New proposal for production of bioactive compounds by supercritical technology integrated to a sugarcane biorefinery

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Abstract An integrated biorefinery is designed for the production of a broad range of products (e.g., bioactive compounds, biofuel, heat and bioelectricity) via multiple conversion pathways and technologies, being supercritical technology applied for the recovery of bioactive compounds from natural sources. In this study, first the effects of the extraction conditions from Brazilian ginseng (*Pfaffia glomerata*) roots including pressure (10-20 MPa), temperature (323-363 K) and CO_2/ethanol proportion ratio (90:10 %, 50:50 % and 0:100 %, w/w) on the β-ecdysone content in the extracts was evaluated. Afterward, a stand-alone bioactive compounds production using supercritical CO_2 with 10% ethanol as co-solvent (optimized conditions) is compared with integrated first and second generation ethanol production from sugarcane. Simulations were developed using the commercial simulator ASPEN PLUS® to represent the different scenarios, which provided data for thermal and economic comparisons. Furthermore, a sensitivity analysis was performed to identify the critical parameters of the proposed integrated biorefinery. Results show that the construction of a supercritical fluid extraction (SFE) plant inside or in close proximity to a sugarcane biorefinery is very promising, since the SFE plant could use directly the ethanol, CO_2, heat and electricity already available, avoiding logistics costs. Another interesting point of this new proposal, which can be extended for other bioactive compounds sources besides Brazilian ginseng, is the possibility of the use of the cogeneration system of the sugarcane biorefinery to burn the leftover extracted material and its unused parts left in the field after harvesting, contributing to its integral valorization.

Keywords Biorefinering, Biomass valorization, Sustainable Technologies, Process Integration, Supercritical Technology, Bioactive compounds

Introduction

Supercritical fluid extraction (SFE) has proven to be technically and economically feasible, presenting several advantages, including environment benefits, when compared to traditional solid–liquid extraction methods. However, after three decades of development, of the over 200 commercial plants in the world, none is located in Latin America (Prado et al. 2011). The high cost of investment when compared to classical low-pressure equipments, of steam distillation and organic solvent extraction, is pointed as the main drawback for the installation of a SFE industrial unit. However, the cost of manufacturing (COM) products by SFE, when all costs involved in the process are taken into account, can be extremely competitive with the COM of extracts obtained by traditional extraction techniques depending on the bioactive compounds source (Meireles 2008; Pereira and Meireles 2010).

Cost of manufacturing (COM) estimation is important to evaluate the feasibility of an industrial project. The most used COM estimations for industrial processes are based on Turton methodology. The economic evaluation consists in determining the parameters influences in the COM: capital investment (FCI), cost of operational labor (COL), cost of raw material (CRM), cost of utilities (CUT) and cost of waste treatment (CWT) (Turton et al. 2003). Generally, for a SFE process the raw material cost is related to the plant material and the solvent lost during the process. If a by-product is used as the bioactive compounds source, for instance, its value can be considered zero. CO_2 loss is mainly due to depressurization of the extractor at the end of each batch and co-solvent loss, if employed, is lost in the residue stream and in the condenser. Pre-processing costs involve drying and comminution of raw material. Utility costs comprise producing heat exchange agents and the electricity used in the processes. The cost of waste treatment may be neglected in SFE because the residue of the process is a dry solid vegetable matrix that may be incorporated into the soil or commercialized as a by-product, as it does not contain any residue of toxic solvents. The CO_2 and co-solvent lost needs no treatment because presents no harm to the environment or human health in small quantities (Prado et al. 2013; Pereira and Meireles 2010).

Nowadays, the image of a sustainable society is focused on a society that has a decentralized local-scale production based on local characteristics of the environment so that chemicals and energy flows can be supplied from diverse biomass and other renewable resources. In this sense, supercritical technology is being considered to be one key in the realization of decentralized processes (Arai et al. 2009). The possibility of constructing a SFE plant in close proximity to an alcoholic fermentation facility that produces high purity CO_2 as a by-product and ethanol, preferred co-solvent for coupling with CO_2 was mentioned by some researchers (King and Srinivas 2009), on the other hand, none evaluation was done until the present date.

This work is a part of a project that aims at providing a way to valorize the Brazilian ginseng plant. In an effort to increase revenues from the feedstock, we assumed that co-products would be extracted by SFE under optimized conditions (determined in this study) prior to the thermochemical conversion. In this study, we studied the integration of the SFE process into a sugarcane mill producing first and second generation ethanol to provide comprehensive perspectives on the possibility of constructing the first industrial SFE unit in Brazil SFE in this location. Critical parameters of the proposed integrated biorefinery, such as cost of raw material (CRM), cost of utilities (CUT) and cost of waste treatment (CWT), was changed for evaluating the thermal and economic benefits gained with this new arrangement.

