gc01153h.

[27] F. Chang, L. Lin, C. Ko, H. Hsieh, B. Yang, W. Chen, W. Hwang, Life cycle assessment of bioethanol production from three feedstocks and two fermentation waste reutilization schemes, J. Clean. Prod. 143 (2017) 973–979. doi:10.1016/j.jclepro.2016.12.024.

[28] B. Gilani, P.R. Stuart, Life cycle assessment of an integrated forest biorefinery: hot water extraction process case study, Biofuels, Bioprod. Bioref. 9 (2015) 677–695. doi:10.1002/bbb.

[29] P. Gullón, B. Gullón, I. Dávila, J. Labidi, S. González-García, Comparative environmental Life Cycle Assessment of integral revalorization of vine shoots from a biore fi nery perspective, Sci. Total Environ. 624 (2018) 225–240.

doi:10.1016/j.scitotenv.2017.12.036.

[30] G.A. Maul, Y. Kim, A. Amini, Q. Zhang, T.H. Boyer, Efficiency and life cycle environmental impacts of ion-exchange regeneration using sodium , potassium , chloride , and bicarbonate salts, Chem. Eng. J. 254 (2014) 198–209. doi:10.1016/j.cej.2014.05.086.

[31] C. Li, K. Lun, X. Yang, C. Sze, K. Lin, Bio-re fi nery of waste streams for green and e ffi cient succinic acid production by engineered Yarrowia lipolytica without pH control, Chem. Eng. J. 371 (2019) 804–812. doi:10.1016/j.cej.2019.04.092.

[32] AspenTech, AspenTech, (n.d.). https://www.aspentech.com/products/engineering/aspen-plus/.

[33] F. Piccinno, R. Hischier, S. Seeger, C. Som, From laboratory to industrial scale: a scale-up framework for chemical processes in life cycle assessment studies, J. Clean. Prod. 135 (2016) 1085–1097. doi:10.1016/j.jclepro.2016.06.164.

[34] F. Piccinno, R. Hischier, S. Seeger, C. Som, Predicting the environmental impact of a future nanocellulose production at industrial scale : Application of the life cycle assessment scale-up framework, J. Clean. Prod. 174 (2018) 283–295. doi:10.1016/j.jclepro.2017.10.226.

[35] F.G. Fermoso, A. Serrano, B. Alonso-Fariñas, J. Fernández-Bolaños, R. Borja, G. Rodríguez-Gutiérrez, Valuable Compound Extraction, Anaerobic Digestion, and Composting : A Leading Biorefinery Approach for Agricultural Wastes, J. Agric. Food Chem. 66 (2018) 8451–8468. doi:10.1021/acs.jafc.8b02667.

[36] Procecam, PROCECAM, (n.d.). http://procecam.es/.

[37] F.S. Ferro, D.A. Lopez Silva, F. Hideyoshi Icimoto, F.A. Rocco Lahr, S. González-garcía, Environmental Life Cycle Assessment of industrial pine roundwood production in Brazilian forests, Sci. Total Environ. 640–641 (2018) 599–608. doi:10.1016/j.scitotenv.2018.05.262.

[38] C. Turner, P. Turner, G. Jacobson, K. Almgren, M. Waldeba, E.N. Karlsson, K.E. Markides, Subcritical water extraction and b -glucosidase-catalyzed hydrolysis of quercetin glycosides in onion waste, Green Chem. 8 (2006) 949–959. doi:10.1039/b608011a.

[39] M. Machavarapu, M.K. Sindiri, M. Vangalapati, Optimization of physico-chemical parameters for the extraction of flavonoids and phenolic components from the skin of Allium cepa, Int. J. Innov. Res. Sci. Eng. Technol. 2 (2013) 3125–3129.

[40] L. Corell, S. Armenta, F.A. Esteve-turrillas, M. De Guardia, Flavonoid determination in onion, chili and leek by hard cap espresso extraction and liquid chromatography with diode array detection, Microchem. J. 140 (2018) 74–79. doi:10.1016/j.microc.2018.04.014.

