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# **A Thermomechanical Preprocessing For Pectin Extraction From Orange Peel. Optimisation by Response Surface Methodology.**

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## **ABSTRACT**

The instantaneous controlled pressure drop process (or D.I.C process: “Détente Instantanée Contrôlée”) was used as pre-treatment prior to pectin acid extraction from orange peel. This process involves subjecting the orange peel for a short time to steam pressure varying from 100 to 700 kPa, followed by an instantaneous decompression to vacuum at 5 kPa. Effects of processing pressure, moisture content of peels before the thermomechanical treatment and processing time were examined with response surface methodology. The optimal conditions were determined and the responses surfaces were plotted from the mathematical models. The Fisher test and p-value indicated that both processing pressure and the moisture content of peels before the pre-treatment had highly significant effect on the pectin yield. The quadratic effect of processing pressure as well as the interaction effects of the initial moisture content and processing time had also a significant effect on the response. Moreover, the kinetics of pectin extraction showed that after few minutes of hydrolysis, the yields of pectin were systematically higher than that of control sample and this is important from industrial point of view because the hydrolysis of pectin is generally performed in 10-15 minutes.

**Keywords:** Pectin extraction, kinetics, preprocessing, instantaneous controlled pressure drop process, response surface methodology

## 1. INTRODUCTION

Citrus fruit processing produces many by-products with significant value. These wastes could be used for the production of many phytochemicals, pharmaceuticals, food products, essential oils, seed oil, pectin and dietary fibres. These by-products are considered to be rich sources of edible and health promoting agents as polymethoxylated flavonoids or hydroxycinnamates, many of which are found exclusively in citrus peels (Hatamipour et al., 2004). For Schieber et al. (2003), the production of pectin is considered the most reasonable way of utilisation of the juice industry by-product both from economical and ecological point of views. The main sources for commercial pectin production are apple pomace and citrus peels. Some authors (Kar and Arslan, 1999; Yapo et al., 2007) cited also the sugar-beet pulp as a potential high source of pectin. Pectin is used in a number of foods as gelling agent in jam and jellies, thickener, texturizer, emulsifier and stabilizer in dairy products, fruits preparations or in icings and frostings. It is also used in pharmaceutical, dental and cosmetic industries for its jellifying properties (Pagan et al., 2001). It is generally produced by acid extraction of citrus peel followed by filtration and precipitation by alcohol as 2-propanol (Kalapathy & Proctor, 2001). Conventionally, extraction of pectin is performed at about 90°C for at least 1 h (Iglesias and Lozano, 2004). Unfortunately, these conditions lead to protein degradation and are not good for either quantity or quality of pectin extracted.

The pectic polysaccharides are located primarily in the in the middle lamella between cells in higher plant tissues. They are of high molecular weight and closely connected with the other polymer components in the cell walls which inhibit their release from the cell matrix. To extract the pectic substances, preprocessing of the plant material is often applied to facilitate pectin extraction (Kratchanova et al., 2004). The processing methods most often used are enzyme (Bonin et al., 2002; Thibault et al., 1988) or physical treatments (Panchev et al., 1988; Osterveld et al., 1996). Shi et al. (1996) used hot water-washing prior to extraction of pectin from sunflower heads to improve pectin quality but unfortunately the pretreatment resulted in increased pectin loss. Fishman et al. (2000) reported that the pretreatment of fruits material by microwave heating led to a considerable increase in the yield of pectin fruits and Kratchanova et al. (1996) confirmed that the benefits were particularly marked during extraction of pectin from orange peel. The same authors (Kratchanova et al., 1994) argued that the favourable effect of microwave heating on the yield and quality of pectin is assumed to be due first to the partial disintegration of the plant tissue and hydrolysis of protopectin and second, to the rapid inactivation of pectolytic enzymes. More recently Wang et al. (2007) optimized the operating conditions of pectin extraction assisted by microwave. They concluded that the application of microwaves in the extraction of pectin from dried apple pomace dramatically reduced the extraction time. Ralet et al. (1994) used extrusion technique as preprocessing for pectin extraction from lemon. They concluded that the amount of water-soluble pectins was largely increased after extrusion-cooking. The aim of this work is to provide an efficient and economically attractive physical pre-treatment for extraction of pectin from orange peel by a process combining thermal and mechanical treatments: the Instantaneous Controlled Pressure Drop process called "D.I.C" process. It was developed and patented (Allaf et al., 2000) in our laboratory, initially in the field of the drying-texturization of various products of food industry (Rezzoug et al., 1998). It is based on the thermo-mechanical processing induced by a rapid transition of the vegetable product from high steam pressure to a vacuum. This processing allows obtaining a product with more alveolated texture than a dried product with classic methods as hot air; therefore the rehydration is far more rapid. This finding was used to improve the functional and rheological properties of scleroglucan molecule as hydration