Materials and methods

Experimental methodology

A home-made unit, described by Pasquel et al. (2000) was used for the experiments that use CO_2 and ethanol mixtures, while another recently constructed unit was used in the experiments that only ethanol is used. This latter unit consists of a HPLC pump (Thermoseparation Products, Model ConstaMetric 3200 P/F, Fremoni, USA), a 6.57 cm^3 extraction cell (Thar Designs, Pittsburg, USA) containing a sintered metal filter at the bottom and upper parts, an electrical heating jacket and a back pressure regulator (BPR) valve (Model n°26–1761-24–161, Tesco, Elk River, USA). A more detailed description of this unit can be found elsewhere (Santos et al. 2012a). Different amounts of dried (8.9 % moisture) and milled (particles with with a diameter of 7.9 µm) raw material (*Pfaffia glomerata* roots) was placed in each equipment, then, the amount of total solvent was adjusted to keep the solvent mass to feed mass ratio constant (S/F = 50) in all experiments. The criterion adopted in the present study has proved to be efficient for comparison of results obtained in different equipments (Prado et al. 2011). The static and dynamic extraction periods always were 5 min and 1 h, respectively. The assays were done in duplicate.

The β-ecdysone content determination in the extracts were carried out on a High-performance liquid chromatography (HPLC) system (Waters Corp., Milford, MA, USA), consisting of a separation module (2695) with integrated column heater and auto-sampler and a photodiode array detector (2998). Separation of compounds was carried out on a fused-core type column (Poroshell 120 EC-C_{18}, 100 × 4.6 mm, 2.7 µm, Agilent Technologies, Little Fall, DE, USA). UV absorbance was monitored from 200 to 400 nm and injection volume was 10 µL. Identification of β-ecdysone was achieved by the comparison of retention times and UV spectra of separated compounds with the authentic standard. Quantification was carried out by integration of the peak areas at 246 nm using the external standardization method. The standard curve (7 points) was prepared by plotting the concentration (0.1-200 mg L^{-1}) against area of the peak. Regression equations and correlation coefficient (r^2) were calculated using Microsoft Excel 2010 software.

Statistical analyses were performed using analyses of variance (ANOVA). The mean values were considered significantly at $p < 0.05$ and very significantly at $p < 0.01$. Statistica software (release 7, StatSoft, TUL, USA) was used to calculate the effects of the temperature, pressure and CO_2/ethanol proportion ratio on the β-ecdysone content in the extracts.

Process Simulation Methodology

A flowsheeting model of the supercritical fluid extraction (SFE) process was developed in the ASPEN PLUS® software in order to compute the mass and energy balance. A thermal model of the production process was solved in MATLAB based platform (OSMOSE) using state variables obtained in the detailed simulation of all the equipment and conversion steps of the process.

It was analyzed the extraction of Brazilian ginseng roots under two different operational conditions:

Scenario I: the simulation of the process considering the operation of the system under the conditions experimentally studied by Leal at al. (2010);

Scenario II: the simulation of the process considering the operation of the system under the optimized condition determined experimentally in the present study.

The two conditions were evaluated energetically considering three possible scenarios (Fig. 1):

Scenario A: a stand-alone SFE plant, being the heat and electricity supplied by the burning of the aerial parts of Brazilian ginseng, the residue of the SFE extraction (roots) and complementary fuel, if necessary, in a cogeneration system shared with a sugarcane mill;

Scenario B: a SFE plant located inside a sugarcane mill producing first and second generation ethanol, so the heat integration would be performed considering heat exchange between the two processes. The thermal requirements would be fulfilled by a cogeneration unit burning the regular fuels from the mill (Part of bagasse, leaves, hydrolysis waste, biogas from xylose and vinasse, leftover of the SFE extraction (roots).

Simulation of the SFE plant

The simulation of the SFE plant was performed using the commercial simulator ASPEN PLUS®. For the Brazilian ginseng roots extraction, it was considered a prior preparation of the material in which the roots were cleaned, air dried using heated air at 373 K and milled. The prepared roots were introduced in an extraction reactor were ethanol and CO_2 was pumped at the desired proportions, pressure and temperature. Although the extraction process is a non-continuous process, it can be modeled as a steady-state process since it was considered different extraction reactors operating in parallel, which enables a continuous production of extract.

After extraction, CO_2 was recovered through 2 flash tanks operating at 6.5 and 0.1 MPa, respectively. Lower pressure CO_2 was pressurized to 6.5 MPar and liquefied to be reused in the system with a loss of 2 %. Ethanol was separated from the extracted compounds by evaporation and recycled to the process.

The flowsheet of the analyzed process simulated is shown in Fig. 2. The operational conditions used in each step, as well as the extraction yield and β- ecdysone content in the extract, are shown in Table 1. It was considered the operation of the system under the conditions experimentally studied by Leal et al. (2010) and under the conditions obtained experimentally and discussed at the present paper.

Simulation of the sugarcane mill producing first and second generation ethanol

The sugarcane mill model producing first and second generation ethanol analyzed sharing only the cogeneration system with the extraction process (Scenario A) or integrated with the extraction process (Scenario B) is described in Ensinas et al. (2013) and Albarelli et al. (2013).

The simulation of the first generation ethanol production considered the steps of: juice extraction and treatment, concentration and sterilization, fermentation, distillation and dehydration. It was simulated the technologies available in modern ethanol distilleries in Brazil, including sugarcane dry cleaning, concentration in multi-effect evaporators, sterilization of the juice before entering the fermentation system and ethanol dehydration using monoethylene glycol. For the second generation ethanol production, it was considered the use of sugarcane bagasse to ethanol production. It was considered the steps of drying and milling of the material, catalyzed steam explosion pre-treatment flowed by enzymatic hydrolysis. The hydrolyzate was concentrated and mixed with the concentrated extracted juice of the first generation process and sent to the fermentation unit. The xylose steam obtained from pretreatment and vinasse obtained from the distillation were used for biogas production in a biodigestor. Table 2 shows the main parameters considered for the simulation of the sugarcane mill.

