



HAL
open science

Reduction of environmental impacts of caffeine extraction from guarana by using ultrasound assistance

Ramiro Ariel Carciochi, Valentin Dieu, Peggy Vauchel, Delphine Pradal,
Krasimir Dimitrov

► **To cite this version:**

Ramiro Ariel Carciochi, Valentin Dieu, Peggy Vauchel, Delphine Pradal, Krasimir Dimitrov. Reduction of environmental impacts of caffeine extraction from guarana by using ultrasound assistance. Food and Bioproducts Processing, 2021, 127, pp.266-275. 10.1016/j.fbp.2021.02.014 . hal-04549009

HAL Id: hal-04549009

<https://hal.science/hal-04549009>

Submitted on 22 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Reduction of environmental impacts of caffeine extraction from guarana by using ultrasound assistance

Ramiro Ariel Carciochi^(a), Valentin Dieu^{(a), (b)}, Peggy Vauchel^{(a)*}, Delphine Pradal^{(a), (b)},

Krasimir Dimitrov^(a)

^(a) *UMR-T 1158 BioEcoAgro, Univ. Lille, INRAe, Univ. Artois, Univ. Littoral Côte d'Opale, YNCREA, Univ. Liège, Univ. Picardie Jules Verne, Institut Charles Viollette, F-59000 Lille, France*

^(b) *ICAM site de Lille, 6 rue Auber, 59016 Lille Cedex, France*

Abstract

Extraction of caffeine from guarana seeds was studied, comparing conventional extraction (CE) and ultrasound-assisted extraction (UAE). Preliminary studies **permitted the selection of** operating conditions for kinetics studies of both processes (water solvent, 10:1 mL/g liquid-solid ratio). UAE **enabled** strong enhancement of caffeine yields and process kinetics compared to CE at room temperature. At higher temperature (50 and 70 °C), the advantage of UAE over CE was still clear for extraction kinetics, but not for maximal extraction yield. Performing Life Cycle Assessment of both processes permitted to highlight ultrasound assistance ability to reduce extraction duration (up to 4.9 times), energy consumption (up to 6.2 times) and environmental impacts (more than twice for some impact categories) compared to CE at the same studied temperature. Environmental impacts of CE and UAE processes were studied in more detail using three different functional units. It contributed to a better knowledge of extraction process of caffeine from guarana seeds and allowed selecting the operating conditions maximizing benefits provided by ultrasound assistance. The environmental gains of UAE over CE at maximal temperature were relatively small when targeting a caffeine extraction yield close to the maximal attainable (at this temperature), but increased strongly for lower target yields.

Key words: ultrasound-assisted extraction; life cycle assessment; guarana; caffeine; environmental impact; green extraction

1. Introduction

Six caffeine-containing genera are worldwide used to prepare stimulant beverages, namely *Coffea*, *Camellia*, *Theobroma*, *Cola*, *Ilex*, and *Paullinia* (Weckerle et al., 2003). Particularly, *Paullinia cupana* Kunth var. *sorbilis* (Mart.) Ducke, more commonly named “guarana”, is a low-growing bush-type plant native to the Amazon region of Brazil whose seeds are among the richest vegetable sources of caffeine. The naturally occurring content is around 2–6% (dry weight basis), which is 3-5 times higher than in an Arabica coffee bean, 30 times higher than in cocoa bean and 10 times than in yerba tea, other popular stimulant drinks (Santana & Macedo, 2018). The interest on caffeine extracts is related to their stimulant effects on the nervous, muscular and cardiovascular systems such as improved alertness, reaction time, speed of information processing, memory, mood and performance in physical exercises (Machado et al., 2018).

Extraction of caffeine from guarana has previously been investigated, focusing mainly on conventional solvent extraction, using either pure solvents (water, alcohols, methylene chloride, and chloroform) or water-organic solvent mixtures (water-ethanol, water-methanol and water-acetone) (Machado et al., 2018; Majhenic et al., 2007). These methods have some disadvantages since they require several hours for a complete extraction and, generally employ volatile, toxic and flammable solvents, leading to several human risks and safety issues and to a poor environmental performance. To overcome these difficulties, other environmental-friendly technologies have been used as alternative methods, such as supercritical fluid extraction (Marques et al., 2016), enzyme-assisted extraction (Ribeiro et al., 2012), ionic liquids (Cláudio et al., 2013), and microwave-assisted extraction (Adnadjevic et al., 2017). Among these innovative methods, considerable attention in recent years has been focused on ultrasound-assisted extraction (UAE). UAE has been advantageously applied for the recovery of valuable compounds from different matrices, the main benefits being a shorter and more effective extraction, using moderate temperatures and reducing energy consumption (Carciochi et al, 2017; Chemat et al., 2017; Chemat et al., 2020; Pradal et al., 2016). To the best of our knowledge, only one published work has used ultrasound assistance to intensify caffeine extraction from guarana (Koturevic et al., 2020). In this very recent work the authors have reported a strong reduction of energy consumption due to ultrasound assistance compared to conventional extraction (CE) showing that UAE could be considered as a “greener” alternative. However the environmental impacts of these processes have not been compared. Indeed, till now very few works have reported results to demonstrate the effective reduction of environmental impacts of the extraction processes, generally considered as green, in comparison to conventional ones (Vauchel et al., 2018).

Life Cycle Assessment (LCA) is a methodology based on the concept of sustainable development, providing an effective and systematic mean of assessing the environmental impacts of a product, process or service (Joliet et al., 2015). This assessment tool is applied to various categories of environmental impact such as greenhouse effect, eutrophication, acidification, ozone layer depletion, ecotoxicity, photochemical pollution, human health, exhausting of natural resources, etc. It enables the quantification of potential environmental impacts of a system, taking into account all the activities associated with a product or a service, from the raw materials to the end of life processing (distribution, use, waste disposal, incineration, recycling, etc.). This method consists of listing the consumptions of natural resources, energy and environmental emissions (water, air and soil). The flows of matter entering and leaving at each step of the life cycle are inventoried (life cycle inventory). This inventory of base flows shows the quantities of polluting substances emitted and the resources extracted during the life cycle. From the results gathered, the environmental impacts are assessed by calculating the contribution of each of the flows to the various environmental impacts studied (De Marco et al., 2018; Santiago et al., 2020).

The aim of this work was to elucidate the potential of ultrasound assistance for reducing environmental impacts on the base of caffeine extraction from guarana seeds case study. For this purpose, a gate-to-gate LCA analysis of caffeine extraction without and with ultrasound assistance was carried out. An initial screening on the effect of solvent composition (water-ethanol mixtures) and liquid-solid (L/S) ratio was conducted, followed by a study of CE and UAE performance in terms of caffeine yield kinetics, energy consumption and environmental impacts. CE and UAE were compared at different temperatures and for three different functional units (FU) allowing a better knowledge of the process at whole and an indication of operating conditions with lowest environmental impacts.

2. Materials and Methods

2.1. Materials

Ground guarana seeds (diameter less than 2 mm) were kindly provided by Ortis Laboratoires (Elsenborn, Belgium). Caffeine and concentrated phosphoric acid (85% w/v) were purchased from Sigma (St. Louis, MO, USA). Ultrapure water was obtained using a Milli-Q system (Millipore, Milford, MA, USA). HPLC-grade solvent acetonitrile was obtained from Merck (Darmstadt, Germany). All other chemicals and reagents were of analytical grade.

2.2. Extraction procedures

Preliminary experiments evaluating the influence of solvent composition and liquid-solid ratio on the yield of caffeine were performed in an incubator shaker (model Multitron Standard, Infors HT, Bottmingen, Switzerland). According to each single factor experiment, a certain amount of ground guarana (2 to 6 g) was suspended in 30 mL specific solvent media (0, 20, 40, 60, 80, or 100 % ethanol in water (v/v)) and then submitted to extraction at 30 °C and 160 rpm agitation speed for 90 min. Afterwards, samples were centrifuged at 10,000 rpm for 10 min (Eppendorf Centrifuge 5804 R, Hamburg, Germany) and the supernatant was carefully removed for further analyses. All extractions were performed in triplicate.

The kinetics of caffeine extraction without and with ultrasound assistance at different temperatures were performed in another series of experiments. For all studies of extraction kinetics (CE and UAE) 70 g guarana seed powder was mixed with 700 mL of distilled water (L/S ratio of 10:1, mL/g) at room temperature (20 °C) and then submitted to extraction at 20, 50, or 70 °C for 60 min.

The CE at room temperature (20 °C) was carried out in a simple 1 L glass cylinder vessel.

