Mechanistic modeling to address process analysis: Carob pods (*Ceratonia Siliqua*, L.) extraction.

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ABSTRACT

The daily challenge on operating a process is to attain the objectives. Process management requires the use of tools adapted to the system complexity. In order to obtain real time results, simplified mechanistic modelling offers a way to deal with. With this aim, the carob pods (*Ceratonia Siliqua*, L.) extraction are addressed in this work. They are a source of different valuable components and show not only a complex structure but also large variability on components concentration. The components considered are sugars and soluble polyphenols. Obtaining the extracts with an optimal composition on a particular component, while avoiding or limiting other components in the extract, is a challenge to be addressed. Two steps can be considered solubilization and diffusion. The solubilization step was modelled by a first order reaction and the diffusion one considering a slab geometry. By considering a particular kibble size and composition, the optimal processing time and temperature are obtained.

Key words: Process management, optimization, extraction, carob

1- INTRODUCTION

When running a process the challenge is how to manage it in order to obtain the output according to the needs/objectives. This is a continuous challenge because the inputs if they involve natural products are time changing, mainly linked to natural variability of raw materials. Type of cultivar, growing practices, degree of ripeness, bioclimatic indexes among others, are factors of variability in composition.

To address this challenge there is a need of process virtualization. This virtualization can take different forms like the expert who has a mental representation, the use of analogs or numerical if quantification is required. Of course, if optimization to attain objectives is involved, quantification is a must. There are process models that can help for that purpose (Iruyadaraj, 2001; Tijskens et al., 2001)

For process management there is a constraint to obtain real time results to address daily operation, this implies that models should be simply enough in order to fulfill the real time results requirement. To establish these models there is a need of process analysis to identify the relevant main variables or parameters for running the process. Frequently, surface response methodologies are considered due to its simplicity (Tetik and Yüksel, 2014; Turhan, 2011), although many times the complexity of the process do not allow a general approach in changing situations (Bon et al., 2005). The best way to address this aspect is by mechanistic modeling avoiding purely empirical approaches (Rodriguez et al., 2014). Even if these models are rough and constitute a first approach, they will be useful for daily management in the industry.

Mechanistic approach is the way to address process management in order to deal with the variability of raw material and complex situations. This is the case when extraction from complex matrices is addressed. A quite interesting raw material also rich in bioactive compounds is carob pods. Through a kibbling operation the pods are deseeded and then the kibbles could be submitted to the extraction process. For solid-liquid extraction frequently two periods are considered, a very fast at the beginning followed by a slow diffusion one (Bucic-Kojic et al., 2013).

Carob trees (*Ceratonia Siliqua*, L.) are mainly cultivated in the Mediterranean area. The seed of the pods are used to obtain the locust bean gum and the kibbles are quite rich in sugars, around 50%. The aqueous extracts have bioactive compounds (Klenow et al., 2009). There are different valuable compounds like d-pinitol with pharmacological interest; polyphenols also constitute a source of compounds of potential health benefits for humans. The kibbles high sugar content present an interest to obtain traditional products for human consumption (Turhan, I. et al., 2006).

Concentration or purification of compounds of interest could be a cumbersome task due to the existence of many different compounds; for instance d-pinitol is obtained from carob extracts by chromatography (Chafer and Berna, 2014). This is a costly and slow process. Consequently obtaining extracts rich in the kind of compounds sought instead of global ones would simplify downstream operations. Carob powder with low sugar content and rich in phenolics could constitute a product of interest.

Considering that the mass transport characteristics of the particular compounds are different during solubilization and diffusion periods, it could be possible to obtain fractions of extracts richer in particular compounds due to the different internal transport rate of the soluble components. As a consequence, the size of the kibbles will influence the time content variation of the different compounds on the extract. Thus, the size of the kibbles must be fixed in order to manage the process, otherwise if this variable is uncontrolled, it will hinder the differences of diffusivity and avoid a sound extraction process. The kibbling process provides particles of different sizes, small enough to allow deseeding the pods.

