Effect of Temperature on Isobutyric Acid Loss during Roasting of Carob Kibble

Angel Berna,*,† María B. Pérez-Gago,‡ Vicente G. Guardiola,‡ Domingo Salazar,§ and Antonio Mulet‖

Chemical Engineering Department, University of València, Burjassot, València, Spain, AINIA, Parc Tecnològic, Paterna, València, Spain, and Department of Vegetal Production and Department of Food Technology, University Politècnica of València, València, Spain

The high content of isobutyric acid in carob (*Ceratonia siliqua* L.) constitutes a handicap for some of its potential uses due to the undesirable smell produced by that compound. In this study the loss of isobutyric acid during roasting was approached by heating the carob kibble at temperatures from 120 to 180 °C in two local cultivars (Matalafera and Lisa). The initial content of isobutyric acid varied between 6.3 (Lisa) and 9.4 (Matalafera) g isobutyric acid/kg dry solid. Results showed that the process can be described by a diffusive model. The activation energy of the process is about 55 kJ/mol for both cultivars.

Keywords: *Carob pod; roasting; isobutyric acid; diffusion*

INTRODUCTION

Carob (*Ceratonia siliqua* L.) is a leguminous tree typical of the Mediterranean area; Spain is the main grower (Tous and Batlle, 1987) and the Valencia region is the most important area. The tree's fruits, carob pods, have two parts with different applications: the pulp (kibbles) and the seeds (or kernels). Kernels are used to obtain the locust bean gum or carob bean gum. This gum is widely employed as a high-quality thickening agent in the food industry (Camacho et al., 1996). Therefore carob kernels are the most valuable part of carob pods.

Carob kibbles, which represent about the 0.90 mass fraction of whole pods, have some uses (Petit and Pinilla, 1995) related to their constituents, mainly sugars (above all sucrose, with glucose and fructose in smaller amounts) and tannins, nevertheless the kibbles account for less than half of the pod price (Mulet, 1985). Since the carob pods have lost their value as food for animals, the price of pods largely depends on the price of a minor part, the kernels, leading to fluctuations and instabilities in the market mainly due to speculative processes, which is the main problem in the field. Despite the increase in pod prices in recent years, pod production is quite constant due to the lack of confidence of the producers on the market and the long time needed to grow an adult tree (more than 10 years).

The potential economic benefits of this crop and its use mainly for ecological purposes in reforestation in the Mediterranean area have increased the interest in reducing the time needed to obtain pod production as well as in improving the knowledge about cultivars that would allow an increase in pod and kernel yields. At the same time, there is interest in developing the existing applications of carob pulp to help make the market price of the carob pods more steady.

The application of the carob pulp in animal feeds, due to its high sugar content (about half its weight), is limited because of the high tannin content (around a mass fraction of 0.15 in some cultivars [Kumar and Singh, 1984]). For that reason different authors have developed procedures to use the carob kibbles for growing micro-organisms in liquid (Marakis and Karagouni, 1985; Roukas and Biliaderis, 1995) or semisolid culture (Cañellas et al., 1989) to enrich this fodder in proteins.

In foods intended for human consumption the carob pulp has been widely used during famines. Nowadays the production of flour from roasted kibbles (Fito et al., 1985) is used in food technology as a substitute for cocoa or as a stabilizer. Other applications of kibbles are in pharmaceutical products, ethanol production (Roukas, 1994), and sugar extraction (Petit and Pinilla, 1995; Mulet et al., 1988; Roseiro et al., 1991; Marakis, 1992). Flavor and aroma are fundamental attributes of these products, in fact more than 169 volatile components have been identified (MacLeod and Forcén, 1992). Nevertheless in most of the uses described, the smell of the isobutyric acid is undesirable; the off-flavor is partially lost in roasting, thus making this process step a crucial one in the manufacturing process. In that sense it is quite interesting to quantify the phenomenon.

In this work the isobutyric acid loss kinetics during roasting was studied in two different cultivars of the Valencia region (Spain); the influence of temperature on the kinetic process was analyzed.