The CE at higher temperature (50 °C or 70 °C) were carried out in a double-walled glass contactor (1 L) coupled to an external circulating water bath connected to a thermostat. To use less energy for the extraction processes **and minimize their environmental impacts**, the solvent was not previously heated; it was heated during extraction process till the target maximal temperature, then temperature was maintained stable. Initial temperature in the water bath was 20 °C.

The UAE were carried out using a 0.75 L cylinder contactor with radial external transducers fixed around (model NexTgen Lab 750, SinapTec, France) operating at a power of 400 W and frequency of 22 kHz. **At the output power of ultrasound generator of 400 W, the power absorbed in the medium was of 220 W. It was determined by calorimetric analysis as proposed by Both et al. (2014), which corresponded to a specific power density of 314 W/L in the studied conditions (700 mL of solvent).** Initial temperature of the solvent was 20 °C, but sonication provoked a temperature elevation during extraction process. Temperature sensors included into the device allowed to regulate the application of ultrasounds in order to maintain the target maximal temperature (50 °C or 70 °C). For each experimental condition, two temperature levels were fixed: a maximal one (suspension of sonication) and a minimal one (sonication restart). Therefore, in the case of UAE the sonication was initially applied in a continuous mode till the moment when temperature of the extractor overtook the maximal limit, then sonication was applied in a discontinuous mode, maintaining in such a way an almost constant temperature around the target maximal temperature for the studied condition.

In all kinetics studies a mechanical agitator was used at 160 rpm allowing to maintain the guarana particles in suspension. Samples of the extract were taken regularly during extraction and centrifuged (10,000 rpm, 10 min) prior to evaluation of caffeine concentration of supernatants.

For each experiment, energy consumption of the equipment was registered using an electrical meter (Otio, Auterive, France).

2.3. HPLC analysis of caffeine

The chromatographic analyses were carried out using a Waters liquid chromatograph system model ACQUITY H-Class coupled to a PDA detector following the method described by Sharma et al. (2005) with slight modifications. Empower 3 internal software was used for data processing (Waters Corp., Milford, Massachusetts, USA). Separation was carried out in a Grace Vydac 218TP C18 column (250 mm x 3 mm i.d., 5 μ m) using a linear gradient of 0.1% H₃PO₄ solution (A) and acetonitrile (B) pumped at flow rate of 0.6 mL/min as follows: 0 min, 95% A, 5% B; 15 min, 84% A, 16% B; 16 min, 95% A, 5% B. A re-equilibration interval of 5 min at the initial conditions was performed between injections. Injection volume was 1 μ L and detection wavelength used was 272 nm. Quantification was performed using the external standard method and the amount of caffeine was expressed as g caffeine per kg of guarana (dry basis).

2.4. Statistical analysis and modeling of extraction kinetics

The contents of caffeine was analyzed using Empower 2 software used for data processing (Waters Corp., Milford, Massachusetts, USA), and means of the different treatments were separated by least significant difference (LSD) test at a 5% significance level. The extraction kinetics curves obtained were fitted to the equation model proposed by Patricelli et al. (1979). The quality and adequacy of the adjustments was assessed by the determination coefficient (R^2) and normalized root-mean-square error (NRMSE) using Infostat software (Infostat group, Argentina).

2.5. Life Cycle Assessment (LCA)

Life Cycle Assessment was performed to calculate environmental impact of extraction processes. This method allowed to evaluate contribution of environmental performance at different stages of Life Cycle. This analysis must be compliant to the International Standards ISO 14040 and ISO 14044 (2006). Life Cycle Assessment consisted on four main steps;

which are 1) Goal and Scope Definition, 2) Life Cycle Inventory (LCI), 3) Life Cycle Impact Assessment (LCIA), and 4) Life Cycle Interpretation.

2.5.1. Goal and scope definition

The LCA goal of this study was to evaluate the influence of operating conditions on environmental performances for lab-scale extraction process of caffeine from guarana. Firstly, LCA is useful to define optimal operating conditions to improve environmental performance of extraction process. Secondly, LCA was used to compare UAE and CE environmental performances at each experimental condition of kinetics studies. A gate to gate approach was chosen. The studied system and its boundary are presented in Figure 1.

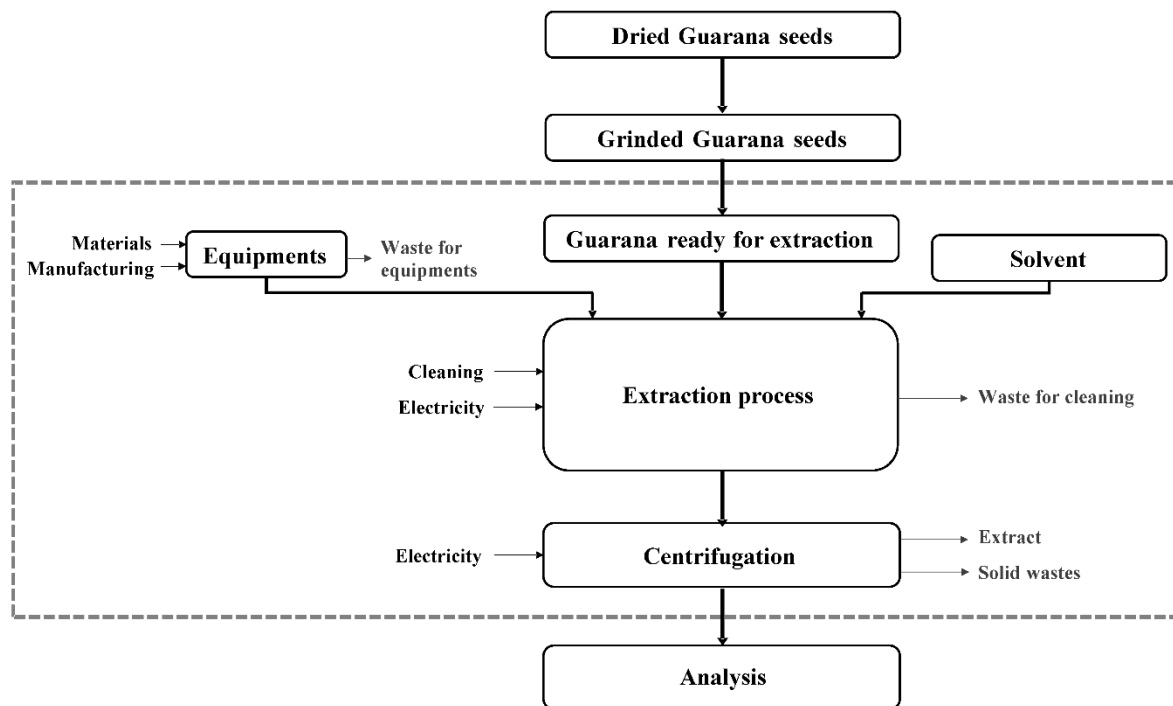


Figure 1. Representation of studied system and its boundaries.

In this study, three functional units have been defined. The first FU was an extraction yield of 21.2 g of caffeine per 1 kg guarana (caffeine extracted from 70 g de guarana by 0.7 L of solvent as a reference flow for the given system). This FU corresponded to the maximum yield achieved in one hour of conventional extraction at room temperature (20 °C). The second FU was 26.4 g of caffeine per 1 kg of guarana with the same reference flow. This FU corresponded to the maximum yield achieved in one hour at 50 °C by both CE and UAE. The last FU was 28.7 g of caffeine per 1 kg of guarana, corresponding to the maximum yield

achieved in one hour at 70 °C by both CE and UAE. The equation obtained for each extraction kinetics using Patricelli model allowed determining extraction time and, respectively, energy consumption for each of these three functional units at each experimental condition.

2.5.2. Life Cycle Inventory (LCI)

The Life Cycle Inventory included all inputs and outputs from areas of the studied system. Data inventory was performed with LCA software SimaPro v8.5 (PRé Consultants). Two types of data were used: experimental data collected during extractions (electricity consumption, extraction duration) and generic data from databases. In this study, “Allocation at the point of substitution” from EcoInvent 3 database was selected as far as possible. ELCD database was used in complement. These databases were used to model inputs (equipment, solvent, electricity, transport) and outputs (waste solvent, end of waste of equipment).

