Industrial Crops & Products 171 (2021) 113836

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Techno-economic assessment of subcritical water hydrolysis process for sugars production from brewer's spent grains

William Gustavo Sganzerla [a], Giovani Leone Zabot [b], Paulo César Torres-Mayanga [c], Luz Selene Buller [a], Solange I. Mussatto [d,*], Tânia Forster-Carneiro [a]

[a] School of Food Engineering (FEA), University of Campinas (UNICAMP), Monteiro Lobato St., n. 80, 13083-862, Campinas, SP, Brazil

[b] Laboratory of Agroindustrial Processes Engineering (LAPE), Federal University of Santa Maria (UFSM), Sete de Setembro St., Center DC, 1040, 96508–010, Cachoeira do Sul, RS, Brazil

[c] Professional School of Engineering in Food Industries, Department of Engineering, National University of Barranca, Barranca, Lima, Peru

[d] Department of Biotechnology and Biomedicine, Technical University of Denmark, Søltofts Plads, Building 223, 2800, Kongens Lyngby, Denmark

A R T I C L E I N F O

Keywords:
Flow-through hydrolysis reactor
Brewer's spent grains
Biorefinery
Subcritical water technology
Scale-up
Techno-economic analysis

A B S T R A C T

Breweries generate a high amount of brewer's spent grains (BSG), which is a valuable feedstock for industrial applications. In the current study, a techno-economic assessment of the flow-through subcritical water hydrolysis reactor to produce sugars from BSG was performed. Simulations were done for a sequential hydrolysis process in three-extractor vessels of 10 L (pilot-plant) and 500 L (industrial-plant), coupled or not to a separation system. The sugar separation system was composed of a five-zone simulated moving bed (SMB) process. A study on the cost of manufacturing (COM), profitability indicators, and sensitivity analysis was conducted to verify the project feasibility. Moreover, the mass and energy balance of the industrial process was accomplished to evidence the main operational parameters. Simulation results indicated that the scale-up process from pilot to industrial scale reduced the COM by approximately 80 %. In the process coupled with the SMB separation system, arabinose and galactose represented 83.68 % of the costs for sugars separation. Arabinose COM decreased from 64.10 USD kg^{-1} in pilot-plant to 7.22 USD kg^{-1} in industrial-plant. The implementation of a separation system recovering six sugars with high added-value can be an advantage in the industrial-plant process when comparing to the process without SMB process, which produces a single hydrolysate fraction with low commercial value. Finally, the integrated subcritical water hydrolysis of BSG coupled with a separation system can be a promising alternative to produce different concentrated sugars in a biorefinery concept.

1. Introduction

The biorefinery concept is based on the integral conversion of agro-industrial residual biomass into innovative value-added products, minimizing environmental impacts, and maximizing renewable resources (Dragone et al., 2020). Therefore, it is possible to design industrial arrangements for waste valorization integrating bioenergy, biomaterials, and active compounds production towards sustainable growth of the bioeconomy (Ioannidou et al., 2020; Ubando et al., 2020). From the biorefinery concept, waste generated during the processing should be used as raw material to produce innovative products. Notwithstanding, there are environmental, economic, and commercial interests related to the use of biomass from agro-industrial processes since lignocellulosic residues can be converted into new products, which decrease the volume of residues improperly disposed (Campos et al., 2020; Ubando et al., 2020).

Nowadays, conventional sugar processing involves complex and distinct unit operations with high energy and chemicals demand. The process can be summarized in raw material processing into raw sugar and then into refined sugar. In the example of sugar cane, a thousand (1000) tons of feedstock produces a hundred (100) tons of refined sugar with an efficiency of only 10 % (El-Haggar, 2007). The electric energy demand is around 440,000 kW h per ton of raw material, which affects the final price of sugar and the greenhouse gas (GHG) emissions (El-Haggar, 2007). In such cases, innovative processes may represent a suitable opportunity to strengthen the economic position of this bioeconomy sector in a biorefinery concept.

Notwithstanding, the use of lignocellulosic materials from agro-

* Corresponding author.
E-mail addresses: smussatto@dtu.dk, solangemussatto@hotmail.com (S.I. Mussatto).

https://doi.org/10.1016/j.indcrop.2021.113836
Received 4 April 2021; Received in revised form 13 July 2021; Accepted 14 July 2021
Available online 23 July 2021
0926-6690/

industrial waste can be a promising alternative to sugar production. In the case of the breweries, brewer's spent grains (BSG) are the main lignocellulosic waste generated (Mussatto et al., 2006). The amount of BSG produced by brewing in Brazil is estimated at 2.8 × 10^6 ton y^{-1} (in wet weight) (Sganzerla et al., 2021), with an average production of 20 kg per 100 L of beer (Mussatto et al., 2013). The lignocellulosic material generated by the brewery is destined to landfills, animal feed, or incinerated to produce heat, a fact that affects GHG emissions (Lynch et al., 2016). From an environmental perspective, the reduction of GHG emissions is an advantage when conducting a better destination of solid residues, driving a sustainable production that addresses affordability, accessibility, sustainability, and equity (Dragone et al., 2020; Campos et al., 2020; Ioannidou et al., 2020).

Nonetheless, one of the limiting steps in the depolymerization of lignocellulosic materials is the hydrolysis of cellulose, hemicellulose, and lignin into monosaccharides and disaccharides (Zhang et al., 2020). Recently, several pretreatments (i.e., acid, alkaline, enzymatic, mechanical, and chemical hydrolysis) have been used to promote the rupture of the lignocellulosic material structures (Kamusoko et al., 2019). However, conventional pretreatments have high costs and generate contaminants after the hydrolysis process, requiring additional steps for the post-treatment of the residue generated, resulting in a non-profitable process for industrial implementation (Cheah et al., 2020). Thereby, emerging eco-friendly technologies with low GHG emissions for the recovery of sugars from agro-industrial waste are arising (Freitas et al., 2021), such as subcritical water hydrolysis (SWH) in flow-through reactor (Lachos-Perez et al., 2020; Oliveira et al., 2020; Abaide et al., 2019a). Through the subcritical system, various chemicals and bioproducts can be produced using water as a solvent. Subcritical conditions can be reached when the water is submitted to temperatures between 100 and 374 °C and pressures up to 20 MPa (Abaide et al., 2019b). Under the conditions mentioned above, the solubility of hydrophobic organic species is significantly increased, which contributes to biomass fractionation into fermentable sugars (Torres-Mayanga et al., 2019).

Previous studies demonstrated the laboratory production of sugars from lignocellulose biomass through SWH in flow-through reactor (Lachos-Perez et al., 2020; Torres-Mayanga et al., 2019; Abaide et al., 2019a; Lachos-Perez et al., 2018; Mayanga-Torres et al., 2017). For instance, orange (*Citrus sinensis*) peel (Lachos-Perez et al., 2020a), sugarcane (*Saccharum officinarum*), bagasse (Zhang et al., 2020), olive (*Olea europaea*), oil pomace (Manzanares et al., 2020), and rice (*Oryza sativa*) husk (Abaide et al., 2019a) were used to produce hydrolysates with high sugar content. Sugars produced from SWH of biomass can be used as a substrate for fermentation processes to produce second-generation ethanol (Oliveira et al., 2020) or other platform chemicals (Abaide et al., 2019a; Zabot et al., 2018), making SWH a promising technology to industrial implementation in a biorefinery concept. From an industrial perspective, Lachos-Perez et al. (2020b) provided a novel economic evaluation related to using SWH technology to produce flavanones and sugars from orange peel, demonstrating that the implementation of industrial-scale reactors decreases the manufacturing costs and can be feasible for future implementation. Nonetheless, there are significant technical and economic challenges before the full implementation of SWH process in biorefineries at industrial scale.

A previous study optimized sugar production from BSG under subcritical water conditions (Torres-Mayanga et al., 2019). The findings obtained in the laboratory-scale flow-through reactor provided new insights into the hydrolysis of BSG and recovery of sugars. However, the scale-up project based on economic evaluation should be the next step before the industrial implementation. Based on simulation studies, the industry can observe the main challenges of industrial plants for a real application, especially regarding the cost of manufacturing (COM). Also, COM values should be examined to understand the cost behavior on a laboratory scale considering the current market conditions. The state of the art of subcritical technology is not entirely elucidated for industrial scale. Consequently, simulation studies may be an alternative to demonstrate the most profitable theoretical routes.

Accordingly, to increase the possibility of finding new technological routes for breweries, SWH can be a promising technology to support an integrated biorefinery, especially to convert BSG lignocellulosic biomass into sugars. In an industrial perspective, a technical point of view should be accompanied by the economic study, which contributes to elucidate some bottlenecks to industrial implementation. In this study, a process based on SWH in flow-through reactor was designed and scaled-up for sugar production from BSG. Additionally, techno-economic assessment, mass, and energy balances were performed to elucidate the novelty presented herein. Finally, considering that external conditions can cause moderate changes in the absolute values, a sensitivity analysis was conducted to exam the uncertainty in simulated data.

2. Materials and methods

2.1. Process description and operational parameters

Torres-Mayanga et al. (2019) designed a flow-through hydrolysis reactor to produce hemicellulose sugars from BSG. A reactor with tubular geometry with an internal volume of 110 mL was constructed. The reactor was heated by a heating jacket to operate at a maximum temperature of 400 °C. A high-pressure liquid pump was used for pressurization and liquid pumping, which allows us to operate at a maximum pressure of 40 MPa. A filter with 2 μm pores was positioned at the outlet of the reactor to minimize particle spillover. The hot effluent exiting the hydrolysis reactor was cooled in a tube heat exchanger coupled to a recirculating bath to obtain a hydrolysate temperature lower than 27 °C. The laboratory process developed was not coupled with a separation system, and the sugars were obtained in the same fraction (called as hydrolysate). Aiming to simulate an industrial sugar-production process, a five-zone simulated moving bed (SMB) process was coupled in the process to obtain liquid isolated sugars. Xie et al. (2005) developed an SMB process based on poly-4-vinyl pyridine (PVP) to recover sugars from biomass hydrolysates, which allows isolating in a liquid fraction six sugars and four impurities (Xie et al., 2005). In better words, the five-zone non-isocratic SMB process may achieve high multicomponent separation of sugars, reaching a processes' yield of 94 % (Xie et al., 2005). The sugars purities can range from 93 to 95 % (Xie et al., 2005). Based on the aforementioned processes, Fig. 1**(a)** demonstrates the laboratory SWH process designed without the SMB separation system, and Fig. 1**(b)** shows the SWH process coupled with a SMB separation system.