Simulation of the cogeneration system

The cogeneration system was developed considering a steam cycle operating in a pressure of 9 MPa with extracting and condensing turbines (Ensinas et al., 2013).

Thermal process integration

All the process design case studies were thermal integrated using the Pinch Method (Linnhoff et al. 1982), aiming at the reduction of process steam requirements. Based on the pinch analysis methodology, the optimal thermal process integration is computed after defining the maximum heat recovery potential between hot and cold streams and considering a minimum approach temperature ΔT_{min}. The energy-integration model is send to the slave optimization, which runs a combined mass and energy integration in order to reduce the operating cost of the system, using a Mixed Integer Linear Programming solver. For the analysis only the hot stream of CO_2 cooling prior to pressurization to introduction at the extraction reactor was not considered for the pinch analysis, as this stream is found at temperature much lower than the process and would not contribute for the heat integration. But, this stream was accounted as a cooling demand for the process at the economic analysis.

Thermal and Economic benefits analysis

The thermal and economic benefits for each scenario were evaluated regarding the cost of raw material (CRM), cost of utilities (CUT) and cost of waste treatment (CWT). Table 3 shows the cost used in the evaluation.

Results and discussion

Effects of experimental condition on bioactive compounds content in the extract

Recently, scientists and executives have shown great interest on Brazilian ginseng (*Pfaffia glomerata*) roots, due to besides similarity in appearance *Pfaffia glomerata* extracts have also demonstrating similar effects to *Panax ginseng* (Santos et al. 2012a). Since the pharmaceutical properties of these *Pfaffia glomerata* roots extracts have been attributed to β-ecdysone content, selective extraction process should be applied. In this context, supercritical fluid extraction (SFE) process has been successfully applied for different bioactive compounds sources, including *Pfaffia glomerata* roots. Leal et al. (2010) obtained an extract employing CO_2+ethanol (90:10 %, w/w) at 20 MPa and 303 K as extracting solvent with a concentration of up to 3.7 % for β-ecdysone (which is 3.8-fold higher to the concentration in the commercial extracts), which indicates the possible use of those extracts directly in the commercial pharmaceutical products. Based on these findings, this work first aims the optimization of β-ecdysone recovery by SFE.

The effects of temperature, pressure and CO_2/ethanol proportion ratio on the β-ecdysone content in the extracts were evaluated. The experimental values at various experimental conditions are presented in Table 4. The use of CO_2/ethanol proportion ratio of 90:10 % (w/w) produced extracts with the highest amount of β-ecdysone. Statistical analysis to evaluate the influence of the studied parameters on the results was performed for better conclusions. CO_2/ethanol proportion ratio was very significantly ($p < 0.01$; $p = 0.00008$) for this response variable, while temperature and pressure showed no influence ($p = 0.212719$ and $p = 0.378168$, respectively).

Leal et al. (2010), studying the SFE from *Pfaffia glomerata* roots using pure CO_2, observed that pressure had different influences on the extraction process at different temperatures. During SFE using CO_2 without any cosolvent, the effect of temperature and pressure on supercritical CO_2 solubilization power depends on the solute vapor pressure and solvent density, being the extraction process strongly affected by the CO_2 density. As the temperature increases at a constant pressure, the solute vapour pressure increases; however, the solvent density decreases. When any cosolvent is added to CO_2 it is not easy to predict the behaviour. The cosolvent effect is normally required to the increase in the concentration of a target compound. A decrease in the cosolvent effect of self-associating cosolvents (cosolvents with both H-bond donor and acceptor properties like ethanol) may occur at high cosolvent concentrations. Seabra et al. (2010) studying the effect of several CO_2+cosolvents mixtures as extracting solvent has demonstrated that extracting solvent composition is the most significant process parameter, corroborating our findings.

Comparing with literature data, the results obtained in this study are very promising. The Patent US6224872 (Shibuya et al. 2001) presents an alternative method for obtaining β-ecdysone-rich extracts from *Pfaffia glomerata.* The extraction technique presented involves water heating at 80 °C for the bioactive compounds source. The processing time reaches 24 h, and the final yield of extract is 0.046 % (dry basis), being the β-ecdysone content in the extract is 1% (dry basis). Meanwhile, in this study the β-ecdysone content in the extracts ranged from 2.54 to 8.08 %.

Analysis of the production of bioactive compounds by supercritical technology

For the production of β-ecdysone-rich extract by supercritical technology the simulations were considering the operation of the system under the conditions experimentally studied by Leal at al. (2010) (employing CO_2+ethanol (90:10 %, w/w) at 20 MPa and 303 K) and under the optimized condition determined experimentally in the present study (employing CO_2+ethanol (90:10 %, w/w) at 10 MPa and 323 K), Scenarios I and II, respectively. Comparing both scenarios, Scenario I presented higher extract production although with lower β- ecdysone content than Scenario II (Fig. 3). On the other hand, It was possible to produce 2.6 times more β-ecdysone in Scenario II, than in Scenario I.

The supercritical fluid extraction (SFE) process is mainly composed by 6 heat streams, 3 cold streams that need heating: i) for raw material drying, ii) for extraction and iii) for ethanol recovery steps and 3 hot streams that need cooling: i) CO_2 cooling prior to pressurization, ii) CO_2 cooling for recirculation and iii) ethanol cooling for recirculation steps.

