SFE FROM *Agaricus brasiliensis*: CURVE MODELING AND COST ESTIMATION

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Abstract. *Agaricus brasiliensis*, popularly known in Brazil as "cogumelo do sol", is widely used in oriental countries as an edible mushroom and extensively studied for its medicinal properties. Due to the cost intensive nature of SFE, the estimation of process cost is necessary to appraise operation viability. The main objective of this work was the modeling of the supercritical fluid extraction (SFE) curve from *Agaricus brasiliensis* and estimate the process cost. The dehydrated mushrooms were submitted to SFE at 200 bar, 313.15 K, 12 g CO_2/min. The Sovová`s model was applied to SFE curve using a derivative-free optimization method. The manufacture and the specific costs of the process were determined according to the methodology by Turton et al. (1998), evaluating SFE unit size and extraction time. The Sovová's modeling showed low mean square error, indicating good adjustment. The values of kya (mass transfer coefficient in fluid phase) were lower than kxa, indicating the higher influence of the diffusion mechanism, compared to the convection. The costs results showed that SFE using a 2 x 400 L unit during the constant extraction rate period is a lucrative process.

Keywords: *Agaricus brasiliensis*, Supercritical CO_2, Modeling, Expenditure.

1. Introduction

Mushrooms are high value food products, with low energetic levels and large amounts of minerals, essential amino acids, vitamins and fibers. *Agaricus brasiliensis* is a top ranking mushroom considering medicinal and culinary aspects [1]. It was formerly known in the literature as *Agaricus blazei* Murril (sensus Heinemann), but after the clarification of its botanical name, many publications refer to *A. brasiliensis* as the cultivated mushroom originated from Brazil [2]. This mushroom has been widely studied in the areas of food science, medicine, biotechnology and pharmacology. Concerning medical aspects, many works have reported that *A. brasiliensis* presents antibacterial, antioxidant, antidiabetic, antiangiogenic, and anticancer activities [3].

Extracts from vegetable and mushrooms sources have important roles on the compositions of high added value food products and supplements, as well as in cosmetics and pharmaceuticals. Supercritical carbon dioxide extraction represents an alternative to classic organic solvent extraction of plants material and mushrooms. SFE has numerous advantages over conventional techniques [4] such as the use of low temperatures and reduced energy consumption, efficiency in solvent use with recycling possibility, prevention of oxidative reactions and high product quality due to the absence of solvent in solute phase, it is a flexible process due to the possibility of continuous adjustment of the solubility and selectivity power of the solvent through the selection of processing parameters.

In spite of the well-known advantages of the process such as high quality product, SFE has an economical constraint due to the high investment cost inherent to high pressure processes. The cost of manufacturing (COM) is influenced by factors that can be divided into three categories: direct costs, fixed costs, and general expenses. The direct costs take into account expenses that depend directly on the production rate, such as raw materials, utilities and operating labor, among others. The fixed cost does not depend directly on the production rate and must be considered even if the operation is interrupted. In this cost are included the depreciation, taxes and insurance, etc. General expenses are overheads of the plant needed to maintain the business and consist of the administrative cost, sales expenses, and research and development, among others [5, 6].

This work aimed to apply mathematical model in the supercritical fluid extraction (SFE) process from *A. brasiliensis* mushroom. In addition, the cost estimation of the process was also determined in function of unit volume and extraction time.

2. Materials and methods

2.1 Sample preparation

The dried *A. brasiliensis* mushrooms were provided by Mushroom Research Center of São Paulo State University (UNESP), São Paulo, SP, Brazil. The mushrooms, with moisture content of 6.6%, were ground in a knife mill (De Leo, Porto Alegre/RS - Brazil). The samples were stored at 255.15 K in a domestic refrigerator until the extractions were performed.