The laboratory-scale hydrolysis of BSG was performed under the following conditions: temperature of 140–210 °C; water flow rates of 10 and 20 mL min^{-1}; solvent/feed (S/F) ratio of 64, 80, and 112 (w/w); constant pressure of 15 MPa; and 5 g of raw material (Torres-Mayanga

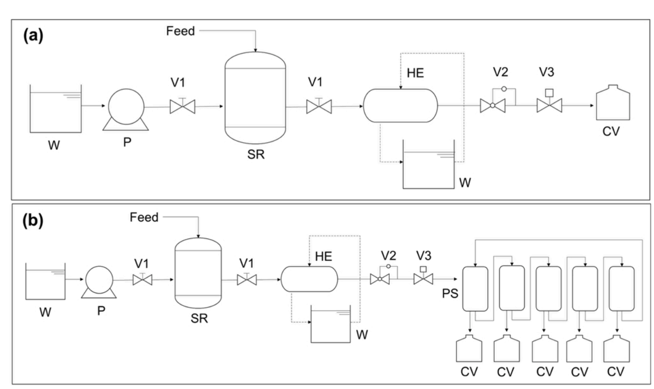

Fig. 1. Laboratory-scale diagram of the subcritical water unit: (a) process without sugar separation (SWH); and (b) process coupled with a SMB system for sugar separation (SWH-P).

et al., 2019). Based on the most suitable operational condition to obtain the highest sugar yield, a hydrolysis temperature of 160 °C, the water flow of 10 mL min^{-1}, and S/F of 112 g solvent g^{-1} feed was used in the SWH process. These data were used to simulate the scale-up process to sugars production in a pilot-plant and industrial-plant.

For the scale-up process, pilot (3 × 10 L) and industrial-scale (3 × 500 L) hydrolysis vessels were considered. Table 1 demonstrates the base costs for each part of the subcritical water process. The adoption of three hydrolysis vessels was based on the fast feedstock residence time inside the reactor. The simulation was based on a process without the SMB separation system (coded as SWH), and a process coupled with the SMB separation system (coded as SWH-P), in accordance with Torres-Mayanga et al. (2019) and Xie et al. (2005). In the SWH process, the final product is a single hydrolysate composed of five sugars. Otherwise, in the SWH-P process, the final products are six different hydrolysates, composed of one isolated sugar per hydrolysate.

Beyond, an additional assumption in the present scale-up analysis is based on the process simulation with low S/F. In industrial projects, it is most suitable to use low S/F instead of high S/F, since high S/F impacts process instrument performance, such as pumping and heat exchanger efficiency (Hatami et al., 2020). When using S/F of 112 g solvent g^{-1} feed (used in the laboratory-scale experiments), the water demand on an industrial scale is not suitable for real implementation. Based on the concern that in an industrial plant, low S/F is required, the scale-up process was accomplished with an S/F of 4 g solvent g^{-1} feed, and the flow conditions were adjusted to maintain a properly subcritical reactor configuration. The assumption to decrease the S/F from 112 (laboratory process) to 4 g solvent g^{-1} feed (industrial process) is based on a mandatory parameter's optimization from the technical point of view for an industrial process. Additionally, the selection of S/F around 4 g solvent g^{-1} feed is supported by other studies (Abaide et al., 2019a, Abaide et al., 2019b; Santos et al., 2020; Vedovatto et al., 2021a, b). For instance, Abaide et al. (2019a) tested S/F values of 15 and 7.5 g solvent g^{-1} feed and concluded that higher yields were obtained when using the lowest S/F. Vedovatto et al. (2021a) concluded that lower water flow rates returned higher yields of sugars because the solvent could reach the desired temperature more rapidly in the flow-through reactor, and the residence time was sufficient for having a substantial dissociation of hemicellulose and cellulose.

2.2. Simulation flowsheet and Gantt chart

The simulation flowsheet and Gantt chart were performed using SuperPro Designer 9.0® software (Intelligen Inc., Scotch Plains, NJ, USA). The flowsheet was designed to represent the industrial process without the SMB separation system (SWH) (Fig. 2**(a)**), and the same process coupled with the SMB separation system (SWH-P) (Fig. 2**(b)**). For representation purposes, the Gantt charts for SWH and SWH-P were designed (Fig. 3**).** In this study, the scale-up project was simulated with three hydrolysis vessels and one separation vessel. The flowsheet also contains cooler, mixers, splitter pumps, and piping. For the SWH process, dried and ground BSG was loaded in the SWH vessel (P − 4/H−101, P − 5/H−102, or P − 6/H−103). Water was pumped (P − 1/PP − 101), heated (P − 2/HE−101), and split to the subcritical reactors. After the hydrolysis condition is reached in the extraction vessel, the liquid was cooled (P − 8/HX−102) to a temperature lower than 27 °C. A pressure valve was used in the process (P − 9/GTV−101), and then, the liquid phase containing the hydrolysate was collected (P − 10/V−102). For the SWH-P process (Fig. 2**(b)**), the same method previously mentioned was adopted. After the pressure stabilization (P − 9/GTV−101), the hydrolysate was submitted to a five-zone non-isocratic SMB process (separation system) to produce different fractions of sugars. Five vessels were selected to promote the hydrolyzed sugars circulation and separation. The individual recovery of arabinose, galactose, glucose, xylose, fructose, and sucrose was obtained with an operational time of 46.8 min per zone of the SMB process. In this simulation, it was assumed that six sugars were isolated in a separation system composed of five-zones, optimized by Xie et al. (2005) and adjusted to the current process. The adoption of the mentioned process has been chosen due to the operational parameters described in the literature (Xie et al., 2005), and the possibility to obtain a similar process on a commercial scale[1] with separation zones adjusted to each process.

2.3. Economic assessment

The economic assessment was performed using SuperPro Designer 9.0® software (Intelligen Inc., Scotch Plains, NJ, USA). For evaluating the profitability parameters, the selling price of non-concentrated sugars was estimated as 3 USD kg^{-1} (Lachos-Perez et al., 2020b), based on the worldwide average selling price. For individual sugars after separation, the selling price was calculated based on a final product with a commercial-grade higher than 90 % purity. The selling price of concentrated sugars was estimated based on the worldwide average selling price of isolated and purified sugars[2] : 59 USD kg^{-1} for arabinose; 21 USD kg^{-1} for galactose; 9 USD kg^{-1} for xylose; 1.2 USD kg^{-1} for glucose and sucrose; and 4.4 USD kg^{-1} for fructose. These values were used to simulate the profitability parameters related to all of the processing scales evaluated in this study. For all the different scales, both labor and production shifts were adequately addressed. Table 2 shows the parameters used for techno-economic simulation.

2.3.1. Itemized cost estimation

Laboratory equipment installation cost was obtained by the market price. For the scaled-up process (pilot and industrial scale), implementation costs were calculated considering the equipment cost and equipment attribute, as shown in Eq. 1 (Turton et al., 2003).

$$C_2 = C_1 \times \left(\frac{A_2}{A_1}\right)^M \tag{1}$$

where: C_1 is the reference cost; C_2 is the adjusted cost for the proposed process; A_1 is the reference equipment production capacity; A_2 is the related production capacity; and "M" is a cost parameter collected in the literature to each equipment (Turton et al., 2003).

In addition, to consider the change in equipment cost over time, the chemical engineering plant cost index (CEPCI) was used for the SMB separation system, according to Eq. 2.

$$C_2 = C_1 \times \frac{CEPCI_2}{CEPCI_1} \tag{2}$$

where: C_1 is the reference cost obtained from 2005; C_2 is the adjusted cost for the proposed process in 2020; $CEPCI_1$ and $CEPCI_2$ were estimated based on the chemical engineering plant cost index, where $CEPCI_2$ /$CEPCI_1$ ratio was considered as 6.

The five major components of the cost of manufacturing (COM) were determined based on the sum on the main components in the process (direct costs, fixed costs, and general expenses), according to the method described by Turton et al. (2003) (Eq. 3).

$$COM = 0.304 \times FCI + 2.73 \times COL + 1.23 \times (CUT + CWT + CRM) \tag{3}$$

where: FCI is the fixed capital investment; COL is the cost of operational labor; CUT is the cost of utilities; CWT is the cost of waste treatment; and CRM is the cost of raw material (CRM). All the costs were normalized per year of investment to determine the COM. FCI is related to expenses involved in the implementation of the production unit. CRM consists of the costs required to prepare the raw material and the costs of chemicals.

[1] Novasep, Purification processes for cellulosic sugars. Available at www.novasep.com

[2] Gold Biotechnology. Available at: https://www.goldbio.com/

Table 1
Base costs to each part of the subcritical water process for sugar production from brewer's spent grains.

Component	M [a]	Unit base cost (USD)	Num.	Total base cost (USD)		
				Laboratory plant	Scale-up (3 × 10 L)	Scale-up (3 × 500 L)
HPLC pump	0.55	3,846.00	1	3,846.00	45,945.53	395,072.50
Manometer	0.00	93.33	6	560.00	560.00	560.00
Structural material	0.40	836.67	1	836.67	5,081.54	24,298.72
Exchange heat	0.59	1,116.67	1	1,116.67	15,977.24	160,654.97
Blocking valve	0.40	91.67	9	825.00	5,010.68	23,959.89
Micrometric valve	0.40	260.25	1	260.25	1,580.63	7,558.21
Backpressure valve	0.40	656.24	1	656.24	3,985.71	19,058.72
Temperature controller	0.60	33.33	3	100.00	1,496.80	15,651.15
Control panel	0.60	533.33	1	533.33	7,982.94	83,472.83
Jacketed extraction-hydrolysis vessel	0.82	500.00	3	1,500.00	60,554.90	1,497,285.64
Piping, connectors, crossheads, and splitters	0.60	314.43	1	314.43	4,706.44	49,212.45
Sugar separation system (Five-Zone PVP SMB)	0.60	38,335.83	1	38,335.83	573,811.50	6,000,000.00
Total SWH plant cost (USD)				10,548.59	152,882.43	2,276,785.09
Total SWH-P plant cost (USD)				48,884.42	726,693.93	8,276,785.09

[a] M constant depending on equipment type; SWH, Subcritical water hydrolysis plant without sugar separation; SWH-P, Subcritical water hydrolysis plant coupled with sugar separation in a SMB system.

