COMPARISON OF TWO MONITORING METHODS FOR ALMOND OIL EXTRACTION WITH SUPERCRITICAL CO_2.

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Nuts provide an interesting nutritional supply. However, their high fatty content makes them unattractive for new consumers demanding “light”, low-fatty foods. Among nuts, almonds have a significant economical importance for the whole Mediterranean area. In the last years, high production and competition among productive zones have hardened the commercialisation of this product. On the other hand, almond oil is very appreciated for alternative medicine, cosmetics, etc. Thus, obtaining the almond oil may be an option for expanding the almond market. In this way, using clean process such as supercritical fluid extraction for almond oil extraction may also lead to an almond revalorisation as a “light” product (partially defatted almonds).

In this work, several experiments have been carried out at different conditions, modifying pressure, temperature or flow rate of SC-CO_2. Extraction pressures have been chosen in the 20–28 MPa range. Extraction temperatures have ranged between 30 and 50ºC. Flow rate of supercritical carbon dioxide varies from 2 up to 4 kg/h. All the experiments have been carried out with the same almond variety (Marcona) in the same extractor (0.5 L). For each experiment, the supercritical extraction process has been applied to approximately the same amount of raw, entire, non-peeled almonds. Extraction processes have been monitored by two different methods. By the first method, the cumulated amount of extract obtained at different moments is registered and by the second one, mass loss of the partially deffated almond is determined at different moments. This last monitoring method implies stopping the extraction process, depressurising, and opening the extractor to weight the content of the basket. Extraction curves are obtained by joining several points coming from extractions carried out under the same operating conditions but that have been stopped at different moments. Only slight differences have been observed between results given by the two applied monitoring methods.

INTRODUCTION

Nuts provide an interesting nutritional supply due to their high nutritive and energetic value. However, their high fatty content makes them unattractive for new consumers demanding “light”, low-fatty foods. Among nuts, almonds (*Prunus Amygdalus*) have a significant economical importance for the whole Mediterranean area. The USA is the main almond producer and Spain is the second one. Almonds have a low content in sugar, for that reason they may be included in diet of diabetics. Almonds and other nuts appear to health benefits despite their high fat content [1, 2]. These benefits (reduction of both colon cancer risk [3], and cardiovascular risk [4]) seem to be related to the oil fraction of these nuts. Almonds have also beneficial effects on serum lipids and induce significant reduction in total cholesterol [5, 6].

In the last years, consumer trends to foods with lower fat content, and higher competition among productive zones have hardened commercialisation of this product. On the other hand, almond oil is very appreciated for alternative medicine, cosmetics, etc [7]. Almond oil has also applications as antioxidant [8, 9] because of its free radical scavenger capacity [9].

Thus, obtaining almond oil may be an option for expanding the almond market. This way, using clean processes such as supercritical fluid extraction for almond oil extraction may also lead to an almond revalorisation as a “light” product (partially defatted almonds) [10].

Supercritical fluid extraction (SFE) is a green process with applications in several areas, mainly in food and pharmaceutical sectors. In fact, oil extraction from seeds was one of the first targets for these processes [11, 12]. However, extraction of almond oil with supercritical CO_2 has been only a little studied [10, 13]. In other work presented to this Symposium the effect of high intensity ultrasound on the kinetic of this extraction process is shown [14], and in a previous paper the effect of the extraction on the cell wall composition of almonds has been studied [15].

The objective of this SFE application may be considered as double: on one hand obtaining almonds partially defatted but with good tasting quality; and on the other hand, producing almond oil. Quality of almond oil obtained by SFE may differ from other almond oil obtained by conventional methods because it is produced by a green and mild process [16] and only the first fraction is extracted. Quality of defatted almond depends on texture properties that are directly related to oil content. Thus, oil extraction process must not take place so long such as for going beyond the defatted almond quality limit. Quality of almond oil could depend on several variables in addition to the extraction process, such as the variety of raw material, pretreatments (toasting for example [17, 18]), ageing-conservation process, among others.

Kinetic of the extraction process can be studied from different experimental procedures. The simplest one (Procedure 1) consists on periodically following the process by measuring the extract collected [19]. This procedure may present a transport delay since part of the oil extracted has not been collected yet at the time of taking every sample. For this reason some authors use an alternative procedure, that avoids the lag between the extraction and the sampling. This method consists on periodically measuring the extraction progress by weighing the content of the extractor [20]. This procedure (Procedure 2) is harder and time consuming.
Data experimentally obtained and generally cited in the literature are subjected to the characteristics of the monitoring method chosen. Thus, establishing the extent of the differences due to the monitoring method becomes interesting. This would help to clarify if either monitoring method may be used without distinction or any is preferred. No other study has been found in the literature for this purpose. The aim of this work is estimating the effect of selecting one or other monitoring methods on extraction data. This contribution results from a project related to SFE of almond oil and its improvement by applying ultrasounds.