When carob kibbles are extracted the soluble polyphenols bring an astringent taste. On the one hand, it could be interesting for human consumption to establish the extraction time to recover the maximum amount of sugar while avoiding astringency. On the other hand if a particular compound, like d-pinitol, is of interest by modeling its extraction kinetics a fraction with the required characteristics could be obtained. Defining the fraction of interest will also consider downstream restrictions linked to product purification. In these circumstances, it appears that mechanistic modeling is the key to deal with process virtualization for process management. In this work, a methodology using a mechanistic model, solubilization and diffusion, will be developed to obtain fractions of interest. In a first approach, sugars and soluble polyphenols will be considered.

2- MATERIALS AND METHODS

2.1- Raw material

The raw material considered were carob kibbles from Majorca (Spain). The kibbles were sieved in order to obtain a uniform size. The predominant size of the kibbles was 0.007±0.0005 m side.

The experimental data for temperature influence on sugar extraction from carob kibbles were obtained from literature (Mulet et al., 1988). The water soluble polyphenols were obtained by extraction in a 1 L well stirred temperature controlled vessel (20-100ºC). The analysis of total phenolic content was carried out using the Folin-Ciocalteu procedure (Kil Sun et al., 2012).

2.2- Modeling

The carob pods have a geometry like a parallelepiped (frequently 0.009x0.025x0.20 m). The pods have an external layer that is impermeable. When obtaining the kibbles, if their size is around 5 mm or larger, most of them have two sides covered by this impermeable layer. Thus they can be modeled as a slab, with only one characteristic dimension regarding diffusion.

When putting the kibbles in contact with the extracting water, the soluble components that are located at the external layer are dissolved. The solid components inside the kibbles will be solubilized and diffuse to the external layer. As a consequence, two different mechanisms can be envisioned, thus two mechanistic models should be defined.

The external layer components solubilization is assumed to follow a first order kinetics. This model could be considered for the sugars (Eq. (1)) as well as the polyphenols (Eq. (2)). This mechanism will predominate at the beginning of the extraction process. When sugars or polyphenols on the external layer are being dissolved, the predominant mechanism will be solubilization, afterwards a diffusion like mechanism from internal layers will predominate. The time when this predominant mechanism shift is the critical time (t_{cs}, t_{cp}).

$$C_s(t) = C_{so}\, e^{-k_s t} \quad \leftrightarrow \quad t \le t_{cs} \tag{1}$$

$$C_p(t) = C_{po} e^{-k_p t} \quad \leftrightarrow \quad t \le t_{cp} \tag{2}$$

The second mechanism could be described by an effective diffusion coefficient that include also the effect of solubilization in the internal layers. Because the compounds considered are water soluble the equilibrium concentration was considered to be cero. The model (Mulet, 1994) will be similar for sugars (Eq. (3)) and phenolics (Eq. (4)).

$$C_s(t) = 2C_s(t_{cs}) \sum_{n=0}^{\infty} \frac{4}{(2n+1)^2 \pi^2} e^{-\frac{D_s}{L^2}\frac{(2n+1)^2\pi^2}{4}(t-t_{cs})} \quad \leftrightarrow \quad t > t_{cs} \tag{3}$$

$$C_p(t) = 2C_p(t_{cp}) \sum_{n=0}^{\infty} \frac{4}{(2n+1)^2 \pi^2} e^{-\frac{D_p}{L^2}\frac{(2n+1)^2\pi^2}{4}(t-t_{cp})} \quad \leftrightarrow \quad t > t_{cp} \tag{4}$$

When identifying the model parameters the critical time must be considered as also to be established; for that purpose an optimization problem was formulated. An effective diffusion parameter (D_s, D_p) and a solubilization rate constant (k_s, k_p) for each temperature were considered as decision variables, as well as the critical time. The average value of the relative absolute errors between calculated and experimental data (ER) was considered as objective function. To solve the optimization problem and identify the model parameters the Evolutionary method was applied (Simon, 2013). The initial values for carrying out the calculations and the constraints on the decision variables were established from previous experimental data.

The temperature influence on the kinetic rate parameters (k_s, k_p, D_s, D_p) was evaluated through an Arrhenius-type relationship (Eq. (5) to (8)).

$$k_s = k_{os} e^{-\frac{E_{ks}}{R(T+273.16)}} \quad (5)$$

$$k_p = k_{op} e^{-\frac{E_{kp}}{R(T+273.16)}} \quad (6)$$

$$D_s = D_{os} e^{-\frac{E_{Ds}}{R(T+273.16)}} \quad (7)$$

$$D_p = D_{op} e^{-\frac{E_{Dp}}{R(T+273.16)}} \quad (8)$$

To identify the preexponential terms and activation energy for each parameter the same procedure previously reported for identifying the kinetic parameters was considered.