MATERIALS AND METHODS

Before the roasting operation, the carob pods were kibbled to uniform size particles and the kernels removed.

Roasting was carried out in a well-stirred hot air oven at constant temperature with air renewal. The kibbles were placed inside the oven on a monolayer and periodically sampled to evaluate the isobutyric acid loss. To establish the effect of temperature on the process, experiments were performed between 120 and 180 °C, this being the temperature interval actually used in some carob roasting industries. At different processing times, samples were taken out of the oven

* Author to whom correspondence should be addressed (telephone 34 6 3864316; fax 34 6 3864898; e-mail Angel.Berna@uv.es).

† Chemical Engineering Department.

‡ AINIA.

§ Department of Vegetal Production.

‖ Department of Food Technology.

S0021-8561(97)00136-2 CCC: $14.00

to determine the isobutyric acid content in order to follow the process during the operation. Extracted samples were vacuum packaged and cooled to avoid changes before analysis, mainly from water sorption.

The isobutyric acid was extracted by steam distillation and measured according to the following procedure: roasted kibbles were ground to obtain carob flour. A 20 g sample was introduced in a distillation flask and 175 mL of distilled water and 25 mL 1 N H_2SO_4 was added. Steam was passed through the sample until 200 mL distilled liquid was collected (Abbaticchio et al., 1983).

The isobutyric acid quantitative analysis was determined by gas chromatography in an HRGC 5300 Mega series (Carlo Erba Instruments; Rodano, Milan, Italy) coupled to a flame ionization detector (FID). A glass column (Teknokroma; San Cugat del Vallés, Barcelona, Spain) was used: 6 ft (1.8 m) long and 2 mm i.d., packing 10% AT-1200 and 1% H_3PO_4 on Chromosorb W-AW 80/100. The working conditions were oven temperature, 110 °C; injector and detector temperature, 200 °C; carrier gas, N_2 at 30 mL/min. The isobutyric acid was identified with an external standard: *n*-butyric acid 99% (no. B-2503 Sigma-Aldrich Chemical Co.; Alcobendas, Madrid, Spain).

The experiments were performed using two different cultivars common in the Valencia region [Matalafera (M) and Lisa (L)]. The main characteristics of these cultivars were reported elsewhere (Sánchez-Capuchino et al., 1987; Albanell et al., 1993). The kibble size was set up to yield 10 × 10 mm. The third dimension corresponds to the thickness of the fruits (approximately 5 mm). These dimensions were considered because industrial kibbling yields mainly this size product, making it the likely input for a roasting operation.

RESULTS AND DISCUSSION

A diffusive model was considered to analyze the results. The main features are summarized to illustrate the procedure.

Because the rate of the transport process is controlled by internal diffusion, concentration changes related to time and position could be described through the microscopic mass balance and Fick's law (Skelland, 1974) as shown in eq 1.

$$\frac{\partial c}{\partial t} = D_{\mathrm{e}}\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \tag{1}$$

Isotropic diffusion behavior is assumed in eq 1, nevertheless this hypothesis could be questioned due to the characteristics of the kibbles. The kibbles show a nonuniform appearance, the external surface of the pod consisting of a cuticle. This cuticle is not found in the surfaces obtained from the cut pod, being, thus apparently more prone to diffuse material in that direction. Moreover the internal structure of the pod pulp, observed by magnification, shows the existence of cells, some of which are coated with a similar cuticle. Hence, whenever the size of the kibble is large enough compared to the size of the cells, the existence of the above-mentioned cuticles confers to the kibble a macroscopically observed isotropy. The measurement of the cells in the cultivars considered (almost elliptical shape) gave a size of 2 × 4 mm for the main dimensions, this figure being lower than the size considered for the kibbles; thus, the isotropic behavior hypothesis could be retained.