2.2 Supercritical fluid extraction (SFE)

SFE from *A. brasiliensis* mushroom was performed in a dynamic extraction unit [7]. The extraction procedure [8], consisted of placing 15 g of dried and milled material inside a stainless steel column (329 mm length × 20.42 mm inner diameter, and internal volume of 100 mL) to form the fixed particle bed, followed by the control of the process variables (temperature, pressure and solvent flow rate). The extraction was then performed and the solute collected in amber flasks after 210 min and weighed on an analytical balance (OHAUS, Model AS200S, NJ – USA). The SFE curve using pure CO_2 was performed at 200 bar, 313.15 K and CO_2 flow rate of 12 g/min in order to apply the mathematical mass transfer model (as explained as follow) and to obtain process parameters used in the process cost estimation. The SFE process used 99.9 % pure CO_2 delivered at pressure up to 60 bar (White Martins).

2.3 Mathematical modeling of SFE curve

The SFE curve of *A. brasiliensis* mushroom was obtained by plotting extraction yield *versus* time. For the kinetic analysis of the extraction procedure the modeling of SFE curve was performed using the model of Sovová [9]. The model equations are extensively described by Kitzberger et al. [10]. The Sovová’s model [9] was applied according to a derivative-free optimization method [11].

The applied models require additional information such as: (a) particle diameter (d_p) of raw material, determined by scanning electronic microscopy (JSM-63990LV, JEOL); (b) solid specific mass (ρ_s), determined by helium pycnometry (AccuPyc II 1340, Micrometrics); (c) bed diameter and height of the extraction column; (d) apparent specific mass (ρ_a) of the SFE bed , calculated by the ratio between the mass of raw material and the bed volume;(e) solvent specific mass (ρ_{CO2}), determined according to Angus et al. [12]; (f) bed porosity (ε), determined by the ratio (ρ_s - ρ_a)/ρ_s. Besides that, the application of Sovová’s model [9] also uses the solubility (Y*) of the extract in the supercritical CO_2 as a function of the extraction conditions of temperature and pressure. According to previous studies of our research group, the solubility value plays low influence in the model adjustment, and for its determination it is required a complex study of system phase equilibrium. Therefore, the solubility value determined by Kitzberger et al. [10] for the shiitake mushroom in supercritical CO_2, at the same conditions of temperature and pressure used in this work, was applied for the current modeling analysis.

2.4 Cost estimation of industrial SFE

The methodology of Turton et al. [5], presented by Rosa and Meireles [13], was used to estimate the manufacturing costs (COM), which is influenced by a series of factors that can be subdivided into three categories: direct costs, fixed costs, and general expenses. The manufacturing costs (COM) of SFE from *A. brasiliensis* mushroom were calculated using “Equation 1”.

$$COM = 0.304\,FI + 2.73\,COL + 1.23*(CRM + CWT + CUT) \tag{1}$$

where: COM = manufacturing cost corresponding to one year of operation; FI = capital investment, represented by equipment cost; CRM = raw material cost, composed by CO_2, transport and solid matrix costs; COL = cost of operational labor; CUT = utility cost, formed by energy cost of flash distillation, condenser, pump and heat exchange operations; and CWT = waste treatment cost.

The values of the manufacturing and the specific costs were determined using the software Tecanalysis [14]. The process cost were determined for: two commercial units with distinct work-volumes capacity (3 x 300 L and 2 x 400 L); SFE times of 80 and 210 min, which represents the constant extraction rate period and total time of extraction, respectively, in the operational conditions of 200 bar and 313.15 K.

3. Results and discussion

3.1 Modeling of SFE from *A. brasiliensis* mushroom

The Sovová's modeled curve from *A. brasiliensis* mushroom is compared with the experimental SFE curve and presented in Figure 1. The values of the adjustable parameters and the mean square error (MSE) of the mathematical models applied are presented in Table 1. The shape of the extraction curve indicates that at different stages of the extraction, different mechanisms control the mass transfer. At the beginning of the extraction convection is the main mass transfer mechanism, since there is available solute over the particle's surface. When this solute is depleted, compounds from inside the particles begin to be extracted, so diffusion becomes the controlling mechanism.