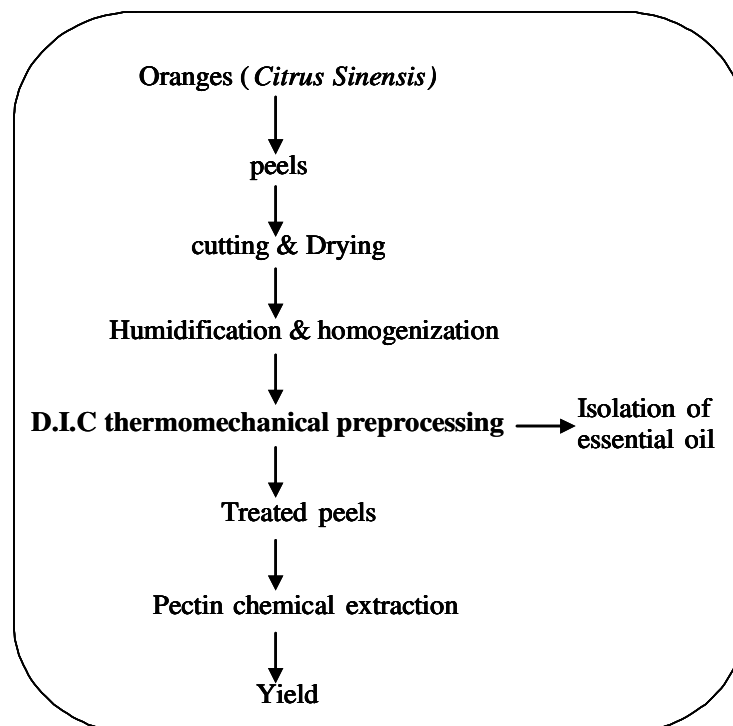
capacity or the developed torque in aqueous solution (Rezzoug et al., 2000a).

Instantaneous controlled pressure drop process was also used for the extraction of essential oils from different substrates as rosemary leaves (Rezzoug et al., 2005) or orange peels (Rezzoug et al., 2000b). In the latter case, after extraction of essential oil, the peels were recovered and pectin extracted by acid hydrolysis of protopectin. Among the processing parameters of D.I.C. process we studied the influence of three independent variables: the processing steam pressure, the moisture content of orange peels before preprocessing and the processing time at fixed saturated steam pressure on the yield of pectin after its conventional extraction. The study was conducted through response surface methodology (RSM) which have as main advantage the reduced number of experimental trials needed to evaluate multiple parameters and their interactions (Giovanni, 1983). A statistical model seems particularly appropriated in the case of a complex and multi-components as natural food products. A kinetic model is nevertheless proposed for pectin acid extraction, after preprocessing.

## 2. EXPERIMENTAL PROCEDURES

In a previous study (Rezzoug et al., 2000b), the D.I.C. thermomechanical treatment was used for the extraction of essential oil from orange peels. After extraction of essential oil, the peels were recovered, dried and the quantity of the residual pectin was determined after acid extraction (fig.1).