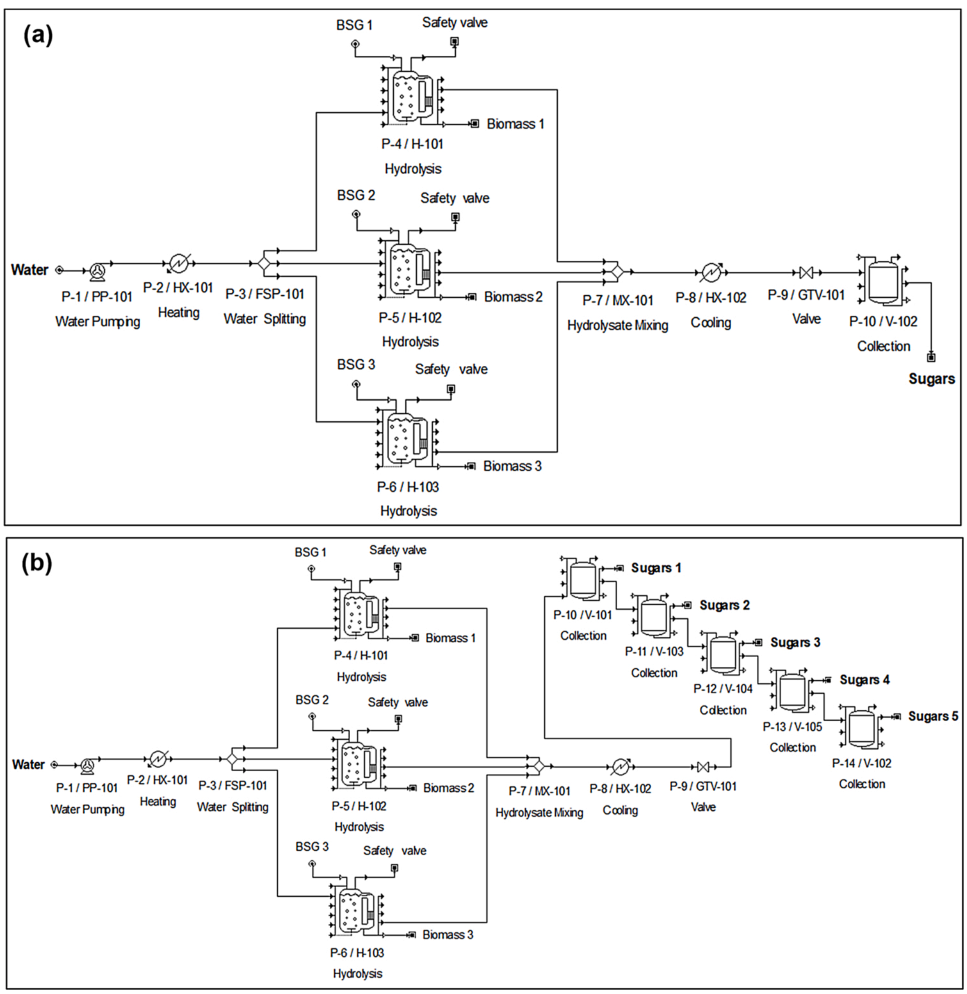

Fig. 2. Simulation flowsheet designed for sugar production and separation using subcritical water hydrolysis of brewer's spent grains: (a) SWH and (b) SWH-P.

COL is related to operators (number and wage) of the unit. CUT considers the energy and cleaning water used in the process, among others. CWT is the residue generated by this process, considered as zero in this study. In this study, more operators were used in the process with separation because this operation requires more activities and control. Consequently, the total cost of operating labor is higher for the SWH-P process. Beyond, in terms of the increase in process size, the same required labor was maintained, assuming similar handling of the processes, with mechanical loading and unloading of reaction vessels.

2.3.2. *Project feasibility*

Gross profit (USD year^{-1}), annual operating cost (USD year^{-1}), and main revenue (USD year^{-1}) were estimated to SWH and SWH-P processes. To evaluate the feasibility of the proposed scenarios, gross

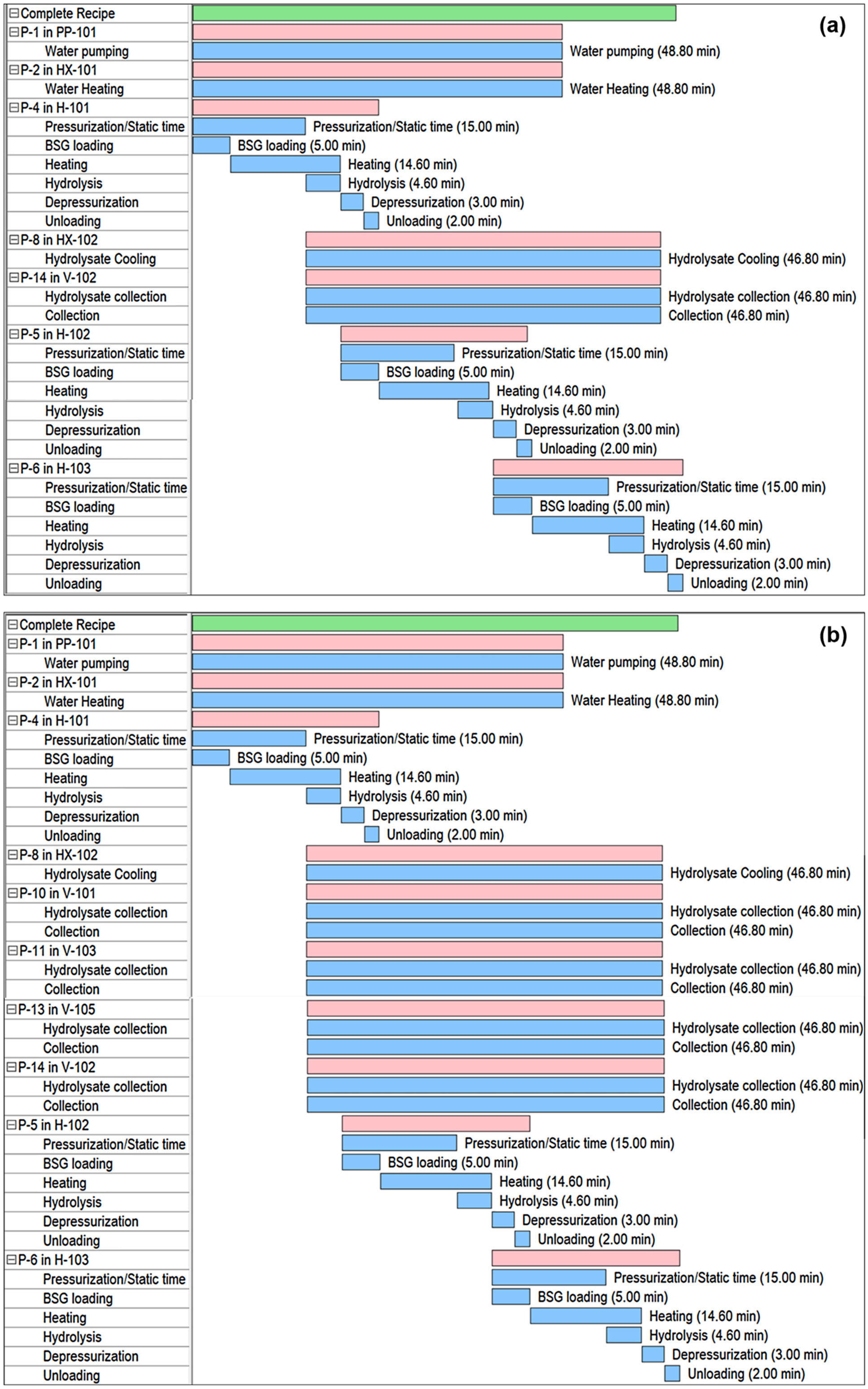

Fig. 3. Gantt chart designed for sugar production and separation using subcritical water hydrolysis of brewer's spent grains: (a) SWH and (b) SWH-P.

margin (GM), return on investment (ROI), the yearly rate of return (ROR), net present value (NPV), and payback time were evaluated for the project implementation. These parameters are the most common indicators to assess the profitability of a new project. GM is the difference between revenue and cost of goods sold. NPV is the sum of the projected discounted cash flows minus the initial investment. ROI measures the return on each unit of money invested in the project, indicating the investment cost-benefit. Yearly ROR is computed by looking at the value of an investment at the end of one year and comparing it to the value at the beginning of the same year. Payback time is the number of years to recover the initial investment. As soon as the investment is recovered, the project is profitable. Payback occurs at the moment when the sum of the terms of the cash flow is positive.

Table 2
Input economic parameters used for the economic simulation in the SuperPro Designer 9.0® software.

Parameters	Scale-up plants		Unit
	3 × 10 L	3 × 500 L	
BSG	10.00	8.00	USD ton^{-1}
SWH plant cost	152,882.43	2,277,000.00	USD
SWH-P plant cost	726,693.93	8,277,000.00	USD
Water (process)	2.00	2.00	USD ton^{-1}
Water (cooling)	0.10	0.05	USD ton^{-1}
Steam	12.00	4.00	USD ton^{-1}
Electric energy	0.20	0.20	USD kWh^{-1}
Wage (with benefits)	8.00	8.00	USD wage $^{-1}$ h^{-1}
Workers per shift (SWH process)	1	1	workers shift^{-1}
Workers per shift (SWH-P process)	4	4	workers shift^{-1}
Operational time	7920	7920	h year $^{-1}$
Apparent density	0.50	0.50	kg BSG L^{-1} reactor
S/F	4	4	g water g^{-1} BSG
Project lifetime	25	25	year
Inflation	4	4	% year^{-1}
Low NPV interest	7	7	%
Depreciation period	15	15	year
Loan period for equipment	12	12	year
Loan interest for equipment	6	6	% year^{-1}
Loan	100	100	%

BSG, brewer's spent grains; SWH, Subcritical water hydrolysis plant without sugar separation; SWH-P, Subcritical water hydrolysis plant with sugar separation system; S/F, solvent mass to feed mass ratio (kg solvent kg^{-1} feed); NPV, net present value.