The modeled curve presented a good adjustment to experimental data, showing the good performance of the Sovová's model [9], not only in the constant extraction rate period (CER period) but also during the falling extraction rate period (FER period) and the diffusional region. Sovová's model [9] presents a strong physical representation of the mass transfer mechanisms and considers a vegetable matrix as raw material. Then, the good performance of this model suggests that probably the physical description of solute incorporation in the mushroom particles is similar to a vegetable structure, where the solute is distributed in broken and intact cells. The internal and external mass transfer resistances are evaluated by the values of k_Xa and k_Ya, respectively. Therefore, higher k_Xa value indicates that the convection mechanism is less representative than the diffusional one for the SFE of *A. brasiliensis* mushroom with CO_2. The good behavior presented by the Sovová's model is presented in Table 1 by the lowest values of the mean square error (MSE).

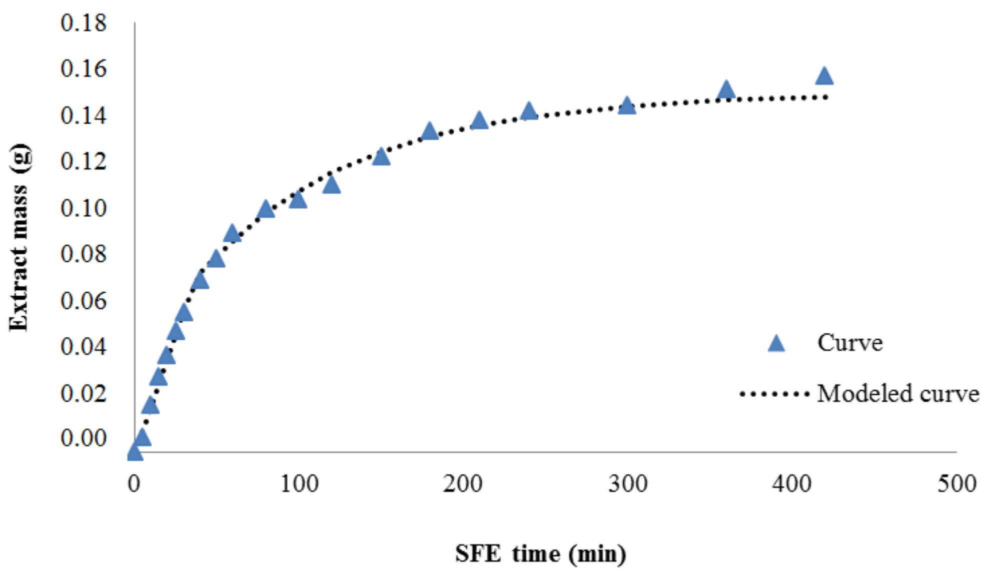


Figure 1. Experimental and modeled curve of SFE from *A. brasiliensis* mushroom.

Table 1. Model coefficients, adjustable parameters, and mean square errors from the modeled curve of SFE from *A. brasiliensis* mushroom

Modeling parameters of Sovová's model[(1)]	
k_Xa (10^{-5} s^{-1})	7.40
k_Ya (10^{-5} s^{-1})	3.36
x_k (g/g)	0.0052
MSE (x 10^{10})	1.99

[(1)]MSE = medium square error; k_Xa = mass transfer coefficient in the solid phase; k_Ya = mass transfer coefficient in the liquid phase; x_k = initial mass of extractable material in intact cells, relative to mass of non-extractable material.

Kitzberger et al. [10] modeled the extraction curves of shiitake mushroom in supercritical CO_2 using the six models. The results showed that the models proposed by Sovova [9], Goto et al. [15] and Martínez et al. [16] were the most effective for modeling the SFE of shiitake oil. The performance of the models to describe the OEC was assessed on the basis of the physical meaning of the parameters, as presented by Sovová [9], and also on the ability of each model to represent the experimental data (Martínez et al., [16]).