Typically, SFE plants are designed as multipurpose plants, where extracts from different raw materials are produced. If the extraction process is considered without energy integration and all heat and electricity source are supplied by electricity, the energy requirement for Scenario I and II would be 339.7 and 164.5 kWh per g of β-ecdysone in the extract, respectively. Heat consumption is responsible for around 35% of the energy requirement for the extraction process; if heat integration is performed the energy consumption per amount of extract produced can be decreased.

Considering the heat integration of these streams through the Pinch Method, it was possible at both Scenarios (I and II) to supply all heat demand by the cooling of the CO_2 for recirculation. In a complete isolated continuous extraction process the CO_2 recirculation system could be used to supply the heat necessary for the process and electricity and cooling utility should be bought from the grid, this would imply in an electricity consumption of 118.3 and 57.7 kWh per g of β-ecdysone in the extract, for Scenario I and II respectively.

It could be an attractive solution for many SFE processes around the world. Although, if the Brazilian scenario is taken into account, the possibility of placing this extraction technology near a very consolidate industrial segment such as the sugarcane sector it could bring even more benefits for the process in terms of energy and economics.

Considering Scenario A, where the SFE plant is located beside a sugarcane mill but as a stand-alone process, using only the cogeneration system to supply heat and electricity for the process, the results for electricity demand, electricity production and the cooling demand under 298 K after heat integration are shown in Table 6.

As previously discussed the heat demand of the system for Scenario IA and IIA is supplied by the cooling of CO_2 for its recirculation. In the energetic point of view the limiting factors to the process are the electricity consumption and cooling demand. As CO_2 need to be compressed to its recirculation, the electricity consumption is high, but its cooling represents the pinch point of the system, supplying heat to all streams at lower temperatures. Fig. 4 shows the Gran Composite Curve for the scenarios, it represents the difference between the heat available and the cold streams in relation to the Pinch point at a corrected temperature (Linnhoff et al. 1982). The heat produced by the burning of the Brazilian ginseng leaves and extraction material leftover is not necessary for the SFE process, therefore, it is used for electricity generation in a condensing turbine. As the compressed CO_2 has a high temperature, part of its cooling was also used for steam generation when integrated with the steam network, which increased the electricity production. Although, electricity is produced by the burning of the residues, it is not enough to supply the requirement of the process and it is necessary to buy external electricity.

Analysis of a SFE plant integrated to a sugarcane biorefinery

Another configuration that could bring benefits to the SFE process might be its integration to the sugarcane biorefinery producing first and second generation ethanol from sugarcane. It could be an interesting solution to the sugarcane biorefinery to have a multipurpose extraction unit operating *in situ* as it could be used to add value to its residue as the case of extraction of bioactive compounds from the filter cake created at the juice treatment for ethanol production (Prado et al. 2011). The interaction can also benefit the extraction process, as CO_2 and ethanol are available at the sugarcane biorefinery with lower cost. The CO_2 produced during fermentation could also be used to enhance the growth of different biomass material that can be used as raw-material to the extraction process. Recently it was demonstrated that CO_2-enriched atmosphere improves growth of *Pfaffia glomerata* (Saldanha et al. 2013). The integration of the heat streams of these systems could also be an advantage for the both processes.

Integrating both Scenario I and II to the sugarcane biorefinery, initially, no thermal benefit could be accounted. As the SFE process does not require heat after its integration the only possibility for its integration would be supply the extra heat to the sugarcane biorefinery. Since the scale of the extraction process is much smaller than the biorefinery, the heat contribution to the sugarcane biorefinery is negligible. This difference in the scale could be interesting to the extraction process if lower amount of CO_2 is used for the extraction or even if a pressurized liquid extraction (PLE) is considered. If lower amount or no CO_2 is used during the extraction process, lower heat or no heat would be available from its recirculation and therefore the heat demand could be easily supplied by the sugarcane biorefinery. Fig. 5 shows the contribution of the SFE process to the sugarcane biorefinery composite curve (Scenario IIB). The composite curve for the extraction process expressed in red compared to the sugarcane biorefinery, expressed in blue, is drawn as a line due the difference in scale. If a bigger scale extraction process was considered, the composite curve of the process would be shown similar to Fig. 4, and the possibility for integration with the sugarcane biorefinery could be better evaluated. This could be the case when considering the use of sugarcane waste, as the filter cake, for extraction.

Economic benefits

It was analyzed the economic potential of the 4 scenarios evaluated (Fig. 6). The economic potential of the processes can give a good initial estimative of the influence of the studied parameters at the economic feasibility of the process as it takes into account the expenditure and benefit each process analyzed. As both Scenarios I and II present very similar process and it is important to take into account that this would be a multipurpose process, the investment for both scenarios will be very similar, therefore only the economic potential was evaluated to access the scenarios economically.

Scenario II presented 2.5 times higher economic potential than Scenario I when not integrated with the sugarcane biorefinery and 2 times when integrated. The integration with the biorefinery increased in 54% and 21% the economic potential for Scenarios I and II, respectively. Scenario IIB is from the energetic and economic point of view the most attractive alternative for β-ecdysone-rich extract production from *Pfaffia Glomerata* roots.

Some of the assumed costs for raw material and price for the products can vary depending on different assumptions for the market. Therefore, a sensitivity analysis was performed varying the cost of the raw-material, the price for possibly selling the leftover extracted material and price for the extract in terms of β-ecdysone content (Fig. 7).