2.3.3. Sensitivity analysis

A sensitivity analysis was accomplished to evaluate the effects of price uncertainties in the profitability analysis of the best economic scenarios, with a range of ±50 % of the established prices. In this study, the SWH-P implementation cost can be a representative factor in the project feasibility. For SWH-P, the price of SMB separation system can affect the project feasibility since it is a high implementation cost. The cost of raw material (BSG) is a parameter with high uncertainties since each brewery designates the content to an appropriate destination, with a fluctuation in the selling price. Otherwise, the number of wages is a difficult factor to estimate since it is possible to develop a process with high automation or manual working.

2.4. Mass and energy balance

To evaluate the main technical parameters of the SWH-P implementation, a mass and energy balance was fulfilled with the industrial proposed process. For sugar production and separation, the balance considers input, output, generation, consumption, and accumulation. Energy balance was used to identify and quantify the energy consumption, accumulation, transformation to another form, and energy loss in the process (Sandler, 2017). A theoretical steady-state design of SWH-P was provided based on the technological route established, considering the separation process and all the parameters used in the simulation. Initially, the mass balance was defined according to Eq. 4, assuming a steady-state process, in which the accumulation is null.

$$\text{input} - \text{output} + \text{generation} - \text{consumption} = 0 \tag{4}$$

In the SMB separation system, the mass fractions are isolated into a stream of water, impurities, and isolated sugars (Eq. 5). Mass fractions were established based on experimental and simulated conditions.

$$M_7 = \sum_{i=8}^{i=15} M_i \tag{5}$$

For energy balance in the subcritical reactor, the first law of Thermodynamics was adopted at a steady-state, with constant pressure and without shaft work. The variation in kinetic and potential energy was neglected. Thus, the energy balance was expressed according to Eq. 6.

$$\sum M_k(H) + Q = 0 \tag{6}$$

Considering the mass constant in the process ($M_{R1} = M_{R2}$ = constant), the heat required in the subcritical reactor (Q) is the difference of enthalpy (H) (Eq. 7):

$$\frac{Q}{M} = H_2 - H_1 \tag{7}$$

Besides, the enthalpy can be calculated based on the specific heat of the mixture in the reactor. For this, the mass of water >> mass of BSG was considered, and then, it was possible to use the specific heat of water (C_p^*), which is 4.178 kJ kg^{-1} K^{-1} at 25 °C and 4.285 kJ kg^{-1} K^{-1} at 160 °C (Sandler, 2017). In the current process, the pressure was considered constant since a pressure pump was used to regulate it during hydrolysis. In addition, the subcritical reactor maintains the pressure constant along the time and increases the temperature of water from 25 °C to 160 °C. Thus, enthalpy was calculated based on Eq. 8.

$$H\left(\frac{kJ}{kg}\right) = C_p^*\left(\frac{kJ}{kg\ K}\right) \times T(K) \tag{8}$$

3. Results and discussion

3.1. Previous laboratory studies

In the subcritical state, water is a promising solvent for biomass depolymerization. Due to the high hemicellulose content (approximately 40 %) in BSG, the use of a subcritical state may suggest the BSG as a potential source of sugars. Under laboratory-scale studies, a flow-through hydrothermal treatment was optimized for the hydrolysis of BSG (Torres-Mayanga et al., 2019). Total sugars production was 45.2 g kg^{-1} BSG, and the individual fraction of sugars obtained at the optimal operational condition was: 31.3 g arabinose kg^{-1} BSG; 1.5 g galactose kg^{-1} BSG; 2.1 g glucose kg^{-1} BSG; 8.7 g xylose kg^{-1} BSG; 1.6 g fructose kg^{-1} BSG; and 1.4 g sucrose kg^{-1} BSG. Also, in the SWH process, one impurity (8 g furfural kg^{-1} BSG) and two organic acids (3.7 g formic acid kg^{-1} BSG and 6.1 g acetic acid kg^{-1} BSG) were generated. Consequently, the focus of this study has been put on the production and isolation of sugars.

Generally, from the results obtained by Torres-Mayanga et al. (2019), the reducing sugars increase with hydrolysis temperature increase, independently of flow rate. However, with the S/F effect and mild hydrolysis conditions (160 °C), a minor impact on reducing sugars was obtained. The hydrolysis experiment indicated that temperature and S/F are the most important factor governing the carbohydrates hydrolysis contained in BSG. From the individual sugars production, the lowest temperature promoted the highest productivity of arabinose and xylose, which represents 88 % of the total quantified sugar yield.

3.2. Costs analysis

3.2.1. Cost of manufacturing (COM)

For the proposed scale-up study, eight scenarios were simulated with different residences time of BSG inside the subcritical reactor (ranging from 4.4–9.5 min) (Table 3). The S/F of 4 g g^{-1} (fixed-parameter) showed the total carbohydrate production was directly affected by the residence time. Scenario 7 was operated with 4.6 min and 160 °C of hydrolysis temperature and produced 4.36 % of sugars, following the previous laboratory results. In general, scenarios with higher residence time promoted hydrolysate production with a high concentration of active compounds (Hatami et al., 2020, 2019; Zabot et al., 2018). The cost of manufacturing (COM) was calculated at two different production

Table 3
Cost of manufacturing (COM, USD kg^{-1}) for the different scaled-up plants with and without sugar separation.

Scenario	Residence time (min)	Total carbohydrates (%)	COM (USD kg^{-1} sugars)			
			3 × 10 L		3 × 500 L	
			SWH[a]	SWH-P[b]	SWH[a]	SWH-P[b]
1	9.5	2.11	38.98	177.07	6.67	17.08
2	9.3	4.52	18.21	82.22	3.18	8.02
3	9.1	4.41	18.66	83.67	3.33	7.56
4	8.8	4.61	17.87	79.39	3.29	7.96
5	4.8	1.78	35.24	172.43	7.22	17.5
6	4.7	2.50	25.21	122.43	5.27	12.58
7	4.6	4.36	14.49	58.88	2.92	6.63
8	4.4	4.13	15.38	73.33	3.39	7.77

[a] COM calculated based on the production of a single hydrolysate.
[b] COM calculated based on the production of a bulk of isolated sugars.

scales (10 L and 500 L), which were coupled or not with a SMB separation system (SWH and SWH-P). When assessing the influence of SMB separation system in the SWH process, the COM increases up to 3-fold, an expected fact since the implementation cost of SMB process is one of the most representative barriers in the adoption of this technology (Matus et al., 2012). For the SWH process, the COM was determined based on producing a single fraction of hydrolysate. Otherwise, COM of the SWH-P process was related to the production of six isolated sugars, and then additional unit operations are required, affecting the COM (Table 3). Based on the scenarios simulated, the condition established in Scenario 8 was favorable to produce sugars with the lowest COM. For the pilot-plant scale (3 × 10 L) the COM obtained was 14.49 USD kg^{-1} (SWH) and 58.88 USD kg^{-1} (SWH-P), an increase in 4-fold comparing to the adoption of a SMB separation system. On an industrial scale (3 × 500 L), the COM for the SWH process was 2.92 USD kg^{-1}, and with the adoption of SMB separation system, the COM increase to 6.63 USD kg^{-1}. The 50-fold process increase (3 × 10 L to 3 × 500 L), leads to a decrease of approximately 80 % of sugars COM. This fact is a consequence of the scale-up process, corroborating with the literature (Hatami et al., 2020, 2019; Zabot et al., 2018).

3.2.2. *Costs discrimination over the COM*

The contribution of the fixed capital investment (FCI), cost of operational labor (COL), cost of utilities (CUT), and cost of raw material (CRM) discriminated over the COM was determined to evidence the process conditions for the sugar production. Cost's discrimination analysis was conducted with the scale-up plants in all the scenarios tested (Fig. 4). For the 3 × 10 L evaluated scales without the separation system (SWH), the COM contribution was COL > CUT > FCI > CRM, and with the SMB separation process (SWH-P) the contribution was COL > FCI > CUT > CRM. In the 3 × 500 L industrial process, COM contribution for SWH was CUT > FCI > CRM > COL, and for SWH-P was FCI > CUT > COL > CRM.

In the pilot plant (3 × 10 L), the COL was the most expressive in all the scenarios, reaching 50 % in the SWH process and increasing to 70 % in SWH-P. Otherwise, the CUT drastically decreased with the implementation of SMB process, from 25 % (SWH) to 6% (SWH-P). In the industrial-scale plant (3 × 500 L), FCI and CUT were the main costs over the COM. Within the SWH-P adoption on the industrial-scale, the CRM and COL maintain lower than 5% and 15 %, respectively. A decrease was observed comparing the COL for the pilot plant and industrial plant, explained by the high degree of instrumentation in industrial plants. The adoption of automation plants requires a relatively lower number of operators to conduct the process, corroborating with the literature (Viganó et al., 2017; de Aguiar et al., 2020). In addition, the cost profile obtained in this study is related to the highest equipment cost, where the SMB separation system demands high FCI; and, therefore, high energy cost (CUT) due to the high process temperature adopted, which requires high electric energy.