3.2 Process costs of SFE from *A. brasiliensis* mushroom

The SFE has been applied in the processing of several natural products. In order to transfer this technology to an industrial scale, an analysis of the economic feasibility is required. The SFE data used for the costs determination were selected according to the present study results and the literature [6, 13]: time of annual operation of 24 hours/day during 330 days/year; operational labor cost of US$ 3.00/hour; raw material cost equal to US$ 270,00; transportation cost equal to zero, considering that the SFE industry was located on same place that mushroom processing industry; initial moisture content is equal to the final moisture content because raw material was already dried; pre-treatment cost of US$ 30.00/$ton_{raw\ material}$ (considering milling and drying cost); CO_2 cost of US$ 0.15,00 per kgCO_2; CO_2 lost during extractions of 2 %; electric cost of US$ 0.0703/Mcal; water refrigeration cost of US$ 0.0837/Mcal; steam cost of US$ 0.0133/Mcal; equipment depreciation of 10 %/year; SFE temperature and pressure of 313.15 K and 200 bar; CO_2 separation pressure of 40 bar, considering that in this condition all extract is liquid; constant ratio between raw material mass and CO_2 flow rate as scale-up criterion; batch specific mass of 730 kg/m^3; SFE times of 80 min (t_{CER}) and 210 min (total SFE time) and respectively extraction yields of 0.71 and 0.92 %; CO_2 flow rate of 10.5 (equipment 3 *x* 300 L) and 14 ton/hour (equipment 2 *x* 400 L); and no wastewater treatment because of the remaining solid matrix can be used as animal feed after its use in SFE.

The results from the cost estimation analysis are presented in Table 2, which indicates that, for both equipments used, the contributions of FI, COL and CUT for COM values are lower at shorter extraction times. The time reduction leads to higher CRM because of the increase in the number of the processes performed in a work day, which enhances the amount of raw material and CO_2 used. Thus, it can be additionally observed that CUT, CRM and FI represents the major part of COM for all times and equipments evaluated. The values of CUT and FI are justified by the high cost of the SFE unit, which is made of materials adequate to extract processing and has to be resistant to high pressures and also provide energy supply, pump system, water refrigeration and saturated steam. The cost of raw material is the major factor affecting the COM of plant extracts [17].

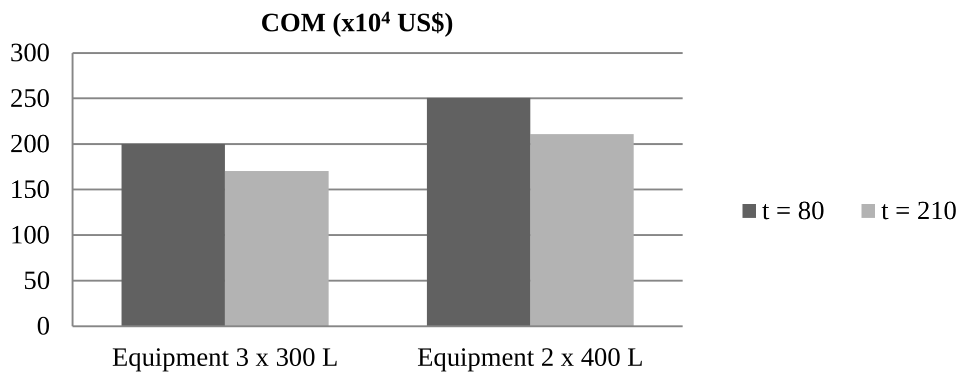
The values for FI, CRM and CUT were lower for the 3 x 300 L unit due to the higher equipment price, higher total volume leading to elevated raw material treatment, and energy expenses [6], respectively. The CWT for all conditions evaluated was zero because the solid residue (after extraction) can be used for different purposes such as fiber source or fuel for boilers. The solvent used leaves the extraction unit as a gas phase, or can be recycled in the system. Because the type of solvent used for the extractions is CO_2, no treatment is required.