2.5.2.1. Equipments

Materials of equipment (stainless steel, plastics, glass, electric and electronic components, etc.), manufacturing of materials, and waste treatment of equipment were modeled. Reactor with radial external transducers, generator of ultrasounds, control tablet, mechanical agitator and centrifuge used for separation of the extract from guarana particles were used for UAE studies. Glass contactor, external circulating water bath with thermostat, agitator and centrifuge were used for CE studies at 50 and at 70 °C. Glass contactor, agitator and centrifuge were considered for CE studies at 20 °C. Equipments were included considering a mass allocation depending on extraction duration at each experimental conditions. The allocated mass of equipment was calculated according to Eq 1.

$$\text{allocated mass (kg)} = \frac{\text{equipment mass (kg)} \times \text{extraction duration (h)}}{\text{equipment lifetime (year)} \times 365 \left(\frac{\text{day}}{\text{year}}\right) \times \text{mean usage duration} \left(\frac{\text{h}}{\text{day}}\right)} \quad (\text{Eq. 1})$$

2.5.2.2. Transport

Among inputs integrated in the system boundaries, only transport of raw material had to be considered. Electricity and deionized water were onsite supplied. Transport was modeled with generic data on the base of raw material mass and traveled distance from supplier.

2.5.2.3. Materials

In this study, drying and grinding of guarana were excluded from the scope of the system. Deionized water was the only solvent used.

2.5.2.4. End of life treatment

After extraction, liquid extracts were centrifuged. Residues were collected, weighed and considered as an incinerated solid waste.

2.5.3. Life Cycle Impact Assessment (LCIA)

Environmental impacts were expressed at midpoint level using ILCD2011 methodology, compliant to ILCD Handbook (2010) recommendations. Sixteen impact categories were expressed: Climate change (CC), Ozone depletion (OD), Human toxicity, non-cancer effects (HTNCE), Human toxicity, cancer effects (HTCE), Particulate matter (PM), Ionizing radiation HH (IRHH), ionizing radiation E (IRE), Photochemical ozone formation (POF), Acidification (A), Terrestrial eutrophication (TEu), Freshwater eutrophication (FEu), Marine eutrophication (MEu), Freshwater ecotoxicity (FEc), Land use (LU), Water resource depletion (WD), Mineral, fossil & renewable resource depletion (RD).

3. Results and Discussion

In order to propose environmentally-friendly processes in this study, it was very important to precisely describe the kinetics of caffeine extraction. It was indeed necessary to find the time needed to reach a target yield in each extraction condition, in order to compare the corresponding energy consumptions as well as the environmental impacts of each extraction process. Experimental design tool has several advantages, such as optimizing several parameters together, minimizing the number of experimental runs and considering the effect of interaction between different operating parameters under study. However, it is not well adapted to precisely determine the optimal extraction time. Indeed, the driving force of the extraction process decreases quasi exponentially in time. Therefore, it was decided to use single-parameter optimization to firstly select appropriate solvent and liquid to solvent ratio, and then study in detail the extraction kinetics with and without ultrasound assistance.

3.1. Effect of ethanol concentration and liquid to solid ratio on the extraction yields of caffeine

Figure 2a shows that extraction of caffeine from guarana seeds was clearly more efficient with pure water than with pure ethanol. However, mixing of these two solvents permitted to

find better conditions for caffeine extraction than the aqueous extraction. An increase in ethanol concentration from 0 % to 40 % (v/v) allowed a 24 % enhancement of caffeine yield. Then, the increase in ethanol content no more improved caffeine yield, and contents higher than 60 % led to a gradual decrease of caffeine extraction. Similar yield tendencies were previously observed by other authors (Jun, 2009; Hu et al., 2016), related to solvent polarity and respective solubility of caffeine. Taking into account that caffeine yield improvement obtained with the addition of ethanol was quite moderate and considering the cost and impact on the environment that implies the use of organic solvents on an industrial scale, it was decided to keep water as extracting solvent in the following experiments.

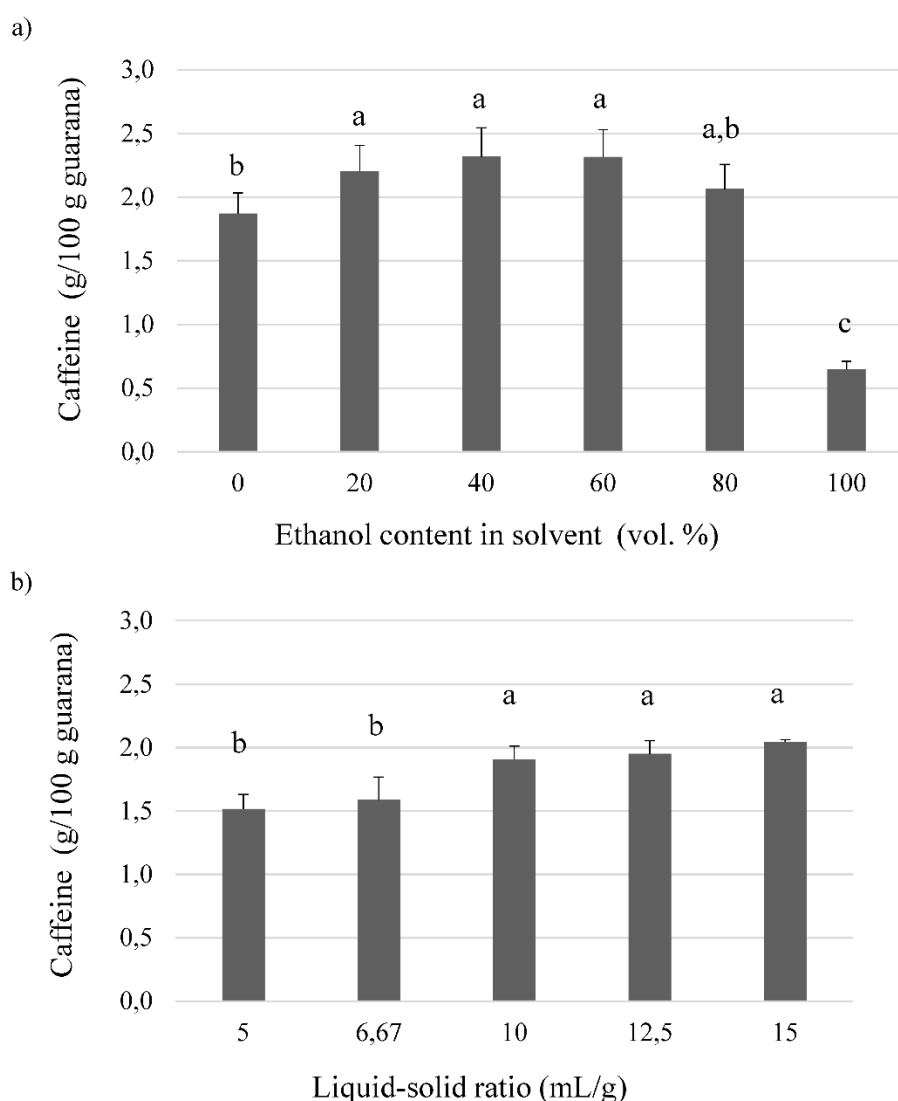


Figure 2. Single-factor effect on the extraction yield of caffeine: (a) ethanol concentration in the solvent system using a liquid-solid ratio of 10:1 mL/g; (b) liquid-solid ratio using water as

solvent. Different letters over the bars indicate significant differences between the means according to ANOVA and LSD tests ($p < 0.05$).

Regarding the effect of liquid-solid ratio (Figure 2b), the yield of caffeine increased progressively when the L/S ratio increased from 5:1 to 15:1 mL/g. From an economical point of view, it would be more advantageous to prioritize the extractions employing lower L/S ratios because of the higher concentrations in such conditions. However, it was observed that the ratios 5:1 and 6.67:1 provided lower yields. Considering that there was no statistical difference ($p < 0.05$) between the extractions performed at L/S ratio between 10:1 and 15:1, thus 10:1 mL/g was selected as the optimum liquid-solid ratio for the following kinetics studies.

3.2. Kinetics studies

Kinetics curves obtained at temperatures of 20, 50 and 70 °C with or without ultrasonic assistance are presented in Figure 3. The simple Peleg model, describing usually well kinetic curves at constant extraction temperature, was not sufficiently adapted in the present case since, in most of the studied extraction conditions, the temperature was not always constant (the extraction started at ambient temperature) and, therefore, solubility and diffusivity also varied during extraction runs. Since Patricelli model involved two simultaneous extraction steps with different kinetics, mathematically traduced by two exponential expressions (Patricelli et al, 1979), it allowed to precisely describe extraction kinetics even when temperature varied (R^2 values in the range 0.996-0.998 and NRMSE below 2 % were obtained with this model). Thus, equations derived from Patricelli model were used to predict the yield of caffeine extracted at a specific time.