[41] A. Fajardo-Romero, Á. Arroyo-Rivera, J.S. Ramírez-Navas, Extraction of total flavonoids of the outer peel of red onion (Allium Cepa), UGCiencia. 22 (2016) 119–126. doi:10.18634/ugcj.22v.1i.599.

[42] EFSA Panel on Contaminants in the Food Chain (CONTAM), Scientific Opinion on the evaluation of the substances currently on the list in the Annex to Commission Directive 96 / 3 / EC as acceptable previous cargoes for edible fats and oils – Part I of III, EFSA J. 9 (2011) 1–61. doi:10.2903/j.efsa.2011.2482.

[43] R.K. Sinnott, G. Towler, Chemical Engineering Design, 5th ed., 2009.

[44] A.J. Braz De Oliveira, R.A. Correia Gonçalves, T. Perez Cantuaria Chierrito, M. Müller dos Santos, L. Mera de Souza, Structure and degree of polymerisation of fructooligosaccharides present in roots and leaves of Stevia rebaudiana (Bert .) Bertoni, Food Chem. 129 (2011) 305–311. doi:10.1016/j.foodchem.2011.04.057.

[45] E. Moreno Ruiz, L. Valsasina, F. Brunner, A. Symeonidis, D. FitzGerald, K. Treyer, G. Bourgault, G. Wernet, Documentation of changes implemented in the ecoinvent database v3.5, Zürich, Switzerland, 2018.

[46] R. Dones, C. Bauer, R. Bolliger, B. Burger, M. Faist-Enmenegger, R. Frischknecht, T. Heck, N. Jungbluth, A. Röder, M. Tuchschmid, Life cycle inventories of energy systems: results fro current systems in Switzerland and other UCTE countries. Ecoinvent report Nº5., Dübendorf, Swizerland, 2007.

[47] Red Eléctrica de España, Avance del informe del Sistema Eléctrico Español, (2017). www.ree.es/sites/default/files/downloadable/avance_informe_sistema_electrico_2017.pdf (accessed September 20, 2009).

[48] M. Pizzol, A. Laurent, S. Sala, B. Weidema, F. Verones, C. Koffler, Normalisation and

weighting in life cycle assessment: quo vadis ?, Int. J. Life Cycle Assess. (2017) 853–866. doi:10.1007/s11367-016-1199-1.

[49] A. Azapagic, Life cycle assessment and its application to process selection , design and optimisation, Chem. Eng. Journalj. 73 (1999).

[50] J.B. Guinée, M. Gorrée, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, L. van Oers, A.W. Sleeswijk, S. Suh, H.A.U. de Haes, Handbook on Life Cycle Assessment - Operational Guide to the ISO Standards, 2002.

[51] P. Consultants, SimaPro Database Manual - Methods Library, (2019). https://support.simapro.com/articles/Manual/SimaPro-Methods-manual.

[52] R. Frischknecht, N.J. Editors, H. Althaus, C. Bauer, G. Doka, R. Dones, R. Hischier, S. Hellweg, T. Köllner, Y. Loerincik, M. Margni, Implementation of Life Cycle Impact Assessment Methods, (2007).

[53] Carbosynth, Carbosynth, (n.d.). https://www.carbosynth.com/.

[54] B. Kumar, K. Smita, B. Kumar, L. Cumbal, G. Rosero, Microwave-Assisted Extraction and Solid-Phase Separation of Quercetin from Solid Onion (Allium cepa L .), Sep. Sci. Technol. 49:16 (2014) 2502–2509. doi:10.1080/01496395.2014.933982.

[55] M. Rutkowska, K. Dubalska, P. Konieczka, J. Mamiesnik, Microextraction Techniques Used in the Procedures for Determining Organomercury and Organotin Compounds in Environmental Samples, Molecules. (2014). doi:10.3390/molecules19067581.

[56] J. Laguerre, V. Tauzin, E. Grenier, Hot air and microwave drying of onions : A comparative study, Dry. Technol. 17 (1999) 1471–1480. doi:10.1080/07373939908917629.