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## 1. Introduction

Chemical peeling is a complex process involving 35 simultaneous heat and mass transfer with chemical reaction. It is used mainly for peeling fruits and vegetables 37 and involves the use of a hot solution of caustic soda in which the product is immersed for a certain period. The lye 39 solution reacts with epidermal and hypodermal cell walls resulting in the separation of the skin (Floros, Wetzstein, & 41 Chinnan, 1987). The rate of peeling is a function of alkali temperature and concentration, peeling time, geometry, 43 peel thickness, and other fruit characteristics; and involves both chemical and thermal treatment. The study of the

- relationship among those variables is important to avoid pulp and weight losses by over-peeling. In the same way,
  the elevated temperature used during peeling could have a cooking effect that affects product texture. Several authors
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<sup>1</sup>Presently with Dr. J.A. Barreiro & Assocs. Professor (R) Universidad Simón Bolívar. have studied the chemical peeling process for various fruits59and vegetables (Barreiro, Caraballo, & Sandoval, 1995;Floros & Chinnan, 1988, 1990; Garrote, Coutaz, Luna,Silva, & Bertone, 1993; Garrote, Coutaz, Silva, & Bertone,611994).63

Barreiro et al. (1995) developed a mathematical model for chemical peeling of fruits with spherical geometry to predict peeling time and texture as a function of the other variables involved. In the development of this model the authors presented the following main assumptions and considerations: 69

- a. The food to be peeled has a spherical geometry.
- b. The reaction mechanism follows an unreacted core model, with the reaction starting at the external surface and proceeding towards the inner part leaving a layer of completely converted reacted material on the surface and a central core of unreacted product in the centre. Reaction takes place uniformly over the product surface and as the reaction proceeds the inner core diameter is reduced. The reaction rate is independent of diffusion of alkali through the reacted product ash, and it is defined as the amount of reacting product proportional to the

1 available surface of the unreacted core (Levenspiel, 1988). This model considers that chemical reaction is the

- 3 controlling step, prevailing over diffusion in the reaction.
- 5 c. Temperature of product at the location being reacted is similar to that of the peeling alkali solution, implying an
- 7 elevated surface heat transfer coefficient. Temperature and concentration of the lye solution remain constant 9 during the peeling process.
- 11 The following equation was proposed to predict peeling time: 13

$$t = b'' \exp(E_a/RT)((R_e - r)/Ca),$$
 (1)

- 15 where t is the peeling time (min), b'' the constant (g mol min/cm<sup>4</sup>),  $E_{\rm a}$  the activation energy for chemical peeling
- 17 (cal/g mol), R the universal gas constant (cal/K g mol), T the peeling temperature (K),  $R_{\rm e}$  the external radius of fruit
- 19 before peeling (cm), r the radius of the product at any moment during peeling (cm), and Ca the alkali concentra-21 tion (g/100 ml).
- The theoretical weight loss after some time of peeling a 23 fruit with spherical geometry was calculated using the following equation:

$$W = \frac{4\pi}{3} R_{\rm o} (R_{\rm e}^3 - r^3)$$
<sup>(2)</sup>

being W is the weight loss during peeling (g),  $R_0$  the 29 average apparent density of the peel (g/cm<sup>3</sup>), and r the radius of peel remaining (cm).

Solving for 31

$$_{33} r = (R_e^3 - (3W/(4\pi R_o)))^{1/3}.$$
 (3)

The authors also presented the following apparent first-35 order kinetic equation to predict the effect of temperature in product texture:

$$\frac{37}{39} \frac{\mathrm{d}T_{\mathrm{ex}}}{T_{\mathrm{ex}}} = K_i \,\mathrm{d}t \tag{4}$$

with

<sup>41</sup> 
$$K_i = K'_o \exp(-E'_a/RT).$$
 (5)

43 Combining Eqs. (4) and (5) and integrating between the limits  $T_{ex}$  and  $T_{exo}$ , and 0 and t, for constant peeling 45 temperature, the following equation was obtained:

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$$\ln(T_{\rm ex}) = \ln(T_{\rm exo}) + K'_{\rm o} \exp(-E'_{\rm a}/RT)t,$$
 (6)

where  $K_i$  is the velocity constant in the texture equation (1/ 49 min),  $T_{ex}$  the texture (mm of penetration),  $T_{exo}$  the initial