UAE are often compared to CE performed at room temperature, without taking into account the fact that sonication provokes not only mechanical effects with cavitation phenomena, but also a heating of the solvent which is also favorable for the acceleration of extraction process and for the enhancement of extraction yields. To elucidate if these advantages of UAE are related to the temperature increase, conventional extractions were also carried out at temperatures of 50 °C and 70 °C as it was done for UAE. Comparing the results obtained without external heating by water bath, it is obvious that the two experimental conditions of UAE provided faster extraction and higher yields than the CE at room temperature. For example, the improvement of extraction yield due to ultrasound assistance (UAE at 70 °C) at 15 min was about 62 %, and then decreased to about 40 % at the end of extraction (at 60 min).

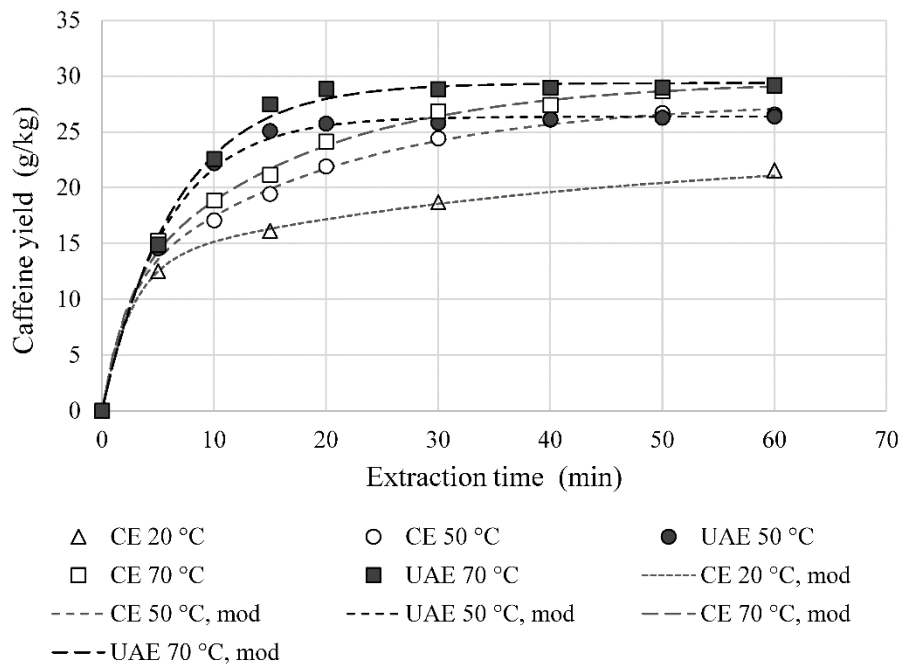


Figure 3. Kinetics profiles of caffeine extraction of extracts obtained with or without ultrasonic assistance at different temperatures fitted by Patricelli's model. Symbols: Experimental data; lines: Model fitting curves.

A positive effect of temperature was observed since the extraction yield after 1 h CE at 50 °C was 28 % higher than at 20 °C. Further increase from 50 °C to 70 °C provided a quite lower enhancement. The observed positive effect of temperature is coherent since, in general, the solubility increases at higher temperature. In addition, an increase in temperature correlates also with improvements in extraction kinetics due to the decrease of viscosity and tension of the solvent that leads to a better solvent diffusion into the vegetal matrix and higher diffusivity of the extracted solutes, finally enhancing the mass transfer.

Then, the comparison of CE and UAE kinetics carried out at the same temperature showed that the application of ultrasounds had a positive impact on the extraction kinetics, since the same yields **were reached** in a shorter time. At 70 °C ultrasound assistance allowed to attain the maximal value for these conditions at 20 min while this value was attained after 60 min in the case of conventional extraction. This positive effect could be related to cavitation phenomena provoked by sonication, that impacts vegetal matrix (local erosion, shear forces, sonoporation, fragmentation, capillary effect, and detexturation) (Khadhraoui et al., 2018) but also to the faster heating of the solvent in the case of UAE. At 15 min, the positive effect of ultrasound assistance was 23 % at 50 °C and 22 % at 70 °C, while after 1 h of extraction there

were practically no difference between extraction yields of CE and UAE at the same temperature.

The positive effect of ultrasound assistance on caffeine extraction is much more evident regarding the relationship between caffeine yield and energy consumption during conventional and ultrasound-assisted extractions (Figure 4). Logically, less energy was consumed in the case of CE at room temperature (20 °C). Therefore, these conditions are favorable if the target extraction yield is up to 20 g caffeine / kg guarana. In this case, only energy for agitation is needed. However, if higher yields are targeted, other energy inputs are necessary. In the case of UAE such additional energy is provided by the sonication with both mechanical (cavitation) and heating effects. In the case of CE at 50 °C and 70 °C, the heating to the target temperature was provided by the water bath. Fig. 4 shows that for the same temperature much more energy was consumed in CE with heating than in UAE. Obviously, ultrasound assistance allowed a strong reduction of energy consumption for the same yield at both studied temperatures (50 °C and 70 °C). Indeed, the 2 L water of the water bath that provided heating of the extraction solvent needed more energy to be heated and pumped through the double wall of the extractor compared to the energy furnished by sonication directly into the 700 mL solvent in the case of UAE. Heat losses are also probably higher in the case of CE taking into account higher contact area with the environment. Therefore, ultrasound assistance allowed to reach a target extraction yield using less energy and at reduced extraction duration (Table 1). For the three target extraction yields (the maximal ones for 1 h CE at 20 °C, for both CE and UAE at 50 °C, and for both CE and UAE at 70 °C), one can see that at 50 °C ultrasound assistance permitted to reduce the energy consumption between 2.0 and 2.4 times, and at 70 °C this reduction varied between 2.1 and 6.8 times. Such strong reduction of energy consumption due to ultrasound-assistance (more than 4 times) was reported by Koturevic et al. (2020), but the energy efficiency in the present study was much higher. For example, at 15 min UAE, only 246 kJ were needed to obtain 1 g caffeine in the present study (UAE at 70 °C), while 2000 kJ/g caffeine were reported by Koturevic et al. (2020). This higher energy efficiency could be explained by the much lower L/S ratio in the present study (10:1) against 80:1 mL/g in Koturevic et al. (2020) study, and probably partially by the difference between the equipments and experimental conditions used.

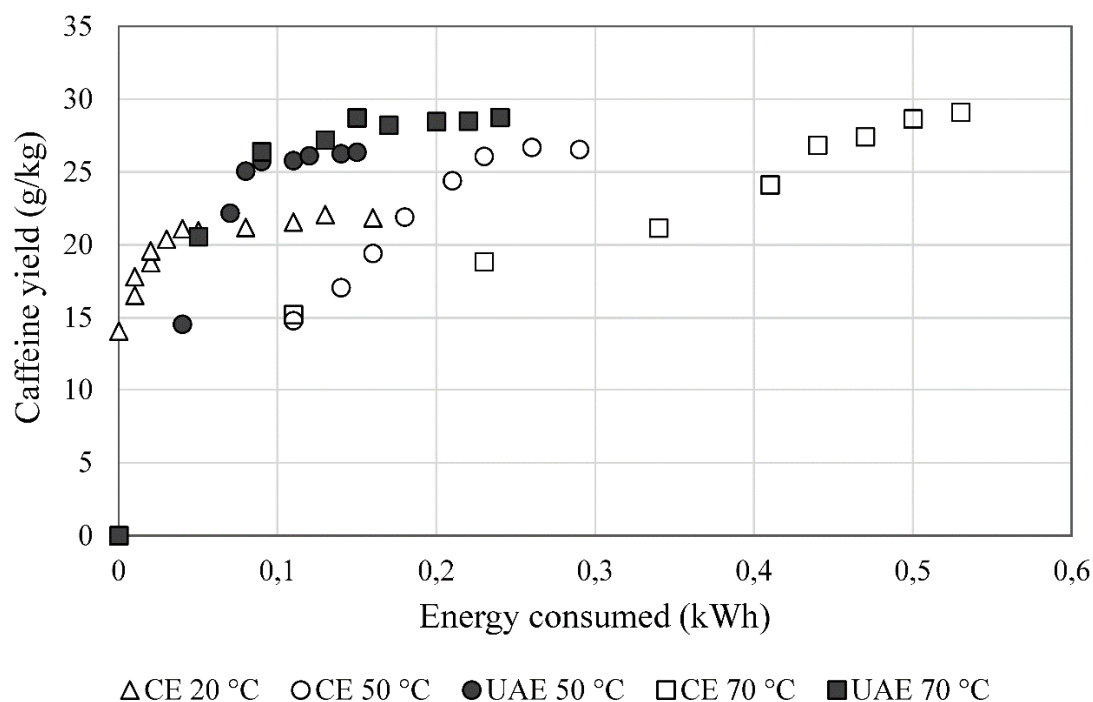


Figure 4. Relationship between caffeine yield and energy consumption during conventional extraction at 20 °C, 50 °C and 70 °C and ultrasound-assisted extraction at 50 °C and 70 °C (L/S of 10:1 mL/g).