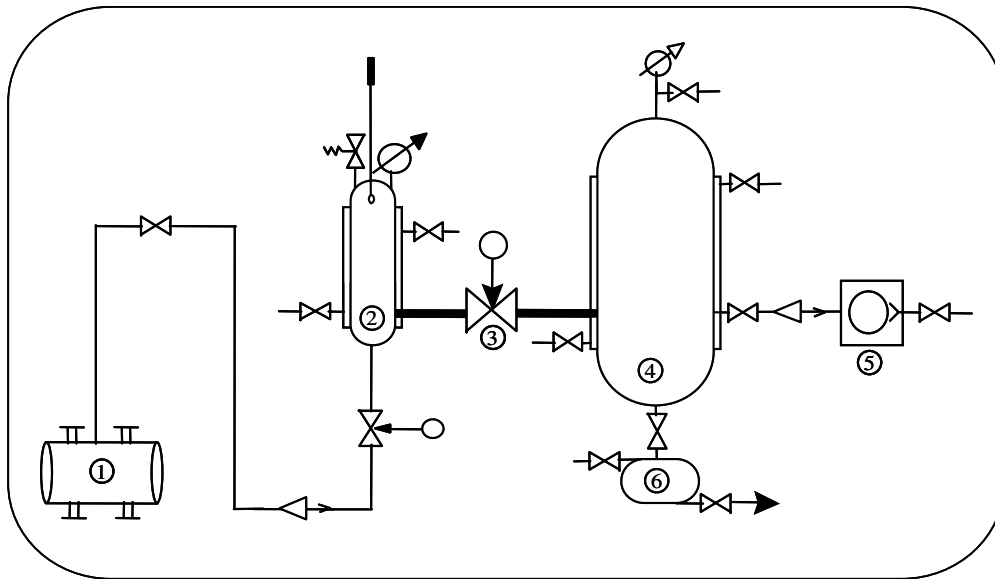
**2.1- Plant material:** The oranges used in this study were *Citrus sinensis* L., grown in Valencia (Spain). The peel was separated from the endocarp by cutting with a hand knife and cut into 6-8 pieces giving yield of 17 % (w/w) of orange peel with respect to the whole fruit. The peels were firstly dried at 50 °C in a pilot through flow air dried. After drying, the orange peel was placed in hermetically sealed bags and stored in a cold chamber until the thermomechanical preprocessing. The moisture content of dehydrated orange peel, measured by using a Mettler LP16 Infrared balance, was 6.8 % (or g/100 g dm).



**Figure 1. Diagram of the different steps of the present work, from the fresh oranges to the calculation of the yield of extracted pectin.**

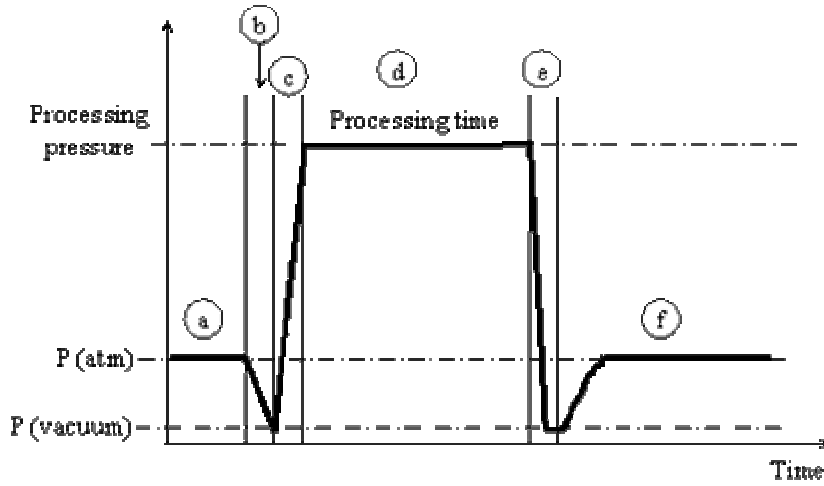
**2.2- Experimental set-up for D.I.C. processing:** The experimental set-up (fig. 1) was largely described in a previous study (Rezzoug et al., 1998) it is composed of three main elements:

- The processing vessel (2) where the samples were placed and treated.
- The vacuum system which consists mainly from a vacuum tank (4) with a volume (360 l) 130 fold greater than the processing vessel (12 l), and a vacuum pump (5). The initial vacuum pressure of the vacuum container was maintained at 5 kPa in all experiments.
- A pneumatic valve (3) that separate the processing vessel from the vacuum tank. It can be opened in less than 0.2 seconds; this ensures a rapid decompression within the reactor.



**Figure 2. Schematic of apparatus (stainless steel made) for the proposed thermomechanical preprocessing of orange peel. 1. Boiler, 2. D.I.C. reactor, 3. Valve communication, 4. Vacuum container, 5. Vacuum pump, 6. Extract container.**

**2.3- Protocol of orange peel pre-treatment by instantaneous controlled pressure drop process :** Orange peels are firstly placed in the D.I.C. vessel (I) which is maintained under a vacuum ( $\sim 50$  mbar) through its connection to a vacuum container (fig. 3a). The vacuum allows a better diffusion of the heating fluid through the plant and consequently heat transfer between the steam and peels is improved and the time to reach the desired processing pressure (or processing temperature) is shortened. After closing the electropneumatic valve (3) which connects the reactor (2) to the vacuum tank (4), an atmosphere of saturated steam pressure (between 100 and 700 kPa in this study) is created within the D.I.C. reactor (fig. 3c). After a processing time at fixed processing pressure (fig. 3d), the thermal treatment is followed by a rapid decompression resulting in a rapid drop in pressure (fig. 3e). The equilibrium pressure after decompression depends on the operating pressure: the higher the processing pressure, the higher the equilibrium pressure. The created steam in orange peel by autovaporization induces mechanical strength capable of causing deformations and micro cavities whose amplitude depends on rheological properties of the vegetable product at initial moisture content and temperature. The evaporation, which is effected in adiabatic conditions, induces a rapid cooling of the residual product. The final temperature must be commensurate with the final pressure.