In the current study, CRM was the lowest significant cost over the COM. However, according to the literture, CRM is the component with the maximum contribution to the COM in their study (Osorio-Tobón et al., 2016). In the mentioned study, when the CRM decreased from 7.27 to 1.59 USD kg^{-1}, the COM proportionally reduced from 112.70 to 64.97 USD kg^{-1}, representing a decrease of 42 %. For the proposed process with fast residence time, the amount of feedstock required by the process is too high; however, the market price of BSG can be considered low. Considering that the brewery disposes of the BSG in landfills or animal feeds, this feedstock can be easily implemented in an industrial biorefinery (Sganzerla et al., 2021). In addition, to decrease the COM in

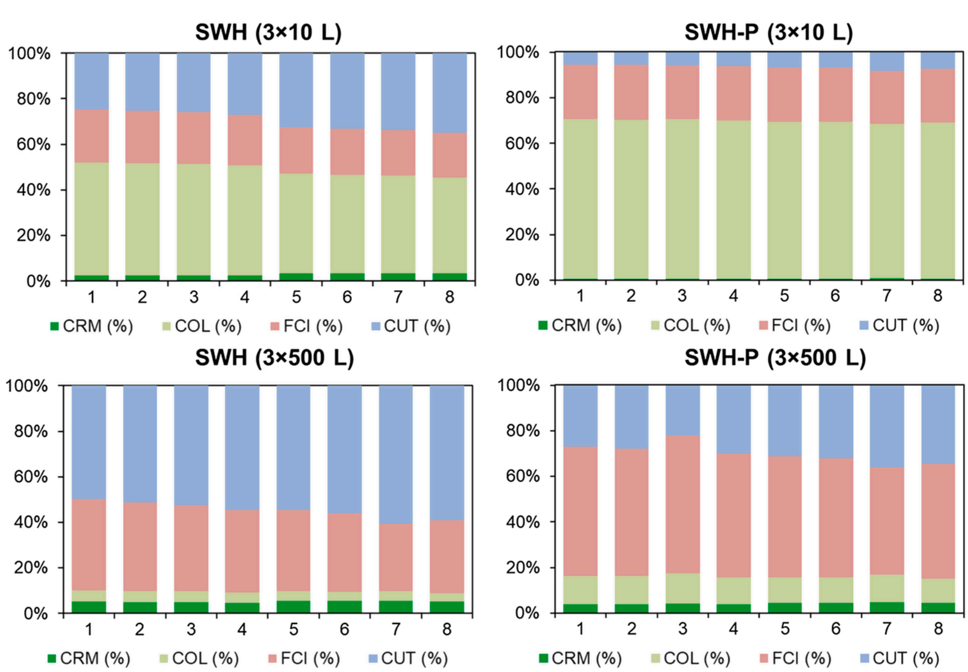

Fig. 4. Contribution of each cost discriminated over the COM to obtain sugars from subcritical water extraction of brewer's spent grains.

the industrial process, an alternative is adopting innovative technologies to increase the recovery of active compounds since higher productivity will decrease the total COM. The adoption of SWH-P decreased the CUT and increased the FCI, an expected fact since the sugars separation system was the most expensive operation.

3.3. Implementation of SMB separation system in SWH

Supercritical technology allows producing a range of active compounds. However, few studies adopted a separation system to isolate the products. As previously mentioned, this simulation was based on a laboratory study that produced sugars by the subcritical process without the sugar's isolation. The individual profile of sugars can be obtained by many analytical techniques; however, the isolation for commercial purposes should be clarified. Thereby, SMB technology can be industrially applied when conventional separation techniques cannot be applied. SMB is a chromatography-based technique that has been successfully used for sugar separation (Azevedo and Rodrigues, 2000). This technology can be operated in a continuous separation method, recovering sugar products from chemical hydrolysates of biomass with a high separation rate (Caes et al., 2013). Then, SMB is a highly efficient separation process with low demand for solvent and energy and a high potential for the separation and isolation of value-added compounds (Lin et al., 2015).

Aiming to address an innovative process to sugars production and separation, a five-zone SMB process was adopted. The SMB process presents a separation performance of 94 %, which means that 6 % of sugars were lost (Xie et al., 2005). Table 4 demonstrates the individual sugar productivity for all the scenarios tested, and considering the theoretical yield (100 %), and the real yield (94 %) in the process. Adopting a yield lower than 100 % represents that it is possible to achieve the sugar concentration obtained in the laboratory-scale; however, the separation process will lose 6% of sugars (Xie et al., 2005). Scenario 7 (with the lowest COM) can produce a maximum of 60.5 % of arabinose, 18.2 % of xylose, 5.2 % of glucose, 3.8 % of sucrose, 3.5 % of fructose, and 2.9 % of galactose for the pilot (3 × 10 L) and industrial plant (3 × 500 L).

In addition, this study focuses on the evaluation of the production of six sugars from BSG. The contribution of each sugar over the COM for the SWH-P can be shown in Fig. 5. This proportion was attributed based on the current market price of each sugar, and then, the contribution cost of each sugar can be related to the final selling price obtained in the market. Arabinose (61.87 %) and galactose (21.18 %) were the sugars most expensive in the market price and then could represent the most expressive in the subcritical process coupled with the separation system. Glucose, fructose, and sucrose were produced in a lower proportion, and

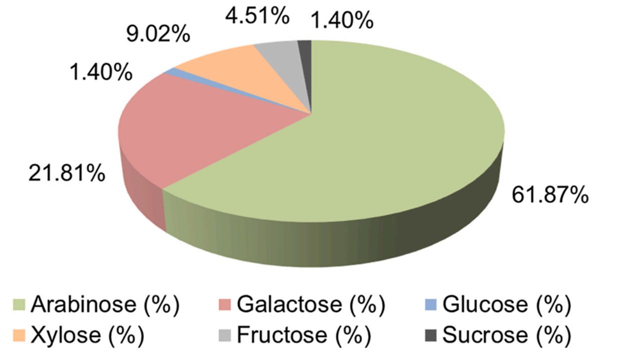

Fig. 5. Percent value of each sugar obtained in the SWH-P processes calculated based on the current market price.

the cost attributed to these sugars represent only 16.32 %. The values estimated over the selling cost were correlated with the market price of each sugar. Arabinose (59 USD kg^{-1}) and galactose (21 USD kg^{-1}) represent 83.68 % based on the sum of all sugars (Fig. 5), in reference to weighted profit. This proportion allows calculating the COM for the SMB separation process, considering 94 % of process' yield for the 3 × 10 L and 3 × 500 L process (Table 5). In the current case (SWH-P), the COM

Table 5
Cost of manufacturing (COM, USD kg^{-1}) for the different scaled-up plants (SWH-P) considering a processes' yield of 94 % and expressed based individual mass of sugar.

Scenario	Arabinose	Galactose	Glucose	Xylose	Fructose	Sucrose
	3 × 10 L (USD kg^{-1} individual sugar)					
1	173.72	1500.14	96.21	113.42	260.63	82.28
2	85.94	622.90	28.80	44.76	120.78	43.12
3	84.75	675.65	29.59	48.40	104.26	82.60
4	133.93	492.31	11.78	24.51	44.95	70.98
5	170.51	1921.78	126.88	96.70	872.26	48.53
6	121.45	1169.78	43.90	77.48	198.25	61.60
7	64.10	468.56	16.86	31.03	81.80	23.20
8	91.48	478.18	17.66	27.46	62.82	374.74
	3 × 500 L (USD kg^{-1} individual sugar)					
1	16.76	144.70	9.28	10.94	25.14	7.94
2	8.38	60.76	2.81	4.37	11.78	4.21
3	7.66	61.05	2.67	4.37	9.42	7.46
4	13.43	49.36	1.18	2.46	4.51	7.12
5	17.31	195.04	12.88	9.81	88.53	4.92
6	12.48	120.20	4.51	7.96	20.37	6.33
7	7.22	52.76	1.90	3.49	9.21	2.61
8	9.69	50.67	1.87	2.91	6.66	39.71

Table 4
Individual sugar productivity for the scenarios tested (SWH-P) scaling 3 × 10 L and 3 × 500 L), considering the theoretical yield (100 %) and the real processes' yield (94 %).

Scenario	Processes' yield	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Fructose (%)	Sucrose (%)
1	100 %	71.4	2.9	2.9	15.9	3.5	3.4
	94 %	67.1	2.7	2.7	15.0	3.3	3.2
2	100 %	67.0	3.3	4.5	18.7	3.5	3.0
	94 %	63.0	3.1	4.2	17.6	3.3	2.8
3	100 %	69.1	3.1	4.5	17.6	4.1	1.6
	94 %	65.0	2.9	4.2	16.6	3.8	1.5
4	100 %	41.5	4.0	10.7	33.1	9.0	1.8
	94 %	39.0	3.7	10.0	31.1	8.5	1.7
5	100 %	70.8	2.2	2.2	18.2	1.0	5.6
	94 %	66.6	2.1	2.0	17.1	0.9	5.3
6	100 %	70.6	2.6	4.4	16.1	3.2	3.1
	94 %	66.3	2.4	4.1	15.2	3.0	3.0
7	100 %	64.3	3.1	5.5	19.4	3.7	4.0
	94 %	60.5	2.9	5.2	18.2	3.5	3.8
8	100 %	56.1	3.8	6.6	27.3	6.0	0.3
	94 %	52.8	3.6	6.2	25.6	5.6	0.3

was calculated based on individual sugar productivity and considering a yield of 94 %. Following the simulation data presented in Table 3, scenario 7 promoted the lowest COM for all individual sugars.

In the tested scales, galactose was the sugar with the highest COM, explained due to the combination of contribution cost of individual sugar in the separation cost (SWH-P) (Fig. 5) with the individual sugar productivity (Table 4). Then, arabinose COM was the second one obtained in the hydrolysis process. For the 3 × 10 L scale in scenario 7, arabinose COM was 64.10 USD kg^{-1}, and in the 3 × 500 L scale, the COM decreased to 7.22 USD kg^{-1}. The results shown in Table 3, arabinose represented up to 60 % in the COM for scenario 7 (SWH-P, 3 × 500 L), which was 6.63 USD kg^{-1}. However, the data presented in Table 3 did not consider 94 % of the SMB separation process. Then, the sum of the COM of Table 5 is different since the last one considered the separation factor and the COM based on the contribution cost of individual sugar in the SMB separation cost (SWH-P). Focusing on implementing a SMB separation system in SWH based on the COM, it is possible to note that the COM at industrial scale (3 × 500 L) is lower than the market price for all sugars, which is a positive indicator for the project feasibility.

3.4. Profitability and sensitivity analysis

3.4.1. Profitability analysis

The evaluation of gross profit, annual operating cost, main revenue, and profitable indicators are the initial parameters to observe the behavior of different scales and designs for the subcritical hydrolysis of BSG (Table 6). For both SWH plants (3 × 10 L and 3 × 500 L), a negative gross profit was obtained per year, which indicated that after all the maintenance and implementation costs, the plant would not return the initial investment. Otherwise, plants with SMB separation process (SWH-P) presented a positive gross profit only for industrial scale (3 × 500 L). For instance, in the SWH-P industrial scale (3 × 500 L), the gross profit ranged from 2,160,000.00 USD (Scenario 1) to 9,921,000.00 (Scenario 7). In addition, from the annual cost, it was clear that Scenario 7 required significant costs to the operational labor. This cost increased with the scale-up and the adoption of a separation system. On an industrial scale (SWH-P, 3 × 500 L), the annual operational cost was higher than 1.5 million USD for all the scenarios.