The cost for the raw material can vary depending different factors as cultivation and environmental conditions, pretreatment before selling the roots and others. Assuming that measures could be taken to enhance this raw-material productivity, as using CO_2 at the cultivation stage, the cost of this material would decrease increasing the economic potential of the scenarios. From the sensitivity analysis, it was found that the cost of 2.42 USD/kg is the maximum cost when the economic potential is positive for all scenarios (Fig. 7a). For the costs of 3.57 and 4.71 USD/kg, representing a raw material possibly already prepared and/or a small cultivation due to seasonal problems, the Scenarios A studied are not feasible as the economic potential is negative. For the highest raw materials cost, only Scenario IIB is still economically feasible.

The leftover extracted material could be sold to different uses, as animal feed, as fuel to cogeneration together with other waste biomass, as a natural biosorbent (Albarelli et al. 2011), and other uses. Therefore its price can vary depending on the use and also its logistics. For Scenario A, it was not considered the selling of this leftover as it was necessary to produce electricity to supply part of the electricity demand of the SFE process, so it was used as fuel for the cogeneration system. For the lowest value studied 0.01 USD/kg, the gain for the selling the leftover is really small, increasing less than 1% the economic potential of Scenario B. According with Ernesto et al. (2009), the value for selling sugarcane bagasse is around of 0.004 to 0.014 USD/kg in dry base, similar to the lowest value assumed for the sensitivity analysis. This low value, probably corresponding to the selling of this waste to be used as fuel or animal feed would not be interesting for the SFE process from the economical point of view. Preview studies (Albarelli et al. 2011) showed that biomass materials could be used as adsorbent, after bioactive compounds recovery, to remove heavy metal ions. Considering a high added-value application as the use of the leftover material as biosorbent the value of it would be higher, increasing the economical potential of Scenarios II, especially Scenarios IIb, due to the higher extraction capacity of β-ecdysone by more adequate extraction conditions employed (Fig. 7b).

Conclusion

Supercritical fluid extraction (SFE) process evaluated experimentally at the present study showed higher β-ecdysone extraction capacity from Brazilian ginseng (*Pfaffia glomerata*) roots, providing an extract with 2.5 times higher β-ecdysone than the results obtained in previous studies. Heat integration of the SFE process diminished energy requirements of the process, as CO_2 recirculation supply the thermal demand necessary for the process, resulting in a final electricity demand of 118.3 and 57.7 kWh per g of β- ecdysone in the extract, considering the SFE process under extraction conditions defined by literature and by optimized condition determined experimentally in the present study.

The integration of the SFE process with a cogeneration system enables the use of process wastes as the Brazilian ginseng aerial parts and the leftover extracted material for heat and electricity production increasing the economic potential of the SFE process. No thermal benefits could be accounted for the integration of the SFE plant to the sugarcane biorefinery producing first and second generation ethanol, but difference at the economic potential could be observed considering different raw-material cost and leftover extracted material price.

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Scenario	**I**	**II**	**Unit**
Raw material processed	29.76	29.76	kg/h
Raw material moisture content	0.66	0.66	%
Raw material cleaning soil removal	60	60	%
Raw material moisture after drying	10	10	%
CO_2 – ethanol mass ratio	10[a]	10[b]	% of ethanol
Extraction pressure	20[a]	10[b]	MPa
Extraction temperature	303[a]	323[b]	K
Solvent mass to Feed mass ratio (S/F)	50	50	
Extraction time	3.5[a]	3.5[b]	h
Extraction yield	0.36[a]	0.26[b]	% (dry basis)
β-ecdysone content in the extract	3.06[a]	8.00[b]	%
Ethanol recovery pressure	0.016	0.016	MPa
Ethanol recovery temperature	348	348	K

[a] experimental data Leal et al. (2010); [b] experimental data of the present study.

Table 1

Table 2

Parameter	**Value**	**Unit**
Juice extraction, treatment and concentration		
Raw material processed	500	t/h
Efficiency of impurities removal on sugarcane cleaning	60	%
Efficiency of sugars extraction on the milling system	97	%
Raw material moisture content	50	%
Recovery of sugars on juice treatment	99.4	%
Second generation ethanol production from bagasse		
Pretreatment catalyzed steam explosion temperature	463	K
Hemicelulose-xylose conversion	61.4	%
Enzymatic hydrolysis temperature	323	K
Reactor solids load	5	%
Cellulose–glucose conversion	69.2	%
Fermentation		
Fermentation yield	89	%
Distillation and dehydration		
Ethanol recovery on distillation and dehydration	99.7	%

data from Ensinas et al. (2013)

Table 3

	Scenario A	**Scenario B**	**Lower**	**Upper**	**Price**
Brazilian ginseng roots	1.5[a]	1.5[a]	0.13[a]	4.71[a]	USD/kg
Ethanol	0.72[b]	0.49*			USD/L
CO_2	0.60[c]	0.30[c]			USD/kg
Electricity	0.07[b]	0.05[b]			USD/ kWh
Price for the extract in terms of β-ecdysone content	86.29[d]	86.29[d]	43.15	172.58	USD/g of β-ecdysone
Leftover Brazilian ginseng roots	--	1.00	0.01[e]	16.00[e]	USD/kg

[a](ddd), [b] Albarelli et al. (2013), [c] Santos et al. 2012b, [d] (dddd), [e] (DDD), * ethanol production cost calculated by the simulation

Table 4: Summary of the process conditions and experimental results (Mean value ± Standard Deviation).