This diffusion problem can be solved using the usual boundary conditions:

(1) Uniform initial composition (initial condition):

$$\text{for } t = 0,\ c = c_{\mathrm{c}}$$

Table 1. Effect of Roasting Time on Isobutyric Acid Concentration in Lisa and Matalafera Cultivars at Different Temperatures

time (min)	isobutyric acid (g/kg dry kibble)					
	Matalafera			Lisa		
	140 °C	160 °C	180 °C	120 °C	140 °C	160 °C
0	9.3	9.3	9.5	6.3	6.2	6.3
5			9.4			
10	8.8	7.5	6.9	5.3	5.8	4.3
15			4.7			
20	8.6	5.0	4.5	5.2	5.2	3.5
25			3.7			
30	6.9	3.8	2.9	5.0	4.7	3.1
40	6.9	3.6		4.9	4.3	2.7
50	6.2	3.2		4.7	4.0	2.5
60	5.4	3.0		4.4	3.9	2.2

(2) Symmetry boundary condition for each direction, for example in direction *x*:

$$\text{at } x = 0,\ \frac{\partial c}{\partial x} = 0$$

(3) Equilibrium boundary condition for each direction in the interface, for example in direction *x*:

$$\text{at } x = L_{\mathrm{x}},\ c = c_{\mathrm{e}}$$

This three-dimensional problem can be separated into three one-dimensional problems by the separation-of-variables method (Arpaci, 1966). The solution for one direction is a well known series development and the three-dimensional solution is the product of the three one-dimensional solutions.

The average concentration can be evaluated by integrating this solution for the entire volume. This is the most interesting form of model solution because the average content at discrete values of time is measured. This equation remains as a series development, but for large values of time only one term of the series is meaningful. In this case the solution for the particle considered is

$$\Gamma = \frac{c - c_{\mathrm{e}}}{c_{\mathrm{c}} - c_{\mathrm{e}}} = \exp\left[-\frac{D_{\mathrm{e}}\pi^2}{4}\left(\frac{1}{{L_x}^2} + \frac{1}{{L_y}^2} + \frac{1}{{L_z}^2}\right)t\right] \tag{2}$$

where *c* is the average concentration of the component transferred, D_{e} is the effective diffusivity, and L_{x} is the half-thickness in the direction *x*. There are similar parameters in directions *y* and *z*. A similar model was previously successfully applied to the extraction of sugar from carob pods (Mulet et al., 1988). The preexponential factor of the complete solution must approach unity in order to achieve the initial condition. Plotting the logarithm of the dimensionless concentration (Γ) versus time should lead to a straight line if the diffusion mechanism prevails.

In order to apply this diffusive model, it has been considered that the equilibrium composition was very small and hence negligible. The initial composition values were 6.3 ± 0.1 and 9.4 ± 0.1 g isobutyric acid/kg dry solid in Lisa and Matalafera cultivars, respectively.

Experimental results of the two cultivars studied are reported in Table 1, which the residual concentration of isobutyric acid is given along the roasting time. If these data are transformed with the corresponding dimensionless values, it can be observed that experimental points can be fitted to straight lines after some

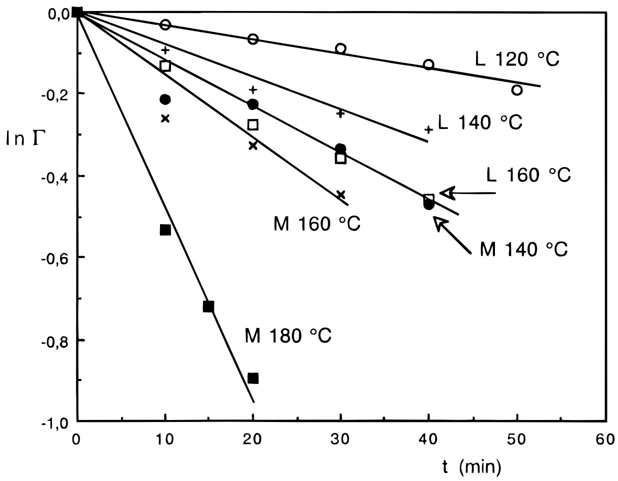

Figure 1. Effect of roasting time on isobutyric acid dimensionless concentration in Lisa and Matalafera cultivars.