I - MATERIALS AND METHODS

Almonds have been selected as raw material because almond oil extraction process is slow, the initial content of extractable material is high, and solubility of oil in supercritical CO_2

is relatively high. Marcona cultivar has been selected because of its wide extension and acceptability. Samples of this cultivar were obtained from a local producer. Almonds are processed as received (with peel), only in one experiment are ground.

Experiments were carried out in a pilot plant described previously [21]. Dry CO_2 was supplied by Abello-Linde (Valencia, Spain), with purity higher than 99 % w. Approximately 0.150 kg of almonds were used in each experiment. In order to clarify the effect of the monitoring method on the kinetic determination, a series of experiments was designed, using whole almonds (with peel) as raw material, and varying the operation conditions. Pressure ranged from 20 to 28 MPa, temperature ranged from 30 to 50ºC and flow rate ranged from 2 to 4 kg/h.

For each experiment, two types of measurements were recorded, each corresponding to a different monitoring method. First monitoring procedure consists on following the process progress by weighing extract mass. Second monitoring method provides kinetic data by measuring the loss of weight of the raw material after the extraction process has been applied. Whereas extract weight may be registered at any time as process goes on, measuring the mass of the partially extracted raw material implies stopping the extraction process, depressurising, getting the basket with the raw material out of the extractor and waiting till constant weight, as it has been already mentioned. As a result, although lag error is avoided, procedure 2 introduces errors associated to each stage and it is more complex and time-consuming.

Following procedure 1, extract samples were weighted at uniformly spaced times. In order to minimise errors associated to method 2, every experiment gave to a unique point of the curve with respect to the loss of weight of the raw material. Thus, several experiments were carried out at the same operational conditions with fresh raw material, changing the duration of the extraction in order to obtain each kinetic curve. Hereinafter, we call as "experiment" each group of experiments carried out at the same operational conditions.

Experimental data were fitted using the Naik model [22], in the following form:

$$e = \frac{e_\infty q}{B + q} \qquad (1)$$

where "e" is the yield (kg extract/100 kg raw material) obtained when it has passed "q" (kg CO_2/kg raw material) and "e_∞" and "B" are the model parameters. "e_∞" represents the solute extractable content in raw material, and B is the kinetic parameter.

II.- RESULTS AND DISCUSSION

Table 1.- List of experiments. Analysis of Variance. Experiments 1 to 7 carried out with whole almonds with peel; and experiment 8, with ground almonds.

Exp. Number	P (MPa)	T (ºC)	M CO_2 (kg/h)	F_{calc}	$F_{0.05}$	Sig. p
1	**24**	**40**	**3**	1.6	4.7	0.24
2	**20**	40	3	0.014	5.3	0.91
3	**28**	40	3	0.069	6.0	0.80
4	24	**30**	3	0.011	5.3	0.92
5	24	**50**	3	1.0	6.0	0.35
6	24	40	**2**	0.014	6.0	0.91
7	24	40	**4**	0.56	5.3	0.47
8	28	50	3	0.69	19	0.49

Table 1 shows the operational conditions at which extraction kinetics by two monitoring methods have been studied. Experiments 1 to 7 were conducted with whole almonds, but experiment 8 was carried out with ground almonds to test the comparison at faster extraction conditions. Results of two of these experiments are shown in Figures 1 and 2. In any case, little difference between data obtained with the two procedures may be observed. The Analysis of Variance (ANOVA) shows that differences are not significant, even when some graphical discrepancies may be seen (Figure 1), as it is observed in Table 1 ($F_{0.05} > F_{calc}$, and $p > 0.05$ for all the experiments).