	Temperature (K)	**Pressure (MPa)**	**CO_2/ethanol proportion ratio (%, w/w)**	**β-ecdysone content in the extract (%)**
E 1	323	10	90:10	7.99 ± 0.28
E 2	323	10	50:50	6.47 ± 0.16
E 3	323	10	0:100	2.54 ± 0.08
E 4	323	20	90:10	8.08 ± 0.36
E 5	323	20	50:50	7.14 ± 0.10
E 6	323	20	0:100	2.65 ± 0.06
E 7	363	10	90:10	8.04 ± 0.08
E 8	363	10	50:50	7.50 ± 0.10
E 9	363	10	0:100	4.50 ± 0.19
E 10	363	20	90:10	7.89 ± 0.30
E 11	363	20	50:50	6.15 ± 0.20
E 12	363	20	0:100	3.55 ± 0.15

Table 5

Scenario	**I**	**II**	
Power consumption	113.4	144.3	kWh
Electricity production	37.7	68.7	kWh
Cooling demand under 298K	91.3	26.9	kWh

Figure 1

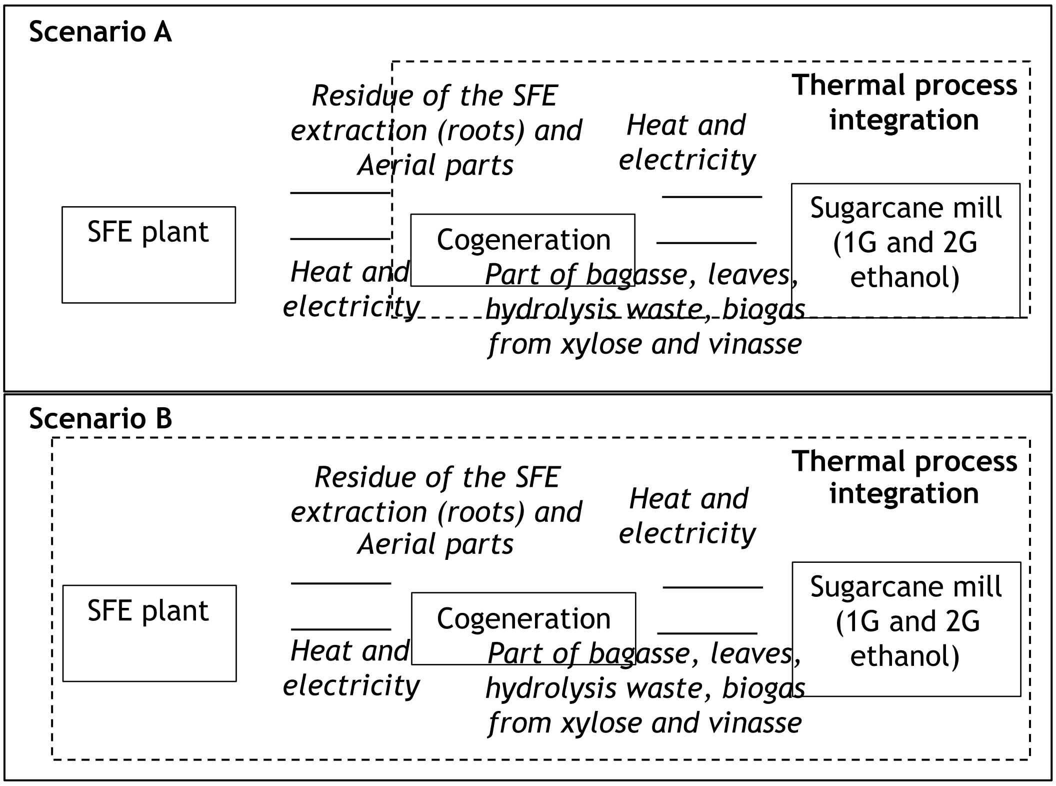

Scenario A
Residue of the SFE extraction (roots) and Aerial parts
Heat and electricity
Thermal process integration
SFE plant
Cogeneration
Sugarcane mill (1G and 2G ethanol)
Heat and electricity
Part of bagasse, leaves, hydrolysis waste, biogas from xylose and vinasse
Scenario B
Residue of the SFE extraction (roots) and Aerial parts
Heat and electricity
Thermal process integration
SFE plant
Cogeneration
Sugarcane mill (1G and 2G ethanol)
Heat and electricity
Part of bagasse, leaves, hydrolysis waste, biogas from xylose and vinasse