The absolute average value of the relative errors (ER) and the explained variance (VAR) were considered to evaluate the accuracy of fit (Bon et al., 2010). The average value of the relative errors (ER) is an index of the random component in the estimation. VAR indicates the proportion of variance that is accounted for by the model.

For managing, to establish the time involved in the first extracting step, the critical time, and consequently the starting of the predominance of diffusion, the amount of sugars dissolved must be estimated. This amount will be proportional to the kibbles surface in contact with water. Thus, one can consider that the relative change in composition is directly proportional to the surface divided by the volume. The models to describe these change in concentration will be for sugar (Eq. (9)) and polyphenols (Eq. (10)). The parameters a_s and a_p will be determined for a particular kibble composition by fitting these models to experimental data.

$$\frac{C_{s0} - C_s(t_{cs})}{C_{s0}} = \frac{a_s}{2L} \quad (9)$$

$$\frac{C_{p0} - C_p(t_{cp})}{C_{p0}} = \frac{a_p}{2L} \quad (10)$$

2.3-Management

For process management an Excel (Walkenbach, 2013) data sheet was developed using the models established. The Excel sheet provides time concentration evolution of both components (sugars and polyphenols) as a function of kibble size and extraction temperature.

A variable that can change in different extraction operations is the size of the kibbles, this being an input data. To select the optimal values of the manageable process variables (temperature and processing time), a decision tool was developed. For that purpose an optimization problem was stablished, considering the manageable process variables as decision variables, and the relative amount of sugars extracted as objective function (Eq. (11)), which should be maximized.

$$OF = 100\frac{C_{s0} - C_s(t)}{C_{s0}} \tag{11}$$

There will be restrictions according to the time allowed in the industry for the extracting operation ($t_t \leq t_l$), the temperatures that could be used ($T_l \leq T \leq T_u$) and also on the minimum amount of polyphenols left on the kibbles ($C_p(t_t) \geq C_{pl}$). To solve this optimization management problem the Generalized Reduced Gradient was considered (Bon et al., 2005)

3- RESULTS AND DISCUSSION

Data to analyze the sugar evolution on kibbles during extraction was obtained from literature (Mulet et al. 1988), experimental data of polyphenol extraction kinetics are presented in table 1 in the range from 20 to 100ºC. From these data the surface solubilization and diffusion like periods could be established for model fitting.

Table 1. Experimental kibbles polyphenol concentration (g/100 g dm) during aqueous extraction at different temperatures.

	T (ºC)					
t (h)	***20***	***30***	***40***	***50***	***60***	***100***
0	3.80	3.80	3.80	3.80	3.80	3.80
0.5	3.38	3.31	3.37	2.98	2.97	2.62
1	3.43	3.40	3.24	2.85	2.82	2.37
2	3.32	3.25	3.08	2.69	2.63	2.04
3	3.24	3.15	2.97	2.57	2.48	1.79
4	3.17	3.07	2.88	2.47	2.36	1.59
5	3.11	3.00	2.79	2.38	2.26	1.41

6	3.06	2.94	2.72	2.30	2.16	1.25
8	2.97	2.83	2.59	2.16	2.00	0.99

The identifying procedure of model parameters from experimental data allowed to establish the influence of the temperature, described according to Arrhenius law (Eqs. (5) to (8)). In Tables 2 and 3 the values obtained when fitting the Arrhenius equations are shown. The diffusion coefficient for polyphenols is in the same order of magnitude that the obtained for grape stalks (García-Pérez et al., 2010).

Table 2. Sugar extraction. Preexponential, activation energy values and statistical results.

		ER (%)	VAR (%)
D_{0s} (m^2/h)	2.298 10^{-6}	3.4	93.0
E_{Ds} (J/mol K)	2704.3		
k_{0s} (h^{-1})	39.1	6.9	99.3
E_{ks} (J/mol K)	9109.1		

Table 3. Polyphenols extraction. Preexponential, activation energy and statistical results.