Notwithstanding, the main revenue was obtained from the sum between gross profit and annual operating cost since a fraction of the revenues are designated to the operating costs, and the other is the gross profit. Thus, the best revenue condition was obtained for the process with SMB separation system on the industrial scale. This fact can be explained by the sugar isolation in the SMB system since the market price increases with the production of isolated sugars, when comparing to the single fraction of sugars obtained in SWH process. The difference in the scenarios and profits are related mainly to yields and the composition of hydrolysates for different reaction times.

Among the eight (08) scenarios evaluated, the plants that produced one hydrolysate (one market product) were not profitable. In the SWH (3 × 10 L and 3 × 500 L), payback time was up to 90 years, and negative GM, ROI, yearly ROR, and NPV were obtained. The current market price of the hydrolysate (3 USD kg^{-1}) does not allow achieving a profitable condition and should not be implemented. Otherwise, with the

Table 6
Results of profitability parameters to obtain sugars from different scaled-up plants (3 × 10 L and 3 × 500 L) considering SWH and SWH-P.

Scenario	GM (%)	ROI (%)	Yearly ROR (%)	Payback (years)	NPV (USD)	Gross profit (USD $year^{-1}$)	Annual operating cost (USD $year^{-1}$)	Main revenue (USD $year^{-1}$)
		3 × 10 L (SWH)						
1	−1193.44	−46.44	−1233	>99	−950,000.00	−74,000.00	80,000.00	6000.00
2	−510.04	−42.39	−567	>99	−871,000.00	−68,000.00	80,000.00	12,000.00
3	−519.67	−42.88	−575	>99	−881,000.00	−69,000.00	81,000.00	12,000.00
4	−497.41	−43.11	−531	>99	−886,000.00	−69,000.00	82,000.00	13,000.00
5	−1079.81	−51.90	−1186	>99	−1,0066,000.00	−83,000.00	90,000.00	7000.00
6	−738,34	−50.43	−810	>99	−1,037,000.00	−81,000.00	91,000.00	10,000.00
7	−383.14	−45.84	−411	>99	−946,000.00	−74,000.00	92,000.00	18,000.00
8	−413.20	−47.31	−422	>99	−976,000.00	−76,000.00	94,000.00	18,000.00
		3 × 10 L (SWH-P)						
1	−363.77	−37.81	−365	>99	−3,695,000.00	−285,000.00	363,000.00	78,000.00
2	−109.85	−25.28	−111	>99	−2,519,000.00	−191,000.00	363,000.00	172,000.00
3	−119.13	−26.30	−119	>99	−2,616,000.00	−198,000.00	364,000.00	166,000.00
4	−107.93	−25.11	−108	>99	−2,503,000.00	−189,000.00	364,000.00	175,000.00
5	−351.63	−37.91	−357	>99	−3,705,000.00	−286,000.00	366,000.00	80,000.00
6	−220.67	−33.57	−221	>99	−3,299,000.00	−253,000.00	367,000.00	114,000.00
7	−54.22	−17.51	−54	>99	−1,794,000.00	−132,000.00	375,000.00	243,000.00
8	−92.06	−23.50	−92	>99	−2,355,000.00	−177,000.00	369,000.00	192,000.00
		3 × 500 L (SWH)						
1	−122.37	−16.24	−122	>99	−5,108,000.00	−376,000.00	683,000.00	307,000.00
2	−6.04	−1.73	−6	>99	−923,000.00	−41,000.00	703,000.00	662,000.00
3	−10.93	−3.08	−11	>99	−1,315,000.00	−72,000.00	724,000.00	652,000.00
4	−9.52	−2.83	−9	>99	−1.249,000.00	−66,000.00	756,000.00	690,000.00
5	−140.73	−19.41	−140	>99	−6,050,000.00	−451,000.00	771,000.00	320,000.00
6	−75.82	−14.74	−75	>99	−4,706,000.00	−343,000.00	795,000.00	452,000.00
7	2.69	1.10	2.72	90.85	−125,000.00	26,000.00	930,000.00	956,000.00
8	12.92	−4.21	−13	>99	−1,661,000.00	−99,000.00	857,000.00	758,000.00
		3 × 500 L (SWH-P)						
1	55.26	25.88	79.26	3.86	25,471,000.00	2,160,000.00	1,749,000.00	8,432,000.00
2	78.99	79.70	78.67	1.25	81,593,000.00	6,661,000.00	1,771,000.00	8,303,000.00
3	80.20	79.88	81.29	1.25	81,578,000.00	6,659,000.00	1,644,000.00	8,785,000.00
4	79.14	83.24	55.05	1.20	85,229,000.00	6,953,000.00	1,832,000.00	4,076,000.00
5	54.17	26.42	67.53	3.79	26,056,000.00	2,208,000.00	1,868,000.00	5,753,000.00
6	67.06	46.15	84.25	2.17	46,626,000.00	3,858,000.00	1,895,000.00	12,032,000.00
7	81.59	118.25	78.14	0.85	121,474,000.00	9,921,000.00	2,111,000.00	9,656,000.00
8	79.65	91.94	76.70	1.09	94,420,000.00	7,691,000.00	1,965,000.00	8,432,000.00

implementation of a SMB separation system, the profitability indicators were positive on industrial scale. Scenario 7 was the most profitable one, corroborating the COM analysis since the lowest productivity cost may increase profitability. The SWH-P industrial-scale (3 × 500 L) of this scenario (SWH-P, Scenario 7) can improve the profitability indicators, which can be considered an advantage to implementation to produce isolated sugars from BSG.

The profitability results obtained in this study are in accordance when comparing with other scale-up studies. For instance, Viganó et al. (2017) studied the scale-up of supercritical fluid and pressurized liquid extraction of phytonutrients from passion fruit (*Passiflora edulis*) by-products. In the mentioned study, the payback time ranged from 0.6 (industrial scale) to 14.9 years (laboratory scale), and the NPV increased to approximately 109 million USD in the industrial scale. Lachos-Perez et al. (2021) evaluated sugars and flavanones production from orange peel using a sequential subcritical water process. The process simulation was conducted at the laboratory (2 × 5 L), pilot (3 × 10 L), and industrial (3 × 500 L) scales. The results demonstrate that the scale-up process decreased the COM and improved the profitability parameters. Zabot et al. (2017) simulated the scale-up process of different supercritical reactors to obtain quercetin-rich powdered extracts from onion (*Allium cepa*) peels. The laboratory-scale obtained negative returns; however, with the implementation of pilot and industrial plant, a satisfactory IRR, ROI, NPV, and payback were obtained, attributing a profitable process. Beyond, Zabot et al. (2018) evaluated the economic feasibility of supercritical fluid extraction coupled to low-pressure solvent extraction to produce tocotrienols oil and bixin extract from annatto (*Bixa orellana*) seeds. On industrial scale, the ROI, GM, and payback obtained were respectively 389.7 %, 66.5 %, and 0.26 years, which suggest an implementation in new production lines.

3.4.2. Sensitivity analysis

The effect of sugar production and purification in the subcritical water process was evaluated by a sensitivity analysis. In the current scale-up project, implementation cost, BSG cost, and wage per shift were evaluated by a sensitivity analysis in the industrial-scale process (3 × 500 L) coupled with the SMB separation system. These variables were adopted since they were the most influencing variables on an industrial scale and directly affected the project feasibility. Thereby, the project condition was evaluated to identify the effects of significant variations

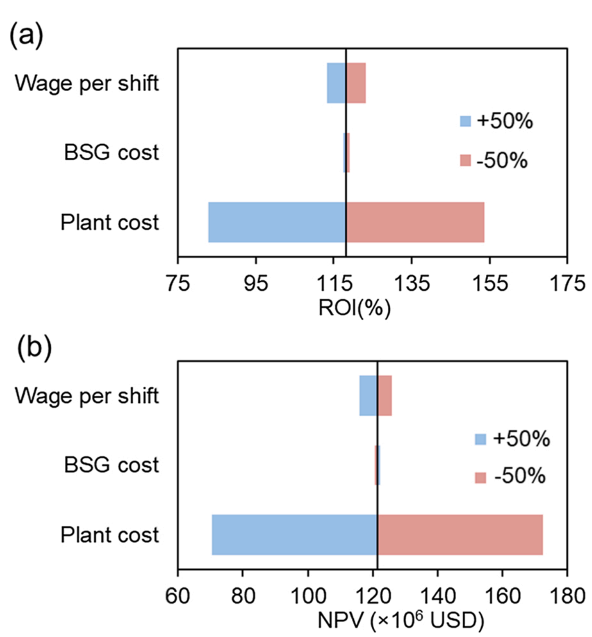

Fig. 6. Sensitivity analysis for the industrial-scale (3 × 500 L) process coupled with the SMB purification system (SWH-P) on the ROI (a) and NPV (b).

on ROI and NPV (Fig. 6). With a variation of ±50 % in the input data, it is possible to observe that plant cost is the most sensitive parameter. This fact can be associated with the highest implementation cost of the industrial process. Otherwise, BSG cost cannot be considered a sensitive parameter since non-significant differences were obtained with a variation in ±50 % for the SWH-P process on the industrial-scale. Notwithstanding, the wage per shift directly affects the SWH-P process since this plant requires a high number of wages to implement the process. The condition evaluated herein may be an alternative to the implementation since the investor can choose the best operational conditions and the market price of the material to construct the most profitable industrial plant.

The adoption of simulated scale-up projects to produce a new product may be accomplished with an economic assessment and a deep sensitivity study. After choosing the best operational conditions on the laboratory scale, the simulated pilot and industrial plant provide an insight related to the adoption of this technology. Therefore, the next step of this study is to conduct the pilot-plant of SWH and extend the technology scope to evidence the operational conditions for an industrial process, transferring successful smaller-scale initiatives to larger-scale processes.