Table 2. Value and COM[(1)] contribution of fraction of investment, raw material cost, operational labor cost, utilities cost and waste treatment cost of SFE from *A. brasiliensis* mushroom

Parameters evaluated		**Equipment 2 x 400 L**		**Equipment 3 x 300 L**	
		t_{CER}[(2)] = 80 min	t_{TOTAL} = 210 min	t_{CER}[(2)] = 80 min	t_{TOTAL} = 210 min
Fraction of investment	($x10^3$) US$/year	2,000.00	2,000.00	1,800.00	1,800.00
	% of COM	24.23	28.80	27.30	32.10
Raw material cost	US$/year	852,984.00	530,866.00	639,738.00	398,149.74
	% of COM	42.00	31.07	39.46	28.86
Operational labor cost	US$/year	43,956.00	43,956.00	43,956.00	43,956.00
	% of COM	4.79	5.70	6.01	7.06
Utilities cost	US$/year	588,368.70	588,368.00	441,276.52	441,276.52
	% of COM	28.97	34.44	27.22	31.99
Waste treatment cost	US$/year	0.00	0.00	0.00	0.00
	% of COM	0.00	0.00	0.00	0.00

[(1)]COM = cost of manufacturing; [(2)]t_{CER} = time of constant extraction rate period.

The values for COM and specific cost, which is the relative cost of COM *per* kg of extract, for SFE from *A. brasiliensis* mushroom, are presented in Figure 2. The highest COM value was obtained for the lowest SFE time, with a decreasing rate similar for both equipments evaluated, behavior also observed by Mezzomo et al. [6] for SFE of peach almond oil. The lower COM value (US$ 1,703,196) was obtained for 3 *x* 300 L unit and 210 min. Alternatively, the specific cost is inversely proportional to the extraction time, as observed in Figure 2. The unit with 3 *x* 330 L provided the lowest cost at 80 min (US$ 167.23/$kg_{extract}$), whereas the 3 *x* 300 L gave the highest value at 210 min (US$ 373.57/$kg_{extract}$). The COM value decreases with the increase in the extraction time, and it is necessary to evaluate the variation in the extraction rate during the process (high extraction rate in the beginning and low extraction rate at the diffusional period).



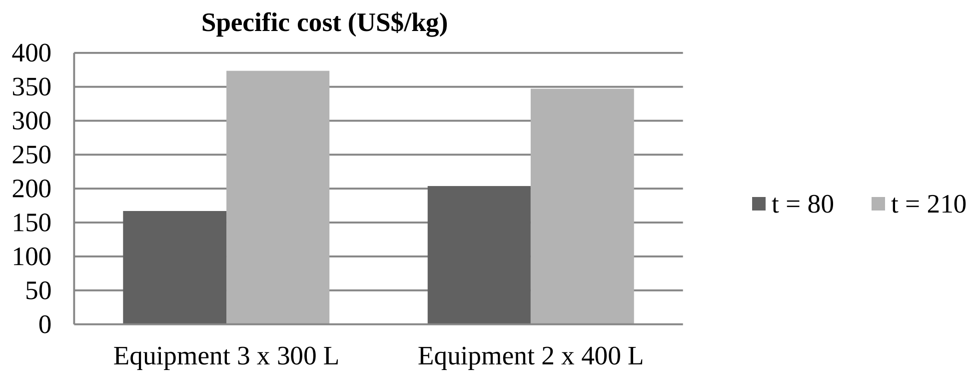


Figure 2. Cost of manufacturing (COM) and specific cost of *A. brasiliensis* mushroom extract obtained by SFE in function of equipment and extraction time.

4. Conclusions

The modeling of SFE from *A. brasiliensis* mushroom showed a very good adjustments achieved by Sovová's model, supplying information about different mass transfer mechanisms involved on the process. The costs results showed that SFE from *A. brasiliensis* mushroom in the CER period, using the equipment of 3 columns with 300 L, presented a low specific cost.

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