		ER (%)	VAR (%)
D_{0p} (m^2/h)	0.0077	7.2	96.5
E_{Dp} (J/mol K)	28143.8		
k_{0p} (h^{-1})	22.7	6.7	95.2
E_{kp} (J/mol K)	12320.8		

For managing purposes the amount of material that would be solubilized must be evaluated (Eq. (9) and (10)). From identified data on critical time concentration, by fitting the models the parameters a_s and a_p were calculated. For the particular case examined the figures were 0.0041 m (a_s) and 0.00045 m (a_p). Of course these values will change according to the raw material (eg. cultivar considered).

Once these values are established the concentration at the critical times for a particular kibble size can be computed (Eqs. (9) and (10)) and afterwards the critical times corresponding to these concentration established (Eqs.(1) and (2)).

In order to assess the goodness of the models in Figs. 1 and 2 are shown the results for the polyphenols and sugar concentrations. Despite its simplicity the models describe well the process, the explained variance being 98.7% (C_p) and 99.6% (C_s).

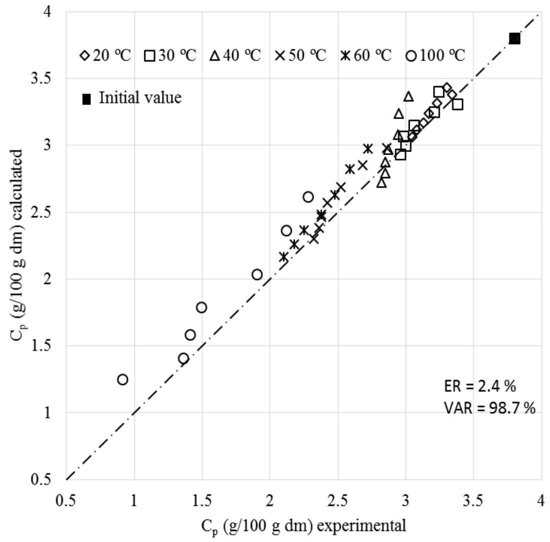

Fig. 1. Goodness of the mathematical model to evaluate the evolution of the kibbles polyphenol concentration.

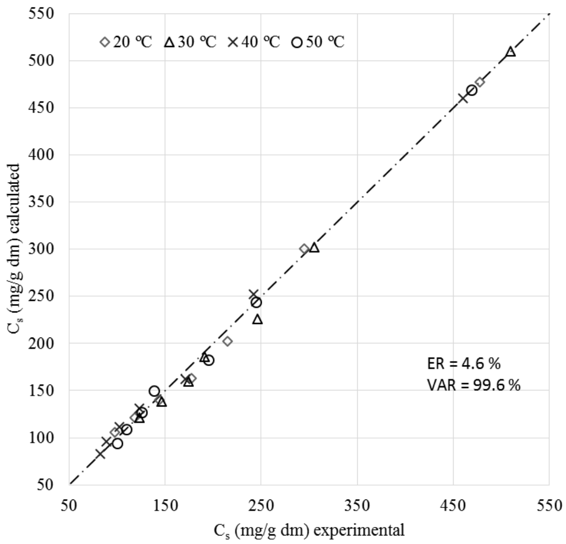

Fig. 2. Goodness of the mathematical model to evaluate the evolution of the kibbles sugar concentration.

In order to manage the process the objective function (Eq. (11)) was considered bounded for temperature, the available time to carry out the extraction ($t_t \leq t_l$) and the concentration of polyphenols left on the kibble ($C_p(t_f) \geq C_{pl}$). Thus, a limit on the polyphenols on the extracts is established.

Then, by fixing the size of the kibbles, the extraction time and temperature will be computed for the particular raw material considered (C_{0s}, C_{0p}) to manage the process. For that purpose, the optimization problem was solved using the Generalized Reduced Gradient (Bon et al., 2005). Using the tool Solver from Excel for solving the optimization problem takes few seconds, thus the restriction of attaining real time results for process management is fulfilled.

Simulations were carried out in order to illustrate the effects of kibble size (L) and polyphenols bounding value (C_{pl}) on optimal temperature (Fig. 3) and extraction time (Fig. 4) for the same initial raw material composition.