**Figure 3.** Typical pressure-time profile for D.I.C. processing cycle. (a) sample at atmospheric pressure; (b) vacuum; (c) steam injection to reach selected pressure; (d) treatment time at selected processing pressure; (e) pressure drop; (f) atmospheric pressure for the sample recovery.

**2.4- Pectin extraction:** Pectin is extracted from orange peel in hot acid solution. The dried orange peels were milled during 20 seconds in a Waring blender mixer. Then the milled product (10 g) was added to 0.1 N HCL solution (200 ml) and boiled in a reflux system at 90 °C for 45 min. 10 ml of the obtained slurry were collected after 1, 3, 6, 9, 15, 20, 30, 45, and 60 minutes and plunged in ice to stop the hydrolysis process. The supernatants were recovered after being filtered on a grid and then frozen. The pectin was precipitated with two volumes of alcohol (ethanol) for one volume of supernatant. The obtained precipitate was washed with 6.6 % alcohol and centrifuged (10000 rpm during 20 min). A portion of the resulted solution undergoes a Mettler LP16 Infrared balance for the pectin assessment. The yields of pectin were expressed in dry extracted material/100 g dry peel.

**2.5- Electron Scanning Microscopy:** Scanning electron micrographs of the control sample and treated orange peel were taken with a Jeol 5410 LV SEM. The samples were first splutter-coated with a thin gold film using a Cressington metallizer.

**2.6- Experimental design:** A response surface methodology was employed for optimizing the operating conditions of the D.I.C. process to give high yield of pectin extracted. This quantity is assumed to be affected by three independent variables,  $\xi_i$  (processing pressure  $\xi_1$ , moisture content of orange peel  $\xi_2$  before D.I.C. preprocessing and processing time  $\xi_3$ ). It is also assumed that one dependent variable (referred to as a response),  $\eta$  (yield of pectin), which was experimentally measured, defined the system.

$$\eta = f(\xi_1, \xi_2, \xi_3) \quad [1]$$

Second degree polynomial equation was assumed to approximate the true function:

$$\eta = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_j \quad [2]$$

where  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are regression coefficients and  $x_i$  are the coded variables linearly related to  $\xi_i$ . The coding of  $\xi_i$  into  $x_i$  is expressed by the following equation:

$$x_i = \frac{2(\xi_i - \xi_i^*)}{d_i} \quad [3]$$

where  $\xi_i$  = actual value in original units;  $\xi_i^*$  = mean of high and low levels of  $\xi_i$ ; and  $d_i$  = difference between the low and high levels of  $\xi_i$ .

A central composite rotatable design (Benoist et al., 1994) with three variables was used. For the three variables, the design yielded 22 experiments with eight ( $2^3$ ) factorial points, six extra points (or star points for the determination of the quadratic effects) to form a central composite design and eight centre points for replications. The range and the centre point were chosen after preliminary trials (Table 1). The model coefficients reflected the linear, quadratic and interactive effects. Response surface were obtained by using the *analysis design* procedure of *Statgraphics Plus for Windows* (5.1 version) software. Contours plot were generated by assigning constant values to one variable and then fitted the solving equations by means of the same procedure of *Statgraphics Plus for Windows*.

Table 1: Coded levels for independent variables used in developing experimental data.

		Coded level				
		$-\alpha$	-1	0	1	$+\alpha$
Processing pressure (kPa)	$x_1$	97	220	400	580	702
Moisture content (%)	$x_2$	9.8	20	35	50	60.2
Processing time (min)	$x_3$	0.32	1	2	3	3.7

$\alpha$ (axial distance) =  $\sqrt[4]{N}$ , N is the number of experiments of orthogonal design, i.e of the factorial design. In this case  $\alpha = 1.6818$ . The moisture content of peels is expressed in % or g of water/100 g dm.

