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Mechanistic modeling to address process analysis: Kibbles of carob (*Ceratonia siliqua*, L.) pod extraction

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ABSTRACT

The daily challenge involved in operating a process is the attainment of the objectives. Process management requires the use of tools adapted to the system's complexity. In order to obtain real time results, simplified mechanistic modeling offers a way to deal with this. To this end, carob pod (*Ceratonia siliqua*, L.) kibbles extraction is addressed in this work. They are a source of different, valuable components and have a complex structure and a highly variable concentration of components. The components considered are sugars and soluble polyphenols. Obtaining the extracts with an optimal composition of 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, modeled by means of a first order reaction and by considering slab geometry. The optimal processing time and temperature are obtained by taking a particular kibble size and composition into account.

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 if the inputs involve natural products, they change over time, mainly due to the natural variability of these materials. The type of cultivar, growing practices, degree of ripeness and bioclimatic indexes, among other things, are factors which lead to variability in composition.

To address this challenge, there is a need for process virtualization. This virtualization can take different forms, such as the expert who has a mental representation, the use of analogs or a numerical value if quantification is required. Of course, if optimization to attain objectives is involved, quantification is a must. There are process models that considering different approaches can help achieve that purpose (Irudayaraj, 2001; Tijskens et al., 2001; Sicard et al., 2011; Trystram, 2012; Marra, 2014).

For process management, there is a constraint to obtain real time results for the purposes of addressing daily operation; this implies that models should be simple enough to fulfill the requirement for real time results avoiding unnecessary complexity for the purpose. To establish these models, there is a need for process analysis to identify the main variables or parameters which are of relevance when running the process. Frequently, surface response methodologies are considered due to their simplicity (Tetik and Yüksel, 2014; Turhan, 2011), although many times the complexity of the process does 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 quite useful for daily industrial management.

A 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. Carob pods represent quite an interesting raw material, one which is also rich in bioactive compounds. Through a kibbling operation, the pods are deseeded and then the kibbles submitted to the extraction process. For a solid–liquid extraction, two periods are frequently considered, a very fast one at the beginning followed by a slow diffusion (Bucic-Kojic et al., 2013).

Carob trees (*Ceratonia siliqua*, L.) are mainly cultivated in the Mediterranean area. The seeds of the pods are used to obtain the locust bean gum and the kibbles are quite rich in sugars, around 50% weight basis. The aqueous extracts have bioactive compounds

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Nomenclature

a_p	surface polyphenol parameter, m	k_{0p}	pre-exponential term polyphenol solubilization, h^{-1}
a_s	surface sugar parameter, m	k_{0s}	pre-exponential term sugar solubilization, h^{-1}
$C_p(t)$	kibbles polyphenol concentration at time, t g/100 g dm	k_p	polyphenol solubilization rate constant, h^{-1}
C_{p0}	Initial polyphenol concentration, g/100 g dm	k_s	sugar solubilization rate constant, h^{-1}
C_{pl}	bound value C_p, g/100 g dm	L	half-thickness of kibbles, slab m
$C_s(t)$	kibbles' sugar concentration at time, t mg/g dm	OF	objective function, %
C_{s0}	initial sugar concentration, mg/g dm	t	time, h
D_{op}	pre-exponential term polyphenol diffusion, m^2/h	t_{cp}	critical time polyphenol solubilization, h
D_{os}	pre-exponential term sugar diffusion, m^2/h	t_{cs}	critical time sugar solubilization, h
D_p	effective diffusion coef. polyphenols, m^2/h	t_l	time limit for extraction, h
D_s	effective diffusion coef. sugars, m^2/h	t_t	total extraction time, h
E_{Dp}	activation energy polyphenol diffusion, J/mol K	T	temperature, °C
E_{Ds}	activation energy sugar diffusion J/mol K	T_l	lower limit of extraction temperature, °C
E_{kp}	activation energy polyphenol solubilization, J/mol K	T_u	upper limit of extraction temperature, °C
E_{ks}	activation energy sugar solubilization, J/mol K		

(Klenow et al., 2009). There are different valuable compounds, like d-pinitol, of pharmacological interest; polyphenols also constitute a source of compounds which have potential health benefits for humans. The high sugar content of the kibbles makes them of interest when obtaining traditional products for human consumption (Turhan et al., 2006).

The 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, low in sugar and rich in phenolics, could constitute a product of interest.

Considering that the mass transport characteristics of the particular compounds are different during the solubilization and diffusion periods, it could be possible to obtain fractions of extracts which are 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 in the kibbles and 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 in diffusivity and avoid a sound extraction process. The kibbling process provides particles of different sizes, small enough to allow the pods to be deseeded.

When carob kibbles are extracted, the soluble polyphenols impart an astringent taste. On the one hand, for human consumption it could be interesting to establish the extraction time in order to recover the maximum amount of sugar while avoiding astringency or conversely obtain higher amounts of polyphenols whit low amounts of sugars in the kibbles. On the other hand, if a particular compound is of interest, like d-pinitol, a fraction with the required characteristics could be obtained by modeling its extraction kinetics. 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 dealing with process virtualization for process management. In this work, a methodology will be developed using a mechanistic model, solubilization and diffusion, in order to obtain fractions of interest. In a first approach, sugars and soluble polyphenols will be considered. The effect of particle size and polyphenols left on the kibbles will be addressed by using a simplified mechanistic model in order to manage the process by obtaining the optimal operating conditions for sugar extraction.

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 the influence of temperature on the extraction of sugar from carob kibbles were obtained from literature (Mulet et al., 1988), the initial sugar content was different in different experiments. The analysis was carried using the colorimetric anthrone method (Snell and Hilton, 1968). The water soluble polyphenols were obtained by extraction in a well-stirred, temperature-controlled 1 L vessel (20–100 °C). The analysis of total phenolic content was carried out using the Folin–Ciocalteu procedure (Kil Sun et al., 2012), the initial content being 3.80 ± 0.26 g/100 g dm.

2.2. Modeling

The carob pods have a geometry like a parallelepiped of different sizes (frequently around 0.009 × 0.025 × 0.20 m), to obtain the kernels the pods are chopped obtaining kibbles of different sizes (Fig. 1). The pods have an external layer that is somewhat impermeable. When obtaining the kibbles, if they are around 5 mm in size 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 placing the kibbles in contact with the extracting water, the soluble components, sugars and polyphenols that are located on the external layer are dissolved. The solid components inside

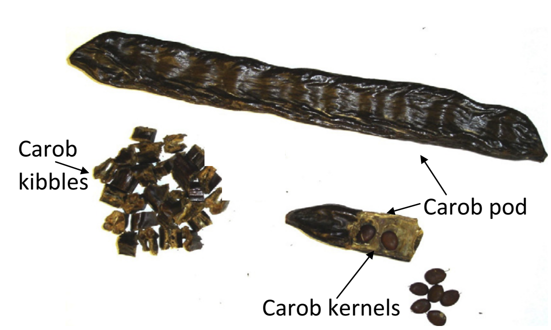

Fig. 1. Plant material: carob pods, kibbles and kernels.