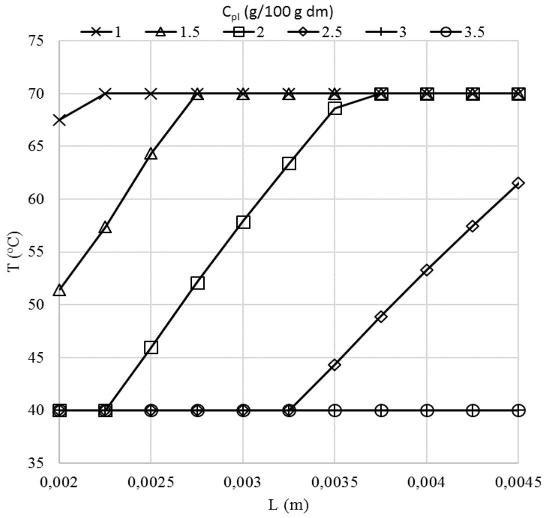

Fig. 3. Influence of the bound value of *Cp* (C_{pl}) and the size of the kibbles (*L*) on the optimal values of the extraction temperature. C_{p0} = 3.8 g/100 g dm; C_0 = 468.7 mg/g dm. Constraints: T $\in$ [40, 70] ºC; t $\leq$ 5h.

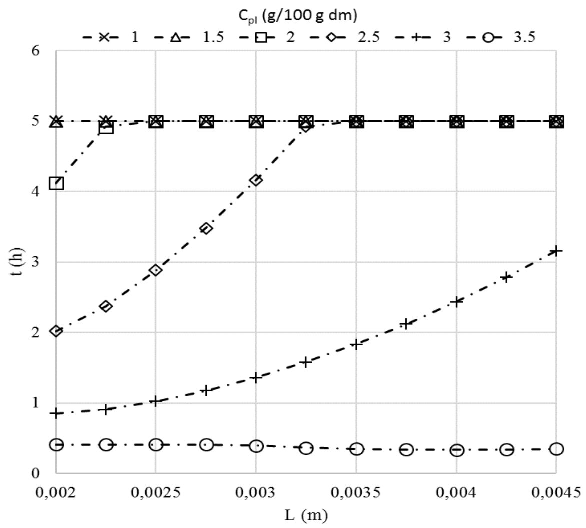

Fig. 4. Influence of the bound value of *Cp* (C_{pl}) and the size of the kibbles (*L*) on the optimal values of the extraction time at the optimal temperature. C_{p0} = 3.8 g/100 g dm; C_0 = 468.7 mg/g dm. Constraints: T ∈ [40, 70] ºC; t ≤ 5h.

As observed in Figs. 3 and 4 the size of the kibbles influences the optimal operating conditions. According to the limits on polyphenols extraction (C_{pl}), there is also a high influence on the extraction time and temperature. When polyphenol extraction is large (C_{pl} low) it is seen (Fig.3) that temperature should be high. In fact for C_{pl}≤1.5 g/100g dm the extraction should be carried always at the maximum allowed temperature (70ºC) for kibble size larger than 0.0027 m. Simultaneously the extraction time (Fig. 4) is large, as seen bounded to the maximum allowed time (5h). When the extraction of polyphenols is low (large C_{pl}) the temperature should be low (Fig. 3) and also the extraction time short (Fig. 4). For intermediate values of C_{pl} there are different complex situations that the mechanistic modelling allow to manage in an optimal way. The different optimal values established arise because not only the diffusion coefficients of sugars and polyphenols are different but also in the solubilization step the amount extracted, linked to the surface per unit volume, is different before the diffusion begins.

Figure 5 shows the optimal values of the objective function attained for different kibble size and limiting value of polyphenols. As a general rule, for a particular kibble size, if the amount of polyphenols extracted diminishes (increase C_{pl}) the objective function also diminishes. For C_{pl}≤2 the amount of sugars extracted increases (OF) when the kibble size decrease. For higher C_{pl}≥2.5 the larger optimal value of OF depends on the size. There is a maximunm of the optimal OF values, that are attained for each particular size depending on C_{pl}. It should be noticed that the effect of carob pod composition both on sugars and polyphenols also will affect the optimization problem.