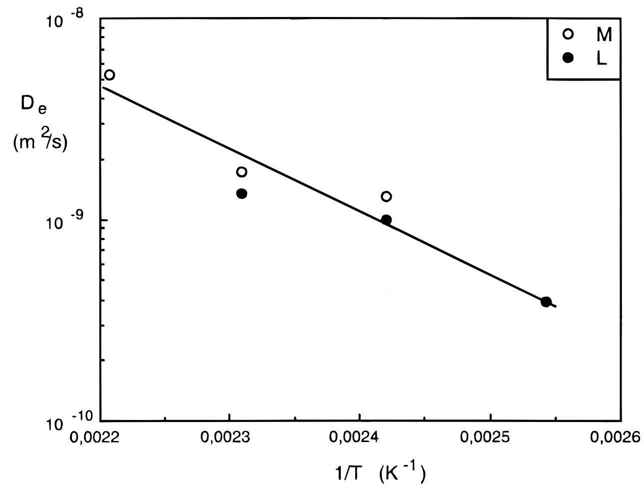

Figure 2. Effective diffusivity variation with temperature in Lisa and Matalafera cultivars.

value of time, in a log plot. The first points could correspond to an induction period during which the main loss of isobutyric acid corresponds to the disrupted cells on the cut surfaces or results for the first points could indicate that the simplifying hypothesis holds only for large enough values of time. In this period the most important mechanism may be the loss of the isobutyric acid on the surface; only when the concentration of this compound in this zone has been depleted is the diffusion mechanism dominant. Equation 2 describes only the diffusional mechanism and consequently other mechanisms are not represented. From inspection by plotting dimensionless concentration versus time it was observed that the initial and the first sample data were not located in a straight line. As a consequence those two data were not considered to be included within the period during which the diffusion mechanism prevails.

In Figure 1 the resulting dimensionless concentration has been represented against time in a log plot. The time scale corresponds to the diffusional period.

The experimental results for the diffusionally described period are shown in Figure 1 for all the temperature values used and the two cultivars considered. From the slope of these straight lines the kinetic parameter of the model was determined. One can appreciate the temperature effect on this slope. The value of the slope for each experiment was determined using a least square technique.

$$\text{slope} = -\frac{D_e \pi^2}{4}\left(\frac{1}{L_x^{\;2}} + \frac{1}{L_y^{\;2}} + \frac{1}{L_z^{\;2}}\right) \qquad (3)$$

For a diffusion driven process the effective diffusivity varies according to the Arrhenius Law. The values of the effective diffusivity were computed from the slopes and log plotted against $1/T$ as shown in Figure 2. It is observed that a straight line fits the data points for both carob cultivars (Matalafera and Lisa). Thus the activation energy (approximately 55 kJ/mol) can be considered to be the same for both cultivars. This value is only a little higher than the values for other diffusional processes: 15 kJ/mol for sugar diffusion in carob kibbles (Mulet et al., 1988) and 12−100 kJ/mol for drying of different fruits and vegetables (Berna et al., 1990; Zogzas et al., 1996).

These results can be used in the process model in order to optimize the overall operation of carob roasting. The higher loss of isobutyric acid will bring a higher sensory quality of the carob powder, which is a factor to consider when establishing the roasting time. Other factors to be considered in the objective function include the energy costs as well as functional properties of the powder as influenced by roasting time and temperature.

LITERATURE CITED

Abbaticchio, P.; Balice, V.; Cera, O. Determination of volatile fatty acids by gas chromatography after a rapid steam-distillation of wastes. *Environ. Technol. Lett.* **1983**, *4* (4), 179−182.

Albanell, E.; Plaixats, J.; Caja, G. Determination of chemical composition of carob pods by near-infrared reflectance spectroscopy. *J. Sci. Food Agric.* **1993**, *63* (3), 309−312.

Arpaci, V. S. *Conduction Heat Transfer*; Addison-Wesley: Reading, MA, 1966; pp 270−307.

Berna, A.; Rosselló, C.; Cañellas, J.; Mulet, A. Drying kinetics of apricots. In *Engineering and Food. 1. Physical properties and process control*; Spiess, W. E. L., Schubert, H., Eds.; Elsevier: London, 1990; pp 682−690.