3.5. Mass and energy balance of the SWH-P process

In the current study, the mass balance was evaluated to obtain equations that observe the mass flow in each step of SWH-P. Energy balance was used to identify and quantify all the energy that flows in the process. A theoretical steady-state design of SWH was provided based on the technological route established, considering the SMB separation process (Fig. 7). Thus, the lists of conventional equipment for the present technical routes were the subcritical reactor, heat exchange, and the separation system.

Additionally, it was still possible to describe some considerations for the current process, considering the laboratory scheme established in Fig. 1 and demonstrated in previous studies (Mayanga-Torres et al., 2017; Lachos-Perez et al., 2017, 2018). The mass balance of the process can be observed in Table 7. For its interpretation, the considerations described herein, and the equation described in the Section 2.4. were the basis to conduct the mass and energy balance of the process:

1) Knowing "M_2" grams of BSG fed into the reactor and knowing the S/F, it is possible to determine the amount of water required using Eq. 9. In the case of the subcritical reactor of 500 L, the amount of BSG used for hydrolysis is 250 kg. Considering the same S/F used in this study (4 g solvent g^{-1} feed) the amount of water per reactor on an industrial scale is approximately one (1) m^3.

$$M_1 = M_2 \times S/F \tag{9}$$

2) The process presents a net extract yield of 56.63 %, and then, "M_3" can be calculated using Eq. 10. The volume of hydrolysate produced in the industrial subcritical reactor of 500 L is 707 L per batch.

$$M_3 = 0.5663 \times (M_1 + M_2) \tag{10}$$

3) The process generates a fraction of waste in the reactor (known as biochar) which can be calculated using Eq. 11. Through the global balance in the reactor, the amount of biochar produced in the industrial reactor is 543 kg.

$$M_4 = 0.4337 \times (M_1 + M_2) = M_1 + M_2 - M_3 \tag{11}$$

4) Under the laboratory experiment, it is known that 5 g of the sample introduced in the reactor produces 2.68 g of residue that remains in the reactor, that is, 53.6 %. Thus, the $m_{4,1}$ fraction should be

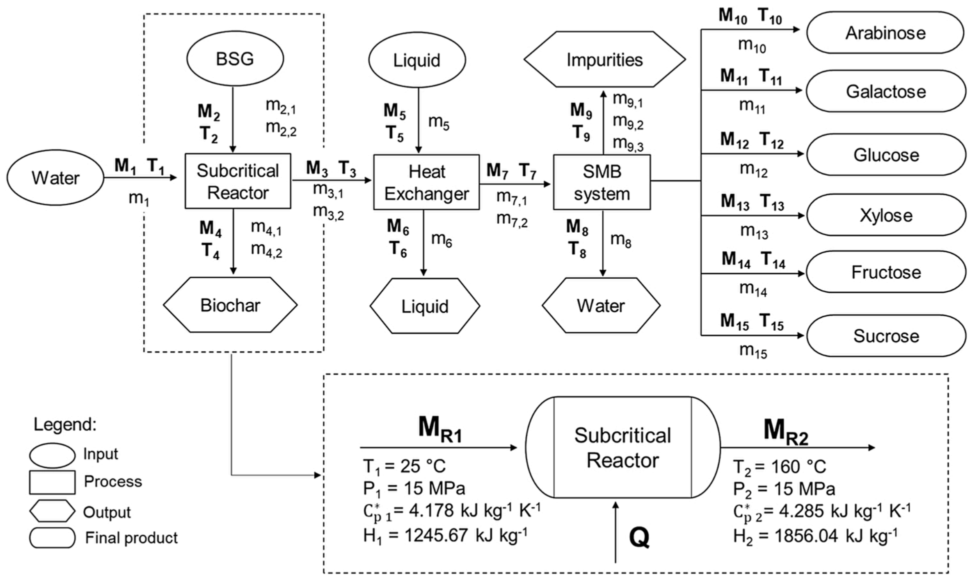

Fig. 7. Representation of the mass and energy balance for sugar production from BSG.

Table 7
Mass and energy balance for the integrated process for sugar production from BSG.

Flow established	Mass fraction		Unit
M_1	m_1	1	g water g^{-1} water
M_2	$m_{2,1}$	0.95	g solids g^{-1} solids
	$m_{2,2}$	0.05	g water g^{-1} water
M_3	$m_{3,1}$	0.007	g solids g^{-1} solids
	$m_{3,2}$	0.993	g water g^{-1} water
M_4	$m_{4,1}$	0.011	g solids g^{-1} solids
	$m_{4,2}$	0.989	g water g^{-1} water
M_5	m_5	1	g water g^{-1} water
M_6	m_6	1	g water g^{-1} water
M_7	$m_{7,1}$	0.007	g solids g^{-1} solids
	$m_{7,2}$	0.993	g water g^{-1} water
M_8	m_8	1	g water g^{-1} water
M_9	$m_{9,1}$	0.45	g furfural g^{-1} furfural
	$m_{9,2}$	0.21	g formic acid g^{-1} formic acid
	$m_{9,3}$	0.34	g acetic acid g^{-1} acetic acid
M_{10}	m_{10}	0.67	g arabinose g^{-1} arabinose
M_{11}	m_{11}	0.03	g galactose g^{-1} galactose
M_{12}	m_{12}	0.05	g glucose g^{-1} glucose
M_{13}	m_{13}	0.19	g xylose g^{-1} xylose
M_{14}	m_{14}	0.03	g fructose g^{-1} fructose
M_{15}	m_{15}	0.03	g sucrose g^{-1} sucrose

approximately 2.68 g, which corresponds to a solid mass fraction of 0.011 w/w, and therefore, 0.989 w/w is the water fraction ($m_{4,2}$) (Table 7).

5) In the heat exchanger, it is possible to assume that there is no degradation of the compounds, only the cooling of the solution, with constant mass. The mass balance can be expressed according to Eq. 12. However, the cooling solution is continuous along the time (Eq. 13), and then, the liquid is constant along in the heat exchanger (Eq. 14):

$$M_3 + M_5 = M_6 + M_7 \tag{12}$$

$$M_5 = M_6 \tag{13}$$

$$M_3 = M_7 \tag{14}$$

6) Also, if 5 g of sample was fed into the laboratory reactor, it is possible to obtain the composition of sugars (Eq. 15) and impurities (Eq. 16), where Eq. 15 is related to the mass entering the reactor with the sugars generated. Eq. 16 is associated with the sample mass entering the reactor with the impurities generated. Thus, the sum of sugars produced on is industrial scale is 11.65 kg, and the impurities mass is 4.45 kg.

$$M_2 \times 0.0466 = \sum_{i=10}^{i=15} M_i \tag{15}$$

$$M_9 = M_2 \times 0.0178 \tag{16}$$

The evaluation of energetic efficiency in a scale-up project is necessary to optimize future implementation in an industrial process. The heat required for the reactor was calculated as 610 kJ kg^{-1}. Generally, in the industrial-scale (reactor capacity of 500 L), the pump operated with a power of 38.36 kW, and an efficiency of 50 %. The heating agent with high pressure was adopted with a rate of 679.65 kg h^{-1}, with an engine's effectiveness in units of work done per unit of fuel as 285 × 10^3 kcal h^{-1}, and an efficiency of 70 %. Finally, in the colling system (heat exchanger), colling water is using at a rate of 27 × 10^3 kg h^{-1}, assuming a heat transfer coefficient of 1 kW m^2 K^{-1}, and an efficiency of 90 %. For continuous operation of SWH-P process, a high amount of energy is required; however, futures studies should be addressed to improve the heat required for an industrial reactor. With the adoption of a mass and energy balance demonstrated herein, it is possible to decrease the COM with the improvement of energetic efficiency drastically.

4. Conclusion

This study allowed to conclude that the flow-through subcritical water hydrolysis of brewer's spent grains followed by a SMB separation system can be a promising technology to produce isolated sugars on industrial scale. The lowest COM was obtained for the process with a residence time of 4.6 min and operating at 15 MPa and 160 °C. The COM for sugars can address a perspective for a future application in a biorefinery. In an industrial-scale (3 × 500 L) of SWH-P, the project implementation is economically applicable, and from the sensitivity analysis, the plant cost is the most affecting parameter. The process efficiency can be intensified from mass and energy balance to produce isolated sugars using subcritical water hydrolysis. Therefore, the technological route simulated and scaled-up is economically viable at the industrial scale. The biorefinery approach can be an alternative for the destination of brewer's spent grains generated by breweries.

CRediT authorship contribution statement

William Gustavo Sganzerla: Methodology, Investigation, Analysis, Validation, Writing - original draft. **Giovani Leone Zabot:** Analysis, Validation, Writing - original draft. **Paulo César Torres-Mayanga:** Analysis, Validation, Writing - original draft. **Luz Selene Buller:** Methodology, Analysis, Validation, Writing - original draft. **Solange I. Mussatto:** Conceptualization, Supervision, Resources, Writing - review & editing, Funding acquisition. **Tânia Forster-Carneiro:** Conceptualization, Supervision, Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

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

Acknowledgments

This work was supported by the Brazilian Science and Research Foundation (CNPq, Brazil) (productivity grants 302473/2019-0 and 304882/2018-6); Coordination for the Improvement of Higher Education Personnel (CAPES, Brazil) (Finance code 001); São Paulo Research Foundation (FAPESP, Brazil) (grant numbers 2018/05999-0, 2018/14938-4, 2019/26925-7, and 2020/10323-5), and the Novo Nordisk Foundation (NNF, Denmark) (grant number NNF20SA0066233).

References

Abaide, E.R., Ugalde, G., Di Luccio, M., Moreira, R.F.P.M., Tres, M.V., Zabot, G.L., Mazutti, M.A., 2019a. Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode. Bioresour. Technol. 272, 510–520.

Abaide, E.R., Mortari, S.R., Ugalde, G., Valerio, A., Amorim, S.M., Di Luccio, M., Moreira, R.F.P.M., Kuhn, R.C., Priamo, W.L., Tres, M.V., Zabot, G.L., Mazutti, M.A., 2019b. Subcritical water hydrolysis of rice straw in a semi-continuous mode. J. Clean. Prod. 209, 386–397.

Azevedo, D.C.S., Rodrigues, A., 2000. SMB chromatography applied to the separation/purification of fructose from cashew apple juice. Braz. J. Chem. Eng. 17, 507–516.