	CE 20°C	CE 50°C	CE 70°C	UAE 50°C	UAE 70°C
Extraction duration (min)					
21.2g of caffeine / 1 kg guarana	60	18	15	10	5.5
26.4g of caffeine / 1 kg guarana	-	50	30	45	10.5
28.7g of caffeine / 1 kg guarana	-	-	51	-	60
Electricity consumption (kWh)					
21.2g of caffeine / 1 kg guarana	0.05	0.17	0.34	0.07	0.05
26.4g of caffeine / 1 kg guarana	-	0.26	0.44	0.13	0.09
28.7g of caffeine / 1 kg guarana	-	-	0.5	-	0.24

Table 1. Extraction duration and energy consumption to obtain 3 different target yields of caffeine during UAE and CE at different temperatures (L/S of 10:1 mL/g)

Some studies have reported a degradation of natural compounds after ultrasonic treatment, mainly due to a long period of ultrasound application (and associated chemical reactions that can take place, such as free radicals production, hydrolysis and oxidation) and also due to high temperatures reached during extraction process (Pingret et al., 2013; Sicaire et al., 2016; Carciochi et al., 2017). In the present study, the extraction kinetics performed with ultrasound assistance (Figure 3) revealed that there was no decrease in caffeine extraction yield after reaching the maximum value for each temperature (50 and 70 °C). Thereby, there was no degradation of caffeine due to heating or sonication. Indeed, thermal stability studies have shown that caffeine is stable at temperatures of up to 150 °C for a pressure of 0.1 MPa (Dichi et al., 2014), a much higher value than the one used in the present study.

3.3. Comparative LCA between CE and UAE at different temperatures

The observed reduction of time and energy suggested lower environmental impacts in the case of UAE compared to CE. However, the equipments used were also different and therefore it was difficult to predict the experimental conditions which are more favorable regarding environmental performance. To compare different scenarios, usually a unique FU is used. However, it is interesting to see if the same conclusions would be made using different functional units for the same processes. In present study it was chosen to compare UAE with CE using three different FU, corresponding respectively to the three maximal extraction yields at each of the studied temperatures: 21.2, 26.4 and 28.7 g of caffeine per kg of guarana, respectively at 20 °C, 50 and 70°C. Energy consumption and time needed to reach these three target extraction yields for each experimental condition was considered in the following LCA of the studied extraction processes, together with the other elements of the life cycle inventory.

Figure 5a presents LCA results considering a FU of 21.2 g/kg. Impacts were expressed as percentages of the maximum impact among all extractions. The operation with highest impact on all categories was the CE at 70°C where much more energy was consumed to attain the yield of 21.2 g/kg (Table 1). The operating conditions of CE at 20 °C and UAE at 70 °C were the most environmental-friendly between the tested ones for this FU. Indeed, the relative impacts for these 2 extraction conditions were very similar. The low impact for CE at 20 °C is related to the simpler extraction equipment used in that case and to the low energy consumption even if extraction duration was long (1 h). The low impacts in the case of UAE at 70 °C are mainly due to the very short extraction time (5.5 min) and corresponding low energy consumption even if the equipment used in UAE was heavier and more complex.

Comparing the impacts at the same temperature for the extraction without and with ultrasound assistance, one can see that all impacts were lower for UAE and that this difference was higher at 70 °C. Therefore, for the FU of 21.2 g/kg, the assistance of ultrasound during extraction allowed the reduction of environmental impacts, extraction duration, and electricity consumption.

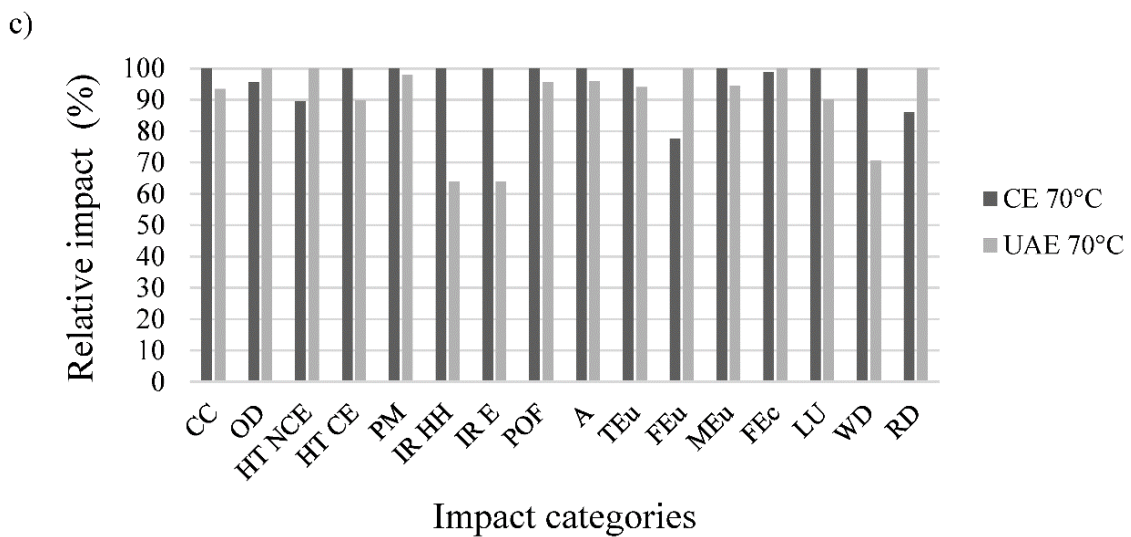
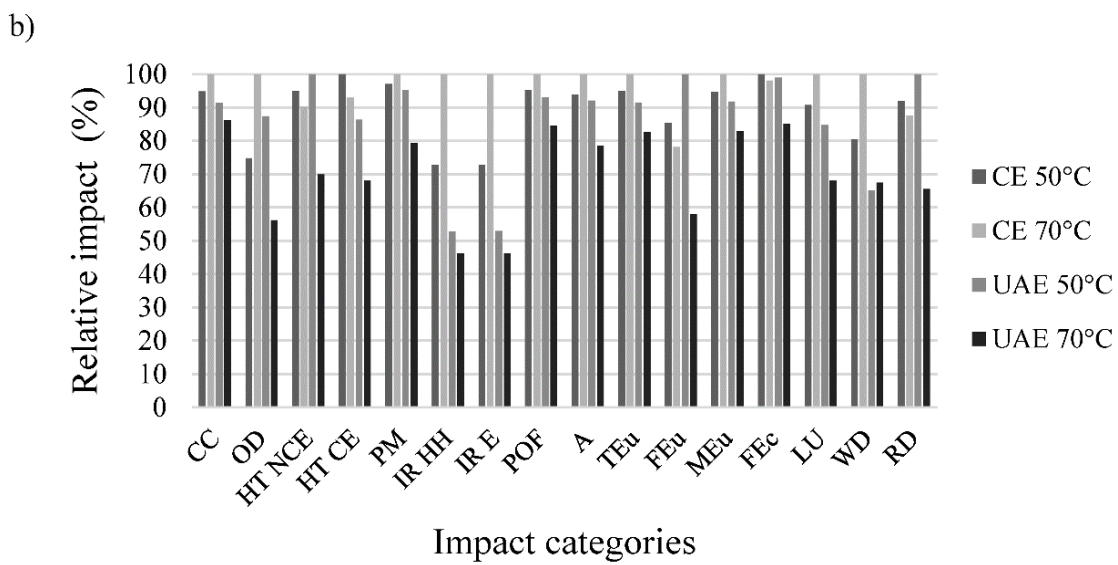
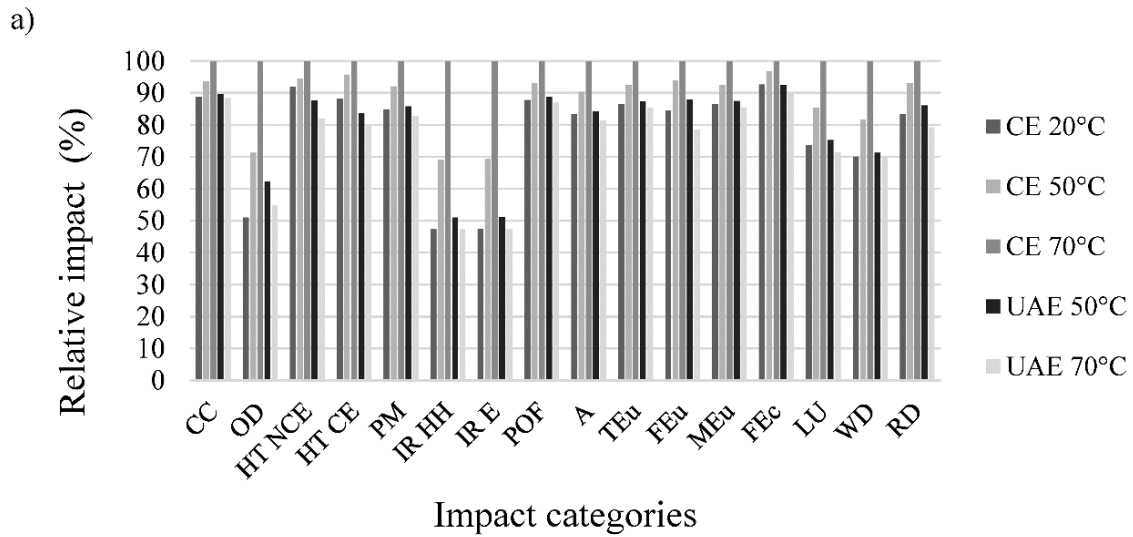