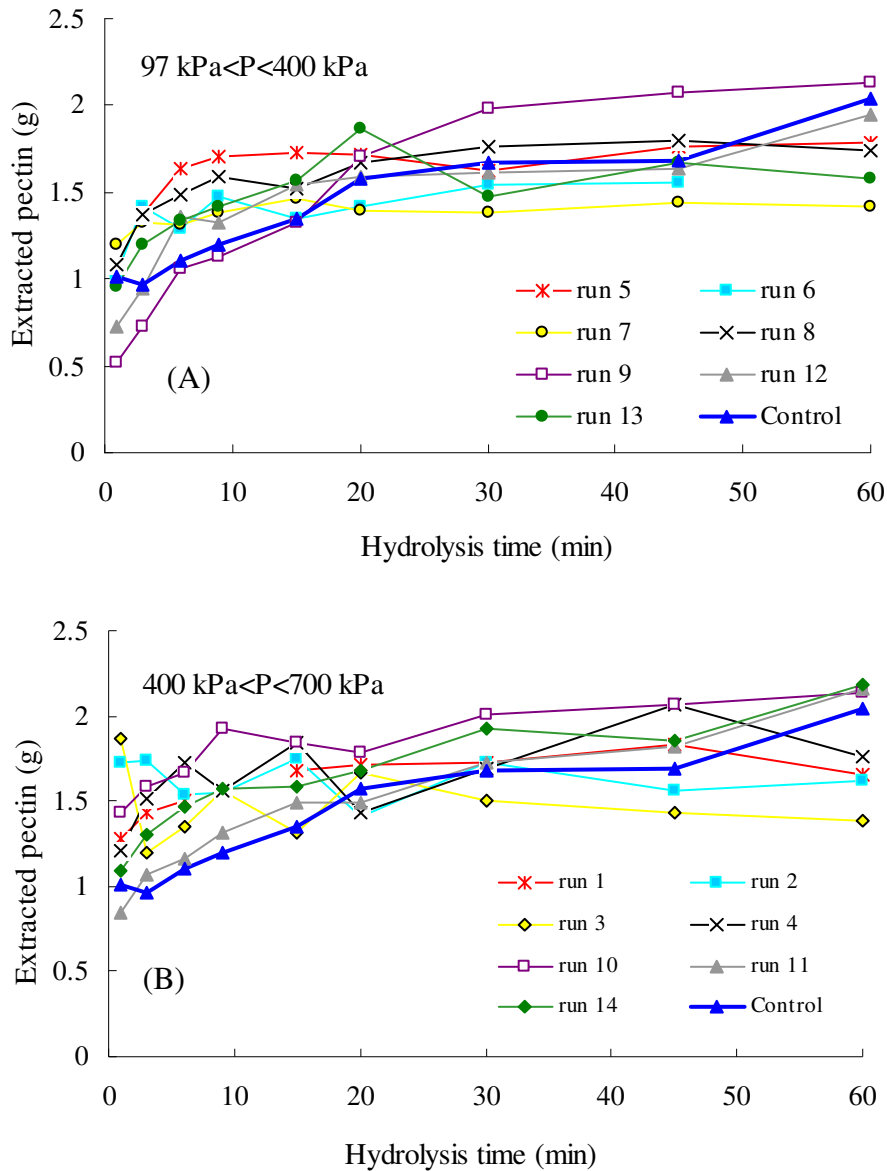
**Table 2.** Observed and predicted values of pectin extraction with different combinations of processing pressure ( $x_1$ ), moisture content of peels before D.I.C.pretreatment ( $x_2$ ) and processing time ( $x_3$ ) used in the randomized central composite rotatable second order design for the response surface methodology.

Run	Variable coded level			Observed	Predicted
	$x_1$	$x_2$	$x_3$		
1	1	1	1	16.7	16.4
2	1	-1	1	17.5	17.8
3	1	1	-1	13.1	13.8
4	1	-1	-1	18.4	18.7
5	-1	1	1	17.3	17.2
6	-1	-1	1	12.1	11.5
7	-1	1	-1	14.6	14.5
8	-1	-1	-1	12.0	12.5
9	$-\alpha$	0	0	13.2	13.4
10	$+\alpha$	0	0	18.4	17.9
11	0	$-\alpha$	0	14.8	14.6
12	0	$+\alpha$	0	15.5	15.3
13	0	0	$-\alpha$	15.6	14.8
14	0	0	$+\alpha$	15.7	16.2
15	0	0	0	16.8	16.3
16	0	0	0	15.9	16.3
17	0	0	0	16.6	16.3
18	0	0	0	14.9	16.3
19	0	0	0	15.7	16.3
20	0	0	0	16.9	16.3
21	0	0	0	16.4	16.3
22	0	0	0	17.0	16.3

### 3. RESULTS AND DISCUSSION

**3.1