- texture (mm of penetration),  $\vec{K}'_{o}$  the constant (1/min).
- The constants in these equations: b'' and  $E_a/R$  in Eq. (1), 51 and  $\ln T_{\rm exo}$ ,  $K'_{\rm o}$  and  $E'_{a}/R$  in Eq. (6), must be obtained
- 53 experimentally for peaches in order to predict peeling time and texture changes during peeling.
- 55 In the same way, Barreiro et al. (1995) presented a procedure to obtain peeling maps, and particularized the

57 model for guava suggesting that its application could be

extended to other food that could be assimilated to spherical geometry.

#### The aim of this work was to apply the above model for the chemical peeling of peaches that were assimilated to 61 spherical geometry, in order to determine experimentally the values of the constants involved in Eqs. (1) and (6), and 63 to develop peeling maps to predict peeling time for various conditions involved in the chemical peeling of peaches, 65 such as alkali concentration, temperature and peel thickness: and to estimate the effect in texture induced by heat 67 treatment during peeling.

## 2. Materials and methods

## 2.1. Raw material

Peaches (Prunus persica L.) variety Amarillo Jarillo, 75 grown in El Jarillo, Venezuela were used in this research work. The fruit, in the early ripening state, was obtained from a commercial wholesaler. Sound fruit resembling spherical geometry was selected and classified according to size.

The selected fruits were washed in a rotary washer (Dayton 2Z153A), provided with water sprays. After washing the fruit was drained and allowed to dry in 83 ambient air.

## 2.2. Laboratory tests

## 2.2.1. Apparent peel density

Peel density was determined in quintuplicate. The fruit 89 peel was carefully removed using a fruit knife and weighed in an electronic balance (Mettler PM  $16-N\pm0.1$  g). The 91 peel was immersed in vegetable oil (25 °C) placed in a graduate cylinder  $(100 \pm 1 \text{ ml})$ . The displaced volume was 93 determined and the apparent density calculated dividing the mass of the peel by the volume displaced. 95

## 2.2.2. Texture

Pulp texture before and after peeling was determined 99 using a bench cone penetrometer (Arthur Thomas Junior Precission,  $\pm 0.1$  mm). The cone and shaft had a total 101 weight of 150 g and an angle of  $15^{\circ}$  with the vertical. To convert penetration measurements in tenth of milimeters to 103 pressure unit (kPa), the equation presented by Vasic and DeMan (1976) can be used after unit conversion. Texture 105 measurements in peaches were carried out in four equidistant points in the periphery of the cheek zone and 107 the results averaged for each fruit.

## 2.2.3. Characteristic dimension

The fruit diameter before and after peeling was measured 111 using a vernier calliper (Tesa $\pm 0.2$  mm) in the midplane perpendicular to the fruit axis. Measurements were carried 113 out in triplicate.

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#### 1 2.2.4. Weight

The fruit lots were weighed before and after peeling, 3 using an electronic balance (Mettler PM 16-N+0.1 g).

#### 5 2.2.5. Peeling solutions

The solutions used for peeling were prepared the same 7 day of the experiment. They were prepared by diluting technical grade caustic soda in tap water (701 for each lye 9 concentration) in the required amount, to obtain solutions of 1.6, 3.2, 5.6 and 7.3 (g/100 ml). The final concentration 11 was standardized by titration with solution of HCl (0.098 Eq/l) using phenolftalein (1 g/100 ml in ethanol) as 13 indicator. The HCl solution was previously standardized with sodium carbonate  $(Na_2CO_3)$  as primary standard 15 using bromocresol green (1g/100 ml in ethanol) as indicator. 17

#### 2.2.6. Neutralizing solution 19

Three g/100 ml citric acid solution was prepared by weighing and diluting technical grade citric acid in tap 21 water.

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## 2.3. Chemical peeling experiments

Eight lots of peaches, with three units each, were used for 27 the chemical peeling experiments. Each lot was packed in a plastic net bag, provided with a string in order to remove it 29 manually after the elapsed peeling time. Each experiment was done by simultaneously immersing the eight lots in hot 31 caustic soda.