Figure 5. Comparative LCA between extractions with and without US assistance: a) for 21.2 g/kg; b) for 26.4 g/kg; c) for 28.7 g/kg.

In Figure 5b are presented LCA results concerning the second FU, 26.4 g/kg. Again the CE at 70 °C exhibited the highest environmental impacts even if for this FU it was less evident (highest impacts for 11 impact categories among 16). Electricity consumption was found to be one of the major contributors among all the impacts except for the categories “HT NCE”, “HT CE”, “FEu”, “FEc” and “RD”. The operation with highest impact on “HT NCE”, “FEu” and “RD” categories was UAE at 50°C. Use of equipment was the major contributor for these categories, and the equipment for UAE was more complex with an important allocation of electronic devices and the duration of UAE at 50 °C was close to that of CE at the same temperature. The operation with the highest impact on “HT CE” and “FEc” categories was the CE at 50°C. The equipment used in CE with heating included more steel than equipment used for UAE (external circulating water bath and thermostat) which was important for these impact categories. For this FU, environmental performances were highest in the case of UAE at 70°C. This extraction condition required a lowest duration (10.5 min) and lowest energy consumption (0.09 kWh) to achieve the target caffeine yield. Therefore, the comparison between CE and UAE was also favorable for UAE especially at 70 °C, but at 50 °C it was less evident (for 12 impact categories among 16, and with lower differences between CE and UAE for most of the categories).

Contribution of different steps of the life cycle to each category of impacts is complex and vary in function of the operating conditions. An example for cumulative impact of life cycle steps on an impact category is presented in Fig. 6 for the FU of 26.2 g/kg. Extraction step influenced by electricity consumption was the highest contributor of impact for the indicator “Ozone depletion”. This figure illustrates also that the contribution of the equipment on this indicator was clearly higher in the case of UAE compared to CE due to the specific equipment for UAE.

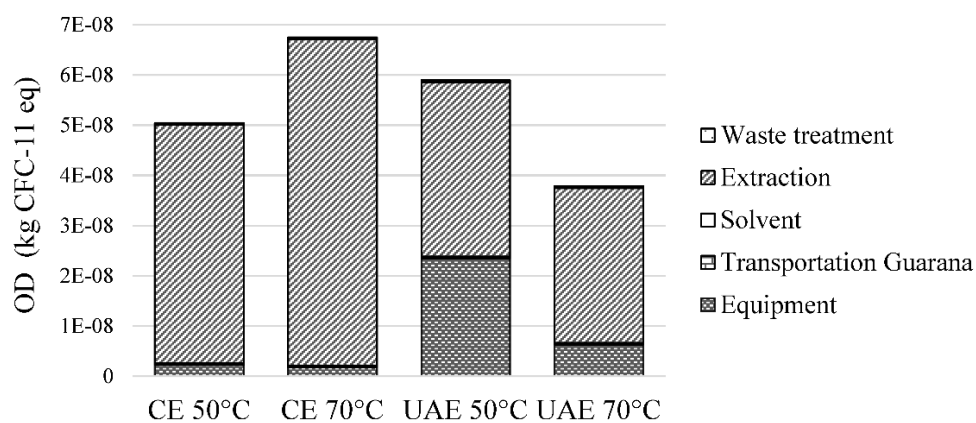
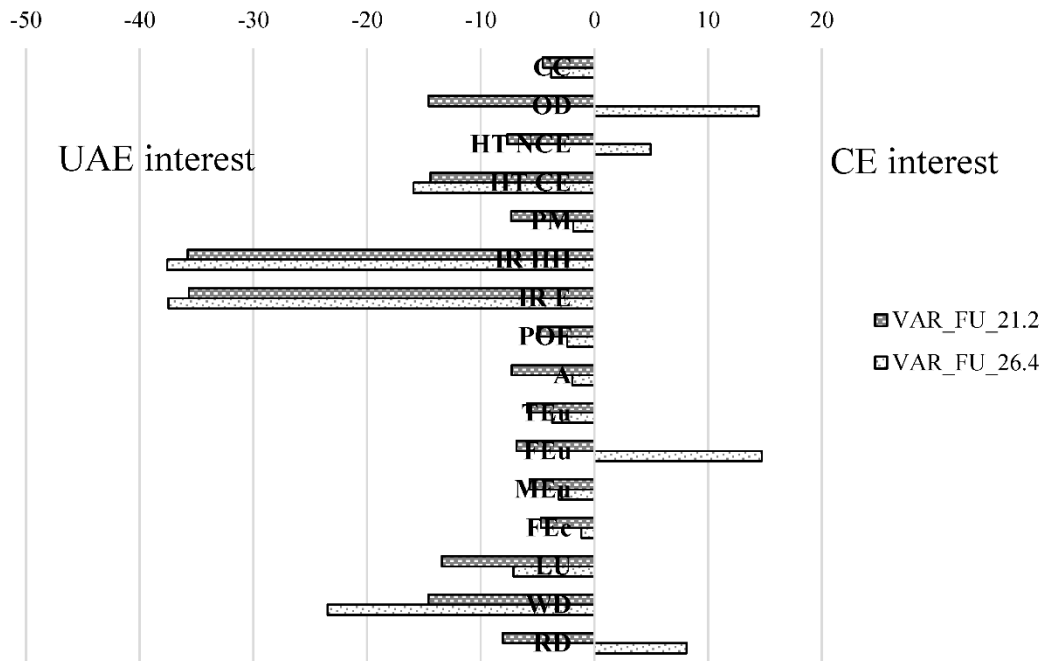


Figure 6. Environmental performance to achieve 26.4 g/kg with Ozone Depletion indicator (kg CFC-11 eq).

LCA results for the last FU (28.7 g/kg) are presented in Figure 5c. Since the extractions at 20 °C and 50 °C did not **permit** to attain this target yield, only CE and UAE at 70 °C were considered. As for the two other FUs, the environmental impacts were higher for CE. However, for this FU the relative impacts for UAE were lower for 11 impact categories only, while for the other 5 (“HT NCE”, “HT CE”, “FEu”, “FEc” and “RD”) CE had lower impact. In addition, the differences between the impacts in CE and UAE at 70 °C were lower for this FU compared to those found for the two other FUs.