Camacho, M. M.; Martínez-Navarrete, N.; Chiralt, A. Functional properties of Locust Bean Gum: A review. *Proceedings of the 3rd International Carob Symposium*, Cabanas-Tavira, Portugal; Facultade de Ciencias de Lisboa: Lisboa, Portugal, 1996; p 32.

Cañellas, J.; Pou, J., Mulet, A. Protein enrichment of carob kibbles after sugar extraction. *Lebensm. Wiss. Technol.* **1989**, *22* (2), 73−77.

Fito, P.; Chiralt, A.; Vidal, D. Obtención de harina de algarroba. Problemática y perspectivas (Carob flour production. Problems and prospects). In *Jornadas sobre el aprovechamiento de la algarroba en el área del Mediterráneo*; Cátedra Ramón Llull: Palma de Mallorca, Spain, 1985; pp 69−80.

Kumar, R.; Singh, M. Tannins: their adverse role in ruminants nutrition. *J. Agric. Food Chem.* **1984**, *32*, 447−453.

MacLeod, G.; Forcén, M. Analysis of volatile components derived from the carob bean *Ceratonia siliqua*. *Phytochemistry* **1992**, *31* (9), 3113−3119.

Marakis, S. G.; Karagouni, A. D. Screening of carob bean yeast chemical composition of Schizosacharomyces versatilis grown on aqueous carob extract. *Biotechnol. Lett.* **1985**, *7* (11), 831−836.

Marakis, S. G. Sucrose syrup from carob pod. *Biotechnol. Lett.* **1992**, *14* (11), 1075−1080.

Mulet, A. Pasado y presente del sector de la garrofa y garrofín. (Past and present of the carob pods and kernel's business). In *Jornadas sobre el aprovechamiento de la algarroba en el área del Mediterráneo*; Cátedra Ramón Llull: Palma de Mallorca, Spain, 1985; pp 1−10.

Mulet, A.; Berna, A.; Heredero, V.; Rosselló, C. Temperature influence on the sugar extraction from carob pods. *Lebensm. Wiss. Technol.* **1988**, *21*, 108−112.

Petit, M. D.; Pinilla, J. M. Production and purification of a sugar syrup from carob pods. *Lebensm. Wiss. Technol.* **1995**, *28* (1), 145−152.

Roseiro, J. C.; Gírio, F. M.; Collaço, M. T. M. Yield improvements in carob sugar extraction. *Process Biochem.* **1991**, *26*, 179−182.

Roukas, T. Continuous ethanol production from carob pod extract by immobilized Saccharomyces cerevisiae in a packed-bed reactor. *J. Chem. Technol. Biotechnol.* **1994**, *59* (4), 387−393.

Roukas, T.; Biliaderis, C. G. Evaluation of carob pod as a substrate for pullulan production by *Aureobasidium pullulans*. *Appl. Biochem. Biotechnol.* **1995**, *55* (1), 27−44.

Sánchez-Capuchino, J. A.; Salazar, D.; García, S.; Martínez, R.; Melgarejo, P. Tipificación pomológica de los algarrobos de la Comunidad Valenciana [Pomologic typification of carob trees in the Comunidad Valenciian (Spain)]. *Proceedings of the 2nd International Carob Symposium*; Generalitat Valenciana: Valencia, Spain, 1987; pp 69−84.

Skelland, A. H. P. *Diffusional Mass Transfer*; Wiley: New York, 1974; pp 28−35.

Tous, J.; Batlle, I. Situación actual y perspectivas del cultivo del algarrobo. (Present situation and perspectives of the carob trees growing). *Proceedings of the 2nd International Carob Symposium*; Generalitat Valenciana: Valencia, Spain, 1987; pp 317−345.

Zogzas, N. P.; Maroulis, Z. B.; Marinos-Kouris, D. Moisture diffusivity data compilation in foodstuffs. *Drying Technol.* **1996**, *14* (4), 2225−2253.

Received for review February 18, 1997. Revised manuscript received June 6, 1997. Accepted June 26, 1997.[⊗]

JF970136P

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.