A chemical peeler (Dixie Canner Equipment Company) 33 was used. The peeler had two compartments, one for the peeling solution  $(0.60 \times 0.45 \times 0.33 \text{ m}^3)$  and the other for 35 the neutralizing citric acid solution  $(0.45 \times 0.45 \times 0.33 \text{ m}^3)$ . The caustic soda solution tank was provided with a heating

37 coil heated by saturated steam. The steam pressure was regulated with a pressure-controlling valve that could be 39 set at the required pressure. The peeling solution tempera-

ture was measured with a copper-constantan thermocouple 41 connected to a temperature recorder (Leeds & Northrup, Speedomax W).

43 Concentrations of 1.6, 3.2, 5.6 and 7.3 (g/100 ml) of caustic soda were experimented at temperatures of 70, 80,

45 90 and 97 °C, for peeling times from 0 to 8 min at 1-min intervals for each of the temperature-concentration combination used. 47

A total of 16 experiments (4 for each concentration at 49 four different temperatures) were carried out. After the established peeling time was elapsed the corresponding lot was removed and immersed in the citric acid solution at 51 ambient temperature in order to neutralize the residues of 53 caustic soda in the fruit surface. After neutralization, each lot was immersed in tap water at ambient temperature to

55 cool down the fruit. The converted ash residues in the surface of the fruit were removed in a rotary washer fitted

57 with water spray (Dayton 2Z153A). Afterwards, the fruit was allowed to dry in air at ambient temperature for 4h before the laboratory tests were done.

#### 61 2.4. Statistical analysis

63 The statistical analysis of the experimental data was done using computer software (Statgraphics, version 6.0). 65

### 3. Results and discussion

The theoretical mathematical model developed by 69 Barreiro et al. (1995) for the chemical peeling of spherical foods was applied to peaches (P. persica L.) variety 71 Amarillo Jarillo. Relevant physical properties assessed for this fruit were (95% confidence interval indicated): 73 apparent peel density  $(g/cm^3)$ : 1.07+0.00; initial texture by penetrometer (mm of penetration): 1.80 + 0.09; fruit 75 radius (cm): 2.02 + 0.02; average peel thickness (cm):  $0.036 \pm 0.009$ . 77

Experimental weight loss during peeling was correlated with the weight loss calculated using Eq. (2), introducing 79 the experimental measurements of the radii of the fruit before and after peeling. For this purpose, the apparent 81 peel density ( $R_0 = 1.07 \,\mathrm{g/cm^3}$ ) was used. The regression analysis carried out for 128 determinations, including 16 83 temperature-concentration values and eight time intervals showed a correlation coefficient ( $R^2 = 0.831$ ). A highly 85 significant linear relationship between the variables tested (P < 0.001) was determined. The results obtained are 87 presented in Fig. 1. For this reason, Eq. (3) was used to



Fig. 1. Linear regression relating the experimental weight loss during 113 peeling of peaches and that predicted by the model (Eq. (2)). Dotted lines represent the 95% confidence and prediction bands.

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(8)

- 1 predict the peel radius as a function of the experimental weight loss in this work. As indicated previously, weight
- 3 loss during peeling is subjected to less variability and it is easier to determine than measurements of the fruit radius5 after peeling.

The evaluation of the constants involved in the linearized 7 form of Eq. (1), (b'') and  $(E_a/R)$ , shown in Eq. (7):

$$\int_{Q} \ln(t/((R_{\rm e} - r)/{\rm Ca})) = \ln b'' + E_{\rm a}/RT$$
(7)

was carried out by considering that the right-hand side of
Eq. (7) depends only on the peeling temperature and therefore, the left-hand side of the equation must be
constant for any given temperature, in such a way that

- variables Ca, t and r in the left-hand side of the equation 15 must change accordingly to make this term constant. For
- each temperature tested, the left-hand side of Eq. (7) was 17 calculated for different values of Ca, t and r, determined
- according to the experimental design presented before. A 19 total of 32 values (four concentrations x eight peeling times) of  $\ln(t/((R_e-r)/Ca))$  were obtained for each tem-
- 21 perature tested. The values of  $\ln(t/((R_e-r)/Ca))$  obtained were plotted as a function of 1/T (Fig. 2). A linear
- <sup>23</sup> correlation coefficient of  $R^2 = 0.981$  was determined. The regression analysis showed a significant linear regression
- 25 between those variables (P < 0.05). Values of  $E_a/R$  of 2.84 × 10<sup>3</sup> K and b" of 0.0345 min g/cm<sup>4</sup> were obtained
- <sup>27</sup> from the slope and intercept of the regression line. By substituting these values in Eq. (1) the mathematical model
- <sup>29</sup> to predict peeling times during chemical peeling of peaches
   was obtained, as follows:

$$t = (0.0345) \exp(2.84 \times 10^3/T)((R_e - r)/Ca)$$

This equation represents the mathematical model for the caustic peeling of peaches adjusted to the physical parameters obtained for this fruit, being  $(R_e-r)$  the thickness of the peel to be removed.



Fig. 2. Linear regression of experimental data to determine constants b'', from the intercept, and  $E_a/R$  from the slope of Eq. (7) for the chemical peeling of peaches.

## 3.1. Changes in texture occurring during the peeling process

It was shown that the change in texture due to the cooking effect during peeling with hot caustic soda was independent of alkali concentration and dependent on temperature and time (Barreiro et al., 1995). Elevation in fruit temperature during peeling had a cooking effect affecting texture. Change in texture was studied by measuring penetration values using a cone penetrometer.

In order to study the effect of time and peeling 67 temperature on texture, the linearized first-order kinetic model was used (Eq. (6)). For this purpose, 32 values of ln 69  $(T_{\rm ex})$  for each temperature were obtained by averaging ln  $(T_{\rm ex})$  for different Ca values (which did not affect texture) 71 at each peeling time. The averaged values for each temperature were represented as a function of peeling time 73 so as to obtain the slope  $(K_i)$  and the intercept  $(\ln T_{exo})$ (values not shown here). Subsequently, the effect of 75 temperature was studied adjusting the  $K_i$  values obtained to the Arrhenius model, representing values of  $\ln K_i$  against 77 1/T (Eq (5)), in order to obtain values of  $K'_{0} = 8.76 \times 10^{-4}$ and  $-E'_{a}/R = 1.72 \times 10^{3}$  K. 79

A linear relationship between the intercept values obtained  $(\ln T_{exo})$ , representing a pseudo initial texture at zero time (not possible to be measured experimentally), and the absolute temperature was determined as suggested by Barreiro et al. (1995). Both relationships were used to obtain the general model describing the effect of peeling time and temperature on texture, as pointed out by the same authors: 87

$$\ln(T_{\rm ex}) = -3.64 + 0.020T$$
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## 3.2. Peeling maps describing chemical peeling of peaches

Peeling maps for peaches Variety Amarillo Jarillo 99 showing the interaction among alkali temperature and concentration, peeling time and peel thickness to be 101 removed during chemical peeling were obtained as described by Barreiro et al. (1995), using Eq. (8) for 103 peaches. The values presented were obtained for values comprised in the experimental ranges of temperature 105  $(70-97 \,^{\circ}\text{C})$  and alkali concentration  $(1.6-7.3 \,\text{g}/100 \,\text{ml})$  used in this work. Peeling maps for four theoretical peel 107 thickness (0.02, 0.03, 0.04 and 0.05 cm) are shown in Figs. 3A-D.

The associated values of texture (measured in mm of penetration) for any time-temperature combination applied during chemical peeling can be estimated using Eq. (9).

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Fig. 3. (A) Chemical peeling maps of peach for peel thickness of 0.02 cm relating the variables involved in the process. The parameters of the line come in g/100 ml of caustic soda. (B) Chemical peeling maps of peach for peel thickness of 0.03 cm relating the variables involved in the process. The parameters of the line come in g/100 ml of caustic soda. (C) Chemical peeling maps of peach for peel thickness of 0.04 cm relating the variables involved in the process. The parameters of the line come in g/100 ml of caustic soda. (D) Chemical peeling maps of peach for peel thickness of 0.05 cm relating the variables
 37 involved in the process. The parameters of the line come in g/100 ml of caustic soda.

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### 4. Conclusions

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In this work, the model presented by Barreiro et al. (1995) for chemical peeling of spherical fruits was applied to peaches. Equations for the prediction of chemical peeling times and texture changes due to the cooking effects during peeling were obtained and peeling maps to estimate peeling times for practical peeling conditions including alkali temperature and concentration and peel

49 thickness were developed.

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