To better illustrate the interest to assist the extraction by ultrasound regarding environmental performance, and the impact of FU choice, different scenarios were compared on couples. Figure 7a demonstrates the interest to apply sonication and how impact categories were sensitive to FU choice at 50°C. Variation was calculated between CE and UAE at this temperature for the two FUs which were attainable. Negative variation meant that UAE **enabled** to reduce environmental impacts compared to CE. On the contrary, positive variation meant that CE was more environmental-friendly than UAE. Ultrasound assistance allowed to reduce all impacts for the FU of 21.2 g/kg with reduction between 5 and 37 % for different categories. For the FU of 26.4 g/kg, UAE had also better environmental performance except for the four categories “Ozone depletion”, “Human toxicity, non-cancer effects”, “Freshwater eutrophication”, and “Mineral, fossil & renewable resource depletion”, which were more influenced by the use of specific UAE equipment.

a)



b)

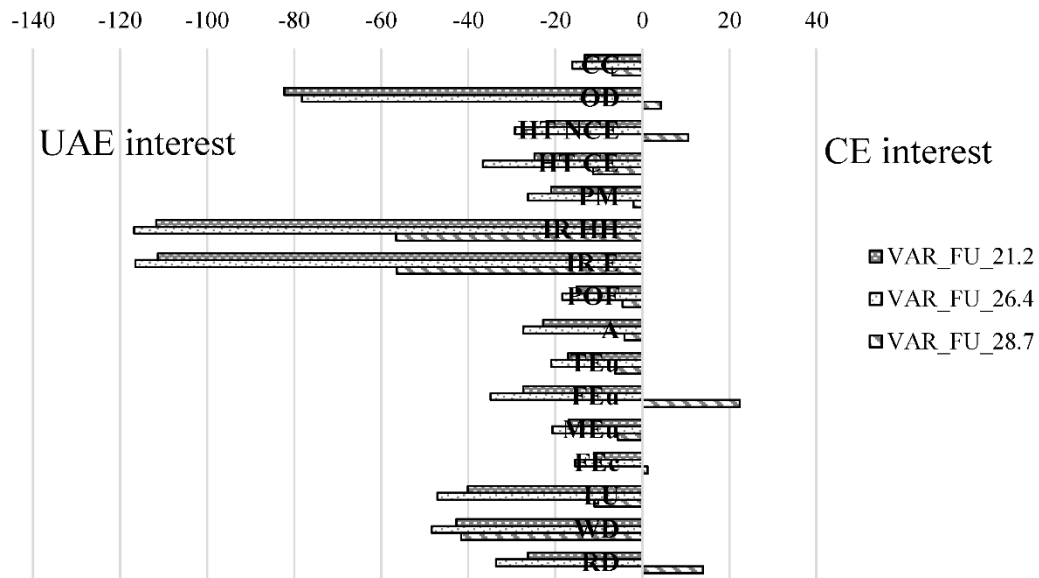


Figure 7. Variation for impact categories between UAE and CE: a) for 50°C; b) for 70°C.

Figure 7b compares CE and UAE at 70 °C showing the variations for the 16 impact categories for the three studied FUs. The results confirmed the clear advantage of UAE at 70 °C for the two lower FUs, due to faster extraction and much lower energy consumption during UAE (reduction of environmental impacts between 16 and 118 %). Similarly to results at 50 °C, the advantage of UAE was lower for FU close to the highest extraction yield at these conditions.

The same four categories were negatively influenced by sonication. For each FU, highest reductions of environmental impacts with ultrasound assistance were observed for the categories “IR E” and “IR HH” both at 50 °C and 70 °C. As a whole, the use of UAE significantly reduced environmental impacts of extraction processes.

It was also interesting to compare the two experimental conditions studied using UAE. Figure 8 shows how impact categories are sensitive to the temperature choice for UAE. Variation was calculated between UAE at 50°C and UAE at 70°C. Negative variation on this figure meant that it was better to work at 70°C to reduce environmental impacts. On the contrary, positive variation meant that 50°C permitted to reduce environmental impacts. The clearly better results observed for UAE at 70 °C were due to reduced electricity consumption and extraction duration (Table 1). Indeed, in the case of UAE at 70 °C the time of sonication before to attain the maximal temperature was longer (15 min for 70 °C and 11 min for 50 °C). This longer cavitation combined to the higher temperature allowed to accelerate the extraction compared to UAE at 50 °C.

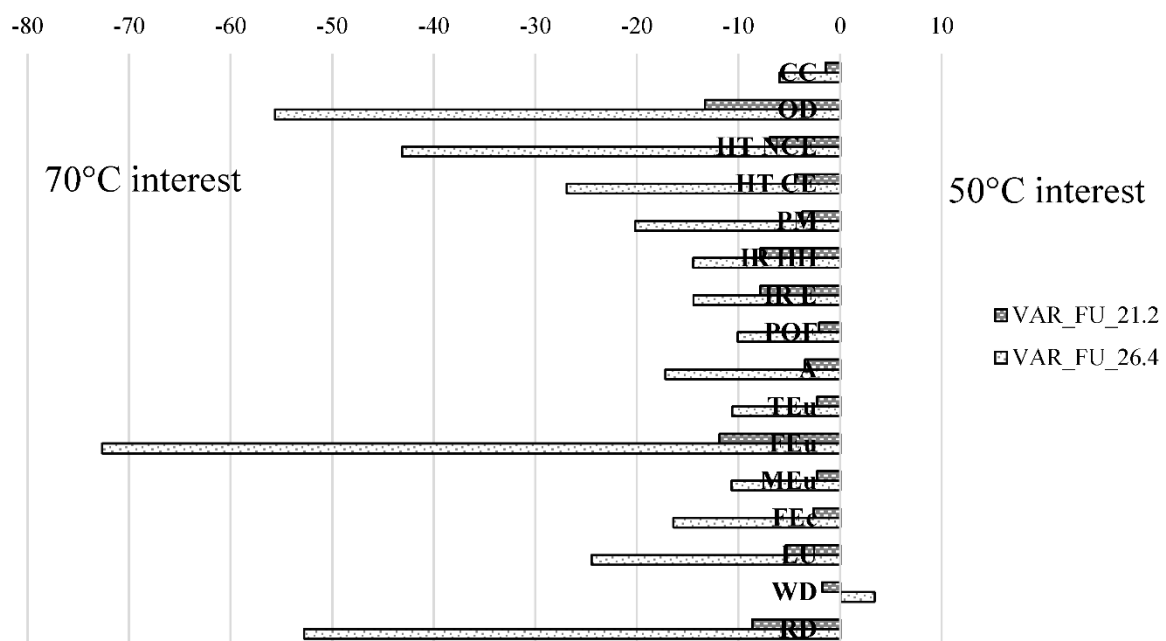


Figure 8. Variation for impact categories between 50°C and 70°C conditions in the case of UAE.

4. Conclusion

Results obtained in the present study showed that UAE is well adapted for caffeine extraction from guarana seeds. Ultrasound assistance provided significant enhancement of extraction

yields and/or kinetics of the process compared to CE, depending on extraction temperature: both caffeine yield and extraction kinetics were enhanced at room temperature, whereas only extraction kinetics were enhanced at higher temperatures (50 and 70 °C). Combining kinetics studies and LCA permitted to highlight other benefits of ultrasound assistance: reduction of extraction duration, energy consumption and environmental impacts compared to CE at the same temperature (especially at 70 °C). Moreover, the proposed UAE process complies with principles n°2 (privilege alternative solvents and principally water and agro-solvents) and n°3 (reduction of energy consumption and environmental impacts using innovative technologies) described in the Principles of the Green Extraction of Natural Products (Chemat et al., 2019). The detailed study of CE and UAE environmental performance using three different functional units contributed to a better knowledge of the process. Operating conditions can be adjusted so as to take real advantage of ultrasound assistance. Indeed, environmental gains of UAE over CE at maximal temperature were relatively small when targeting a caffeine extraction yield close to the maximal attainable (at this temperature), but increased strongly for lower target yields. Hence, combining LCA and more classical process engineering tools such as kinetics studies allowed to get a more detailed knowledge of the studied process. In the framework of green processes development, this enables to make well-founded choices of target yield and operating conditions, so as to optimize process duration, energy savings, and environmental performance of the process. The interest of this kind of approach was shown in the present work for caffeine extraction from guarana seeds, but it could largely be applied to other case studies or processes. The information collected in the present study on the absorbed power and specific power density could serve for further scaling up of the process.

Funding sources

This work has been carried out in the frameworks of INEXUS and Alibiotech projects financed by European Union, French State and the French Region of Hauts-de-France.

Acknowledgements

The authors thank Ortis Laboratoires for the kind providing of guarana seeds.

References

Adnadjevic, B., Koturevic, B., Jovanovic, J., 2017. Comparative kinetic analysis of isothermal extraction of caffeine from guarana seed under conventional and microwave heating. *Chem. Eng. Res. Des.* 118, 61–70. <https://doi.org/10.1016/j.cherd.2016.12.006>.

Both, S., Chemat, F., Strube, J., 2014. Extraction of polyphenols from black tea - Conventional and ultrasound assisted extraction. *Ultrason. Sonochem.* 21 (3), 1030–1034. <https://doi.org/10.1016/j.ultsonch.2013.11.005>.