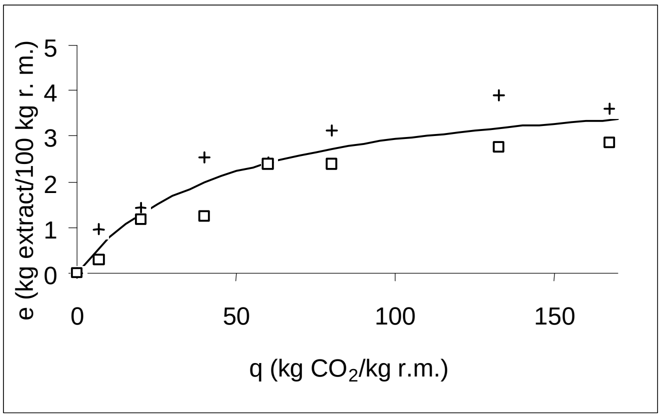

Figure 1.- Kinetic of almond oil extraction. Experiment 1 (24 MPa, 40ºC and 3 kg CO_2/h). □, data obtained by collecting extract (Procedure 1); +, data by weighing loss of raw material mass (Procedure 2); __, model.

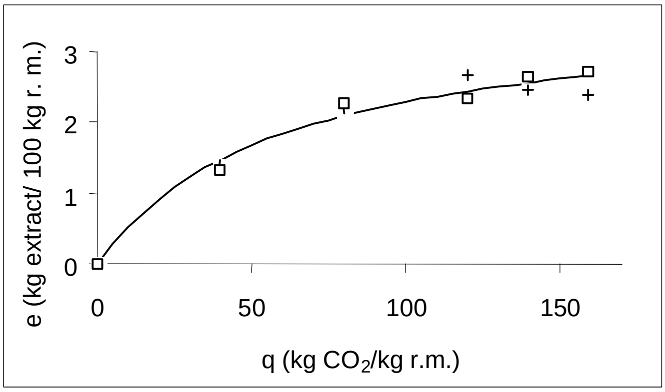

Figure 2.- Kinetic of almond oil extraction. Experiment 2 (20 MPa, 40ºC and 3 kg CO_2/h). □, data obtained by collecting extract (Procedure 1); +, data by weighing loss of raw material mass (Procedure 2); __, model.

In order to test the influence of selecting a monitoring procedure on kinetics study, data has been fit to a particular model. Naik model [22] has been selected because of its simplicity and because its acceptable correlation of the data. Table 2 shows values for Naik model parameters when all the data are considered and when it is applied to different data sets (1 and 2), one for each monitoring procedure. As an example, model parameters for the experiments 1 and 2 (Figures 1 and 2) are presented. As it may be observed, parameters vary slightly between experiments, but within the same order of magnitude. Thus, procedure 1 may be selected for the studied plant without entering significant errors.

In addition, experiment 8 has also been included to show the effect of modifying the particle size on model parameters and extraction kinetics. Only model parameters fitting data (56 points) got by procedure 1 are shown, since this is the selected method and only three data obtained by procedure 2 are available. As it is shown, e_∞ value is much higher than those corresponding to the rest of experiments (e_∞ some 20 times bigger), probably because the reduction of particle diameter increases considerably the amount of extractable oil.

Table 2.**-** Parameters of the Naik model [22] obtained using the different data sets.

Experiment	Data[1]	Parameters		Differences (%)	
		e_∞	B	e_∞	B
1	All	4.29	46.0	-	-
	1	4.64	39.3	8.2	-15
	2	3.94	55.3	-8.2	20
2	All	3.63	58.6	-	-
	1	3.38	48.7	-6.9	-17
	2	3.94	71.1	8.5	21
8	1	77.2	212	-	-

[1] Data used: All: all; 1: data obtained with procedure 1; 2: data obtained with procedure 2.

CONCLUSION

In this work, kinetics of SFE of almond oil has been studied. Extraction processes have been followed by two monitoring methods. By first method, the cumulated amount of extract obtained at different moments is registered. By second method, mass loss of the partially deffated almond is determined at different moments. First method may present errors due to lag between extracting and collecting extracts and to extract losses in tubing, fittings, valves, etc. Magnitude of these errors depends on installation features. On the other hand, second method implies stopping the process and depressurising the whole system. First method is less time-consuming and less complicated, and thus, more desirable if its measures are acceptable.

Both monitoring methods have been applied in a series of experiments in order to compare them. Only slight differences have been observed between results given by the two applied monitoring methods. Statistics tools have been applied to kinetics data and these differences do not seem to be significant. The effect of these differences on the parameters of Naik model [22] is also studied. Experiments carried out at different operating conditions led to model parameters within the same order of magnitude, with slight differences between both monitoring methods. However, order of magnitude changes when particle size is reduced, reflecting that extraction rate of oil increases.

It has been shown that no significant differences have been found between observing the process by monitoring procedure 1 or 2. Thus, because of its advantages, procedure 1 may be selected for experiments carried out in the considered plant. For other plants new experiments should be done.

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