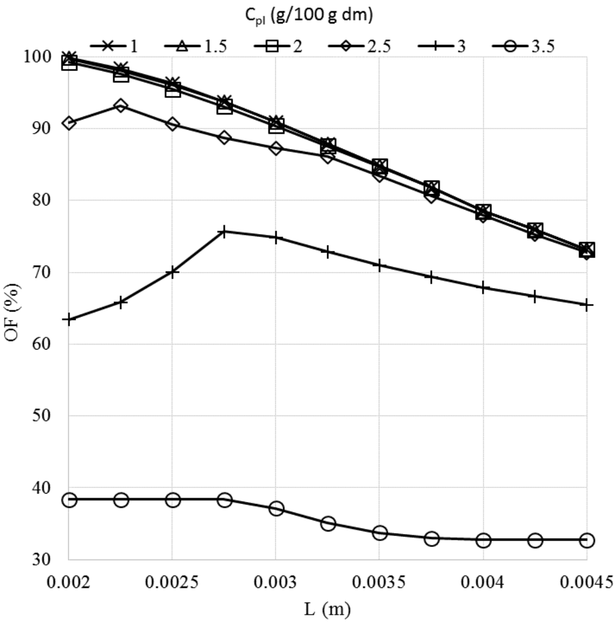

Fig. 5. Influence of the bound value of C_{pl} and the size of the kibbles (*L*) on the optimal values of the objective function. C_{p0} = 3.8 g/100 g dm; C_0 = 468.7 mg/g dm; *T* ∈ [40, 70] ºC; *t* ≤ 5 h.

4- CONCLUSIONS

Carob pods (*Ceratonia Siliqua*, L.) are a source of valuable components. To extract those components a solubilization and an effective diffusion step should be considered. In order to facilitate the use of the extracts, it is important to carry the extraction in such a way that they contain a particular component in maximum amount while minimizing or limiting the presence of other components. For that purpose, based on the different characteristics on solubility and diffusion, a mechanistic model based management can be put on place. This allows the real time operation management according to chemical characteristics, initial composition, and physical characteristics, kibble size. The optimization of the extraction operation considering the cost of down steps of concentration or purification it is also possible. The models can be adapted to different components, as well as the objective function considered, to allow managing the process according to different goals linked to product characteristics, demand, energy, etc. The use of mechanistic models for process management greatly simplify the task while allowing process optimization.

Nomenclature

a_p	Surface polyphenols parameter	m
a_s	Surface sugars parameter	m
$C_p(t)$	Kibbles polyphenol concentration at time t	g/100 g dm
C_{p0}	Initial polyphenols concentration	g/100 g dm
C_{pl}	Bound value C_p	g/100 g dm
$C_s(t)$	Kibbles sugars concentration at time t	mg/g dm
C_{s0}	Initial sugars concentration	mg/g dm
D_{op}	Preexponential term polyphenols diffusion	m^2/h
D_{os}	Preexponential term sugars diffusion	m^2/h
D_p	Effective diffusion coef. polyphenols	m^2/h
D_s	Effective diffusion coef. sugars	m^2/h
E_{Dp}	Activation Energy polyphenols diffusion	J/mol K
E_{Ds}	Activation Energy sugars diffusion	J/mol K
E_{kp}	Activation Energy polyphenols solubilization	J/mol K

E_{ks}	Activation Energy sugars solubilization	J/mol K
k_{0p}	Preexponential term polyphenols solubilization	h^{-1}
k_{0s}	Preexponential term sugars solubilization	h^{-1}
k_p	Polyphenols solubilization rate constant	h^{-1}
k_s	Sugars solubilization rate constant	h^{-1}
L	Half thickness kibbles, slab	m
OF	Objective Function	%
t	time	h
t_{cp}	Critical time polyphenols solubilization	h
t_{cs}	Critical time sugars solubilization	h
t_l	Time limit for extraction	h
t_t	Total extraction time	h
T	Temperature	ºC
T_l	Lower limit of extraction temperature	ºC
T_u	Upper limit of extraction temperature	ºC

Acknowledgements

The support from Generalitat Valenciana PROMETEO/2014/005 is acknowledged

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