Figure 2

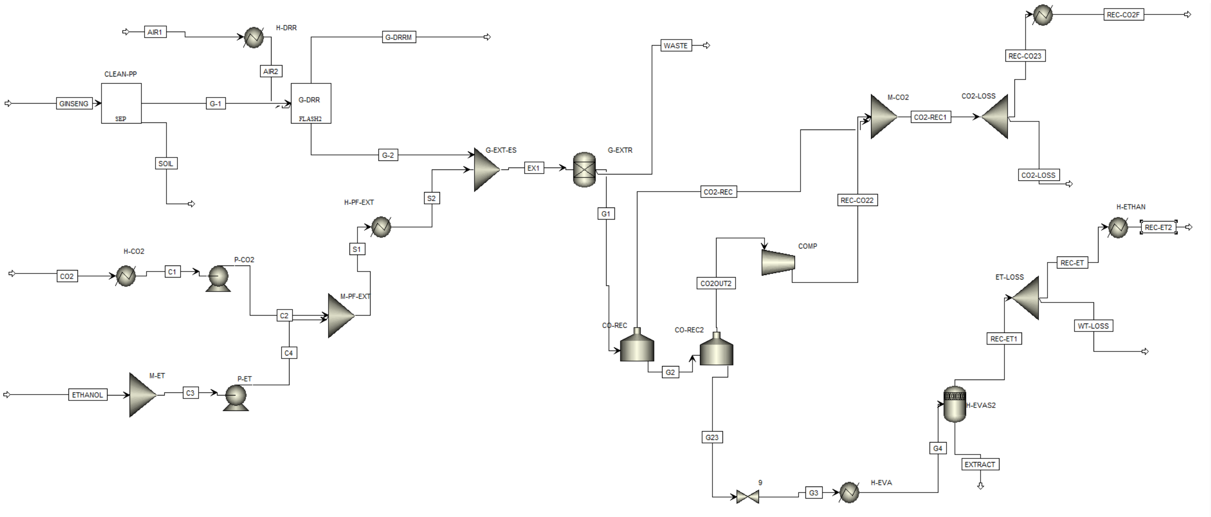

AIR1
H-DRR
AIR2
G-DRRM
CLEAN-PP
GINSENG
SEP
G-1
G-DRR
FLASH2
SOIL
G-2
G-EXT-ES
EX1
G-EXTR
WASTE
H-PF-EXT
S2
S1
H-CO2
CO2
C1
P-CO2
C2
M-PF-EXT
C4
M-ET
ETHANOL
C3
P-ET
G1
CO-REC
G2
CO-REC2
CO2-REC
CO2OUT2
COMP
REC-CO22
M-CO2
CO2-REC1
CO2-LOSS
CO2-LOSS
REC-CO23
REC-CO2F
H-ETHAN
REC-ET2
REC-ET
ET-LOSS
WT-LOSS
REC-ET1
H-EVAS2
G4
EXTRACT
G23
9
G3
H-EVA

Figure 3

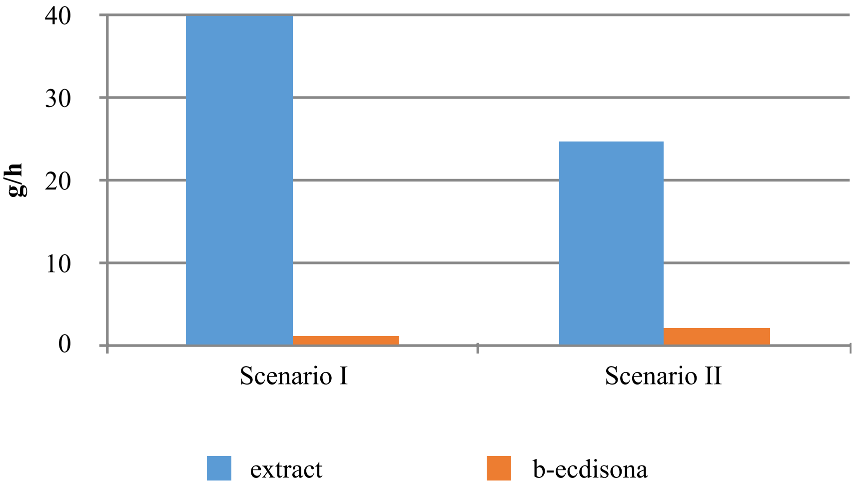


Figure 4

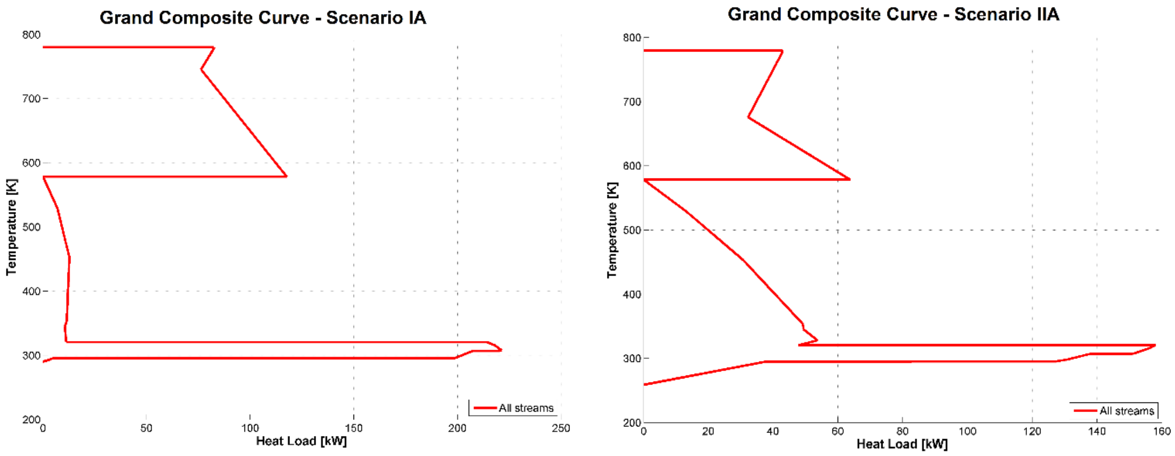

Grand Composite Curve - Scenario IA
Temperature [K]
800
700
600
500
400
300
200
Heat Load [kW]
0
50
100
150
200
250
All streams
Grand Composite Curve - Scenario IIA
Temperature [K]
800
700
600
500
400
300
200
Heat Load [kW]
0
20
40
60
80
100
120
140
160
All streams