Caes, B.R., Van Oosbree, T.R., Lu, F., Ralph, J., Maravelias, C.T., Raines, R.T., 2013. Simulated moving bed chromatography: separation and recovery of sugars and ionic liquid from biomass hydrolysates. ChemSusChem 6 (11), 2083–2089.

Campos, D.A., Gómez-García, R., Vilas-Boas, A.A., Madureira, A.R., Pintado, M.M., 2020. Management of fruit industrial by-products - a case study on circular economy approach. Molecules 25, 320.

Cheah, W.Y., Sankaran, R., Show, P.L., Tg. Ibrahim, T.N.B., Chew, K.W., Culaba, A., Chang, J.-S., 2020. Pretreatment methods for lignocellulosic biofuels production: current advances, challenges and future prospects. Biofuel Res. J. 7 (1), 1115–1127.

de Aguiar, A.C., Osorio-Tobón, J.F., Viganó, J., Martínez, J., 2020. Economic evaluation of supercritical fluid and pressurized liquid extraction to obtain phytonutrients from biquinho pepper: analysis of single and sequential-stage processes. J. Supercrit. Fluids, 104935.

Dragone, G., Kerssemakers, A.A.J., Driessen, J.L.S.P., Yamakawa, C.K., Brumano, L.P., Mussatto, S.I., 2020. Innovation and strategic orientations for the development of advanced biorefineries. Bioresour. Technol. 302, 122847.

El-Haggar, S.M., 2007. Chapter 10 - sustainability of industrial waste management. In: El-Haggar, S.M. (Ed.), Sustainable Industrial Design and Waste Management. Academic Press, Oxford, pp. 307–369.

Freitas, L.C., Barbosa, J.R., da Costa, A.L.C., Bezerra, F.W.F., Pinto, R.H.H., Junior, R.N.C., 2021. From waste to sustainable industry: How can agro-industrial wastes help in the development of new products? Res. Conserv Recy 169, 105466.

Hatami, T., Johner, J.C.F., Zabot, G.L., Meireles, M.A.A., 2019. Supercritical fluid extraction assisted by cold pressing from clove buds: extraction performance, volatile oil composition, and economic evaluation. J. Supercrit. Fluids 144, 39–47.

Hatami, T., dos Santos, L.C., Zabot, G.L., de Almeida Pontes, P.V., Caldas Batista, E.A., Innocentini Mei, L.H., Martínez, J., 2020. Integrated supercritical extraction and supercritical adsorption processes from passion fruit by-product: experimental and economic analyses. J. Supercrit. Fluids 162, 104856.

Ioannidou, S.M., Pateraki, C., Ladakis, D., Papapostolou, H., Tsakona, M., Vlysidis, A., Kookos, I.K., Koutinas, A., 2020. Sustainable production of bio-based chemicals and polymers via integrated biomass refining and bioprocessing in a circular bioeconomy context. Bioresour. Technol. 307, 123093.

Kamusoko, R., Jingura, R.M., Parawira, W., Sanyika, W.T., 2019. Comparison of pretreatment methods that enhance biomethane production from crop residues - a systematic review. Biofuel Res. J. 6 (4), 1080–1089.

Lachos-Perez, D., Tompsett, G.A., Guerra, P., Timko, M.T., Rostagno, M.A., Martínez, J., Forster-Carneiro, T., 2017. Sugars and char formation on subcritical water hydrolysis of sugarcane straw. Bioresour. Technol. 243, 1069–1077.

Lachos-Perez, D., Baseggio, A.M., Mayanga-Torres, P.C., Maróstica, M.R., Rostagno, M.A., Martínez, J., Forster-Carneiro, T., 2018. Subcritical water extraction of flavanones from defatted orange peel. J. Supercrit. Fluids 138, 7–16.

Lachos-Perez, D., Baseggio, A.M., Torres-Mayanga, P.C., Ávila, P.F., Tompsett, G.A., Marostica, M., Goldbeck, R., Timko, M.T., Rostagno, M., Martinez, J., Forster-Carneiro, T., 2020. Sequential subcritical water process applied to orange peel for the recovery flavanones and sugars. J. Supercrit. Fluids 160, 104789.

Lachos-Perez, D., Buller, L.S., Sganzerla, W.G., Ody, L.P., Zabot, G.L., Forster-Carneiro, T., 2021. Sequential hydrothermal process for flavanones and sugars production from orange peel: an economic assessment. Biofpr 15 (1), 202–217.

Lin, C.H., Lin, H.-W., Wu, J.Y., Houng, J.-Y., Wan, H.-P., Yang, T.Y., Liang, M.T., 2015. Extraction of lignans from the seed of Schisandra chinensis by supercritical fluid extraction and subsequent separation by supercritical fluid simulated moving bed. J. Supercrit. Fluids 98, 17–24.

Lynch, K.M., Steffen, E.J., Arendt, E.K., 2016. Brewers' spent grain: a review with an emphasis on food and health. J. Inst. Brew. 122 (4), 553–568.

Manzanares, P., Ballesteros, I., Negro, M.J., González, A., Oliva, J.M., Ballesteros, M., 2020. Processing of extracted olive oil pomace residue by hydrothermal or dilute acid pretreatment and enzymatic hydrolysis in a biorefinery context. Renew. Energy 145, 1235–1245.

Matus, K.J.M., Clark, W.C., Anastas, P.T., Zimmerman, J.B., 2012. Barriers to the implementation of green chemistry in the United States. Environ. Sci. Technol. 46 (20), 10892–10899.

Mayanga-Torres, P.C., Lachos-Perez, D., Rezende, C.A., Prado, J.M., Ma, Z., Tompsett, G.T., Timko, M.T., Forster-Carneiro, T., 2017. Valorization of coffee industry residues by subcritical water hydrolysis: recovery of sugars and phenolic compounds. J. Supercrit. Fluids 120, 75–85.

Mussatto, S.I., Dragone, G., Roberto, I.C., 2006. Brewers' spent grain: generation, characteristics and potential applications. J. Cereal Sci. 43 (1), 1–14.

Mussatto, S.I., Moncada, J., Roberto, I.C., Cardona, C.A., 2013. Techno-economic analysis for brewer's spent grains use on a biorefinery concept: the Brazilian case. Bioresour. Technol. 148, 302–310.

Oliveira, T.C.G., Hanlon, K.E., Interlandi, M.A., Torres-Mayanga, P.C., Silvello, M.A.C., Lachos-Perez, D., Timko, M.T., Rostagno, M.A., Goldbeck, R., Forster-Carneiro, T., 2020. Subcritical water hydrolysis pretreatment of sugarcane bagasse to produce second generation ethanol. J. Supercrit. Fluids 164, 104916.

Osorio-Tobón, J.F., Carvalho, P.I.N., Rostagno, M.A., Meireles, M.A.M., 2016. Process integration for turmeric products extraction using supercritical fluids and pressurized liquids: Economic evaluation. Food Bioprod. Process. 98, 227–235.

Sandler, S.I., 2017. . Chemical, Biochemical, and Engineering Thermodynamics, 5a. ed. John Wiley and Sons.

Santos, M.S.N., Zabot, G.L., Mazutti, M.A., Ugalde, G., Rezzadori, K., Tres, M.V., 2020. Optimization of subcritical water hydrolysis of pecan wastes biomasses in a semi-continuous mode. Bioresour. Technol. 306, 123129.

Sganzerla, W.G., Buller, L.S., Mussatto, S.I., Forster-Carneiro, T., 2021. Techno-economic assessment of bioenergy and fertilizer production by anaerobic digestion of brewer's spent grains in a biorefinery concept. J. Clean. Prod. 297, 126600.

Torres-Mayanga, P.C., Azambuja, S.P.H., Tyufekchiev, M., Tompsett, G.A., Timko, M.T., Goldbeck, R., Rostagno, M.A., Forster-Carneiro, T., 2019. Subcritical water hydrolysis of brewer's spent grains: selective production of hemicellulosic sugars (C-5 sugars). J. Supercrit. Fluids 145, 19–30.

Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., 2003. Analysis, Synthesis and Design of Chemical Process. Prentice Hall-PTR, New Jersey.

Ubando, A.T., Felix, C.B., Chen, W.H., 2020. Biorefineries in circular bioeconomy: a comprehensive review. Bioresour. Technol. 299, 122585.

Vedovatto, F., Ugalde, G., Bonatto, C., Bazoti, S.F., Treichel, H., Mazutti, M.A., Zabot, G.L., Tres, M.V., 2021a. Subcritical water hydrolysis of soybean residues for obtaining fermentable sugars. J. Supercrit. Fluids 167, 105043.

Vedovatto, F., Bonatto, C., Bazoti, S.F., Venturin, B., Alves Jr., S.L., Kunz, A., Steinmetz, R.L.R., Treichel, H., Mazutti, M.A., Zabot, G.L., Tres, M.V., 2021b. Production of biofuels from soybean straw and hull hydrolysates obtained by subcritical water hydrolysis. Bioresour. Technol. 328, 124837.

Viganó, J., Zabot, G.L., Martínez, J., 2017. Supercritical fluid and pressurized liquid extractions of phytonutrients from passion fruit by-products: economic evaluation of sequential multi-stage and single-stage processes. J. Supercrit. Fluids 122, 88–98.

Xie, Y., Chin, C.Y., Phelps, D.S.C., Lee, C.-H., Lee, K.B., Mun, S., Wang, N.-H.L., 2005. A five-zone simulated moving bed for the isolation of six sugars from biomass hydrolyzate. Ind. Eng. Chem. Res. 44 (26), 9904–9920.

Zabot, G.L., Bitencourte, I.P., Tres, M.V., Meireles, M.A.A., 2017. Process intensification for producing powdered extracts rich in bioactive compounds: an economic approach. J. Supercrit. Fluids 119, 261–273.

Zabot, G.L., Moraes, M.N., Meireles, M.A.A., 2018. Process integration for producing tocotrienols-rich oil and bixin-rich extract from annatto seeds: a techno-economic approach. Food Bioprod. Process. 109, 122–138.

Zhang, X., Zhang, W., Lei, F., Yang, S., Jiang, J., 2020. Coproduction of xylooligosaccharides and fermentable sugars from sugarcane bagasse by seawater hydrothermal pretreatment. Bioresour. Technol. 309, 123385.