Carciochi, R.A., Galván D'Alessandro, L., Vauchel, P., Rodriguez, M.M., Nolasco, S.M., Dimitrov, K., 2017. Valorization of agri-food by-products by extracting valuable bioactive compounds using green processes, in: Grumezescu, A., Holban, A.M. (Eds.), *Handbook of Food Bioengineering, Volume 4: Ingredients Extraction by Physicochemical Methods in Food*. Academic Press, London, pp. 191–228.

Chemat, F., Rombaut, N., Sicaire, A.-G., Meullemiestre, A., Fabiano-Tixier, A.-S., Abert-Vian, M., 2017. Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. *Ultrason. Sonochem.* 34, 540–560. <https://doi.org/10.1016/j.ifset.2017.04.016>.

Chemat, F., Abert-Vian, M., Fabiano-Tixier, A.-S., Strube, J., Uhlenbrock, L., Gunjevic, V., Cravotto, G., 2019. Green extraction of natural products. Origins, current status, and future challenges. A review. *Trends Anal. Chem.* 118, 248–263. <https://doi.org/10.1016/j.trac.2019.05.037>.

Chemat, F., Abert-Vian, M., Fabiano-Tixier, A.-S., Nutrizio, M., Režek Jambrak, M., Munekata, P.E.S., Lorenzo, J.M., Barba, F.J., Binello, A., Cravotto, G., 2020. A review of sustainable and intensified techniques for extraction of food and natural products. *Green Chem.* 22, 2325–2353. <https://doi.org/10.1039/c9gc03878g>.

Cláudio, A.F.M., Ferreira, A.M., Freire, M.G., Coutinho, J.A.P., 2013. Enhanced extraction of caffeine from guarana seeds using aqueous solutions of ionic liquids. *Green Chem.* 15, 2002–2010. <https://doi.org/10.1039/c3gc40437d>.

De Marco, I., Riemma, S., Iannone, R., 2018. Life cycle assessment of supercritical CO₂ extraction of caffeine from coffee beans. *J. Supercrit. Fluids*, 133, 393–400. <https://doi.org/10.1016/j.supflu.2017.11.005>.

Dichi, E., Legendre, B., Sghaier, M. 2014. Physico-chemical characterization of a new polymorph of caffeine. *J. Therm. Anal. Calorim.* 115, 1551–1561. <https://doi.org/10.1007/s10973-013-3429-0>.

Hu, C.-J., Gao, Y., Liu, Y., Zheng, X.-Q., Ye, J.-H., Liang, Y.-R., Lu, J.-L., 2016. Studies on the mechanism of efficient extraction of tea components by aqueous ethanol, *Food Chem.* 194, 312–318. <https://doi.org/10.1016/j.foodchem.2015.08.029>.

ILCD Handbook, 2010. General guide for Life Cycle Assessment - Detailed guidance, EUR 24708EN-2010, JRC European Commission.

ISO 14040:2006, 2006. Environmental Management - Life Cycle Assessment - Principles and Framework. International Standard Organisation, Geneva, Switzerland.

ISO 14044:2006, Environmental Management - Life Cycle Assessment - Requirements and guidelines, International Standard Organisation, Geneva.

Jolliet, O., Saade-Sbeih, M., Shaked, S., Jolliet, A., Crettaz, P., 2015. Environmental Life Cycle Assessment, CRC Press, Taylor & Francis Group, Boca Raton.

Jun, X., 2009. Caffeine extraction from green tea leaves assisted by high pressure processing. *J. Food Eng.* 94(1), 105-109. <https://doi.org/10.1016/j.jfoodeng.2009.03.003>.

Khadhraoui, B., Turk, B., Fabiano-Tixier, A.-S., Petitcolas, E., Robinet, P., Imbert, R., El Maâtaoui, M., Chemat, F., 2018. Histo-cytochemistry and scanning electron microscopy for studying spatial and temporal extraction of metabolites induced by ultrasound. Towards chain detexturation mechanism. *Ultrason. Sonochem.* 42, 482–492. <https://doi.org/10.1016/j.ultsonch.2017.11.029>.

Koturevic, B., Adnadjevic, B., Jovanovic, J., 2020. The kinetics of the extraction of caffeine from guarana seed under the action of ultrasonic field with simultaneous cooling. *Green Proc. Synth.* 9, 26–36. <https://doi.org/10.1515/gps-2020-0003>.

Machado, K.N., Freitas, A.A., Cunha, L.H., Faraco, A.A.G., Pádua R.M., Braga, F.C., Vianna-Soares, C.D., Castilho, R.O., 2018. A rapid simultaneous determination of methylxanthines and proanthocyanidins in Brazilian guaraná (*Paullinia cupana* Kunth.). *Food Chem.* 239, 180–188. <https://doi.org/10.1016/j.foodchem.2017.06.089>.

Majhenic, L., Škerget, M. Knez, Z., 2007. Antioxidant and antimicrobial activity of guaraná seed extracts. *Food Chem.* 104(3), 1258–1268. <https://doi.org/10.1016/j.foodchem.2007.01.074>.

Marques, L.L.M., Panizzon, G.P., Aguiar, B.A.A., Simionato, A.S., Cardozo-Filho, L., Andrade, G., Gonçalves de Oliveira, A., Guedes, T.A., Palazzo de Mello, G.C., 2016. Guaraná (*Paullinia cupana*) seeds: Selective supercritical extraction of phenolic compounds. *Food Chem.*, 212, 703–711. <https://doi.org/10.1016/j.foodchem.2016.06.028>.

Patricelli, A., Assogna, A., Casalaina, A., Emmi, E., Sodini, G., 1979. Fattori che influenzano l'estrazione dei lipidi da semi decorticati di girasole, *Riv. Ital. Sost. Gras.* 56, 136–142.

Pingret, D., Fabiano-Tixier, A.S., Chemat, F. 2013. Degradation during application of ultrasound in food processing: A review. *Food Control* 31, 593–606. <https://doi.org/10.1016/j.foodcont.2012.11.039>

Pradal, D., Vauchel, P., Decossin, S., Dhulster, P., Dimitrov, K., 2016. Kinetics of ultrasound-assisted extraction of antioxidant polyphenols from food by-products: Extraction and energy

consumption optimization. *Ultrason. Sonochem.* 32, 137–146.
<https://doi.org/10.1016/j.ultsonch.2016.03.001>.

Ribeiro, B.D., Coelho, M.A.Z., Barreto, D.W., 2012. Obtenção de extratos de guaraná ricos em cafeína por processo enzimático e adsorção de taninos. *Braz. J. Food Technol.* 15, 261–270. <http://dx.doi.org/10.1590/S1981-67232012005000020>.

Santana, A.L., Macedo, G. A., 2018. Health and technological aspects of methylxanthines and polyphenols from guarana: A review. *J. Functional Foods*, 47, 457–468.
<https://doi.org/10.1016/j.jff.2018.05.048>.

Santiago, B., Calvo, A.A., Gullón, B., Feijoo, G., Moreira, M.T., González-García, S., 2020. Production of flavonol quercetin and fructooligosaccharides from onion (*Allium cepa* L.) waste: An environmental life cycle approach. *Chem. Eng. J.*, (in press).
<https://doi.org/10.1016/j.cej.2019.123772>.

Sharma, V., Gulati, A., Ravindranath, S.D., Kumar, V.A., 2005. Simple and convenient method for analysis of tea biochemicals by reverse phase HPLC, *J. Food Comp. Anal.* 18, 583–94. <https://doi.org/10.1016/j.jfca.2004.02.015>.

Sicaire, A.-G., Abert Vian, M., Fine, F., Carré, P., Tostain, S., Chemat, F. 2016. Ultrasound induced green solvent extraction of oil from oleaginous seeds. *Ultrason. Sonochem.* 31, 319-329. <https://doi.org/10.1016/j.ultsonch.2016.01.011>

Vauchel, P., Colli, C., Pradal, D., Philippot, M., Decossin, S., Dhulster, P., Dimitrov, K., 2018. Comparative LCA of ultrasound-assisted extraction of polyphenols from chicory grounds under different operational conditions. *J. Clean. Prod.* 196, 1116–1123.
<https://doi.org/10.1016/j.jclepro.2018.06.042>.

Weckerle, C.S., Stutz, M.A., Baumann, T.W., 2003. Purine alkaloids in *Paullinia*. *Phytochem.* 64, 735–742. [https://doi.org/10.1016/S0031-9422\(03\)00372-8](https://doi.org/10.1016/S0031-9422(03)00372-8).