Figure 5

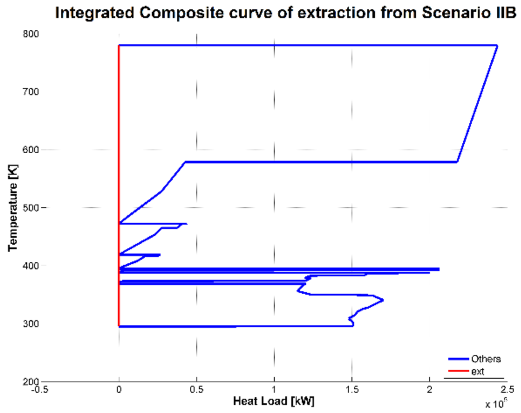

Integrated Composite curve of extraction from Scenario IIB
Temperature [K]
800
700
600
500
400
300
200
-0.5
0
0.5
1
1.5
2
2.5
Heat Load [kW]
x 10^5
Others
ext

Figure 6

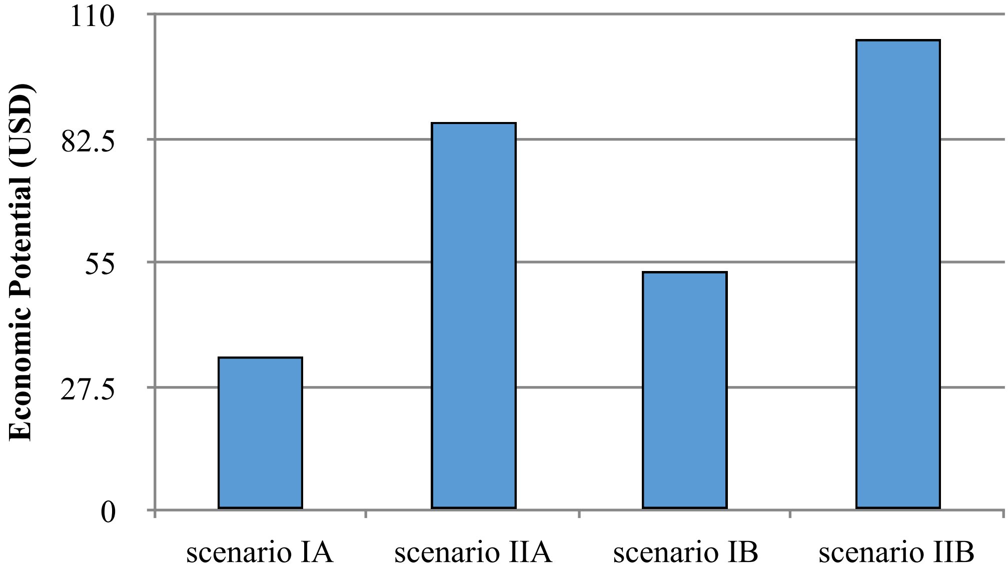
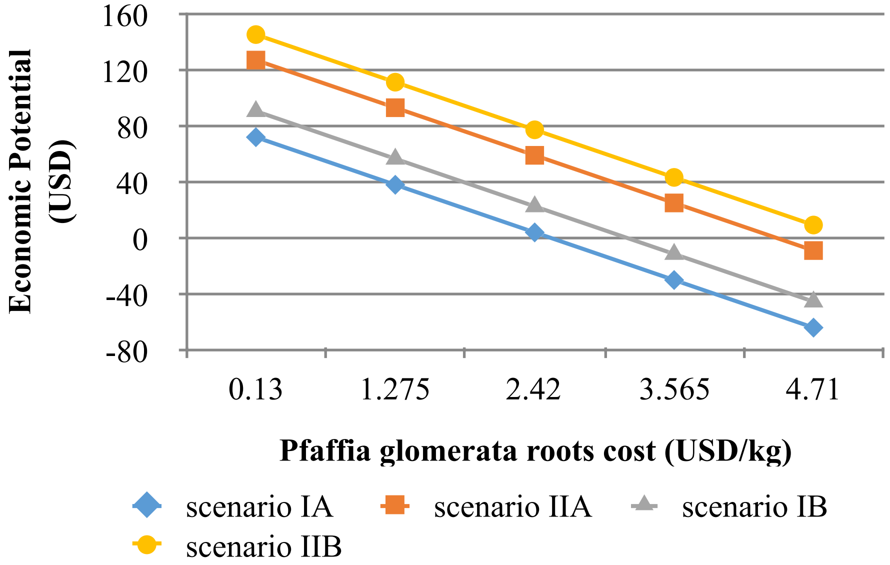

Economic Potential (USD)
110
82.5
55
27.5
0
scenario IA
scenario IIA
scenario IB
scenario IIB

Figure 7



Legend: I – extraction system based in experimental data from Leal et al. (2010); II - – extraction system based in experimental data of the present study; A – stand-alone extraction system with shared cogeneration with a sugarcane mill; B – extraction system integrated with a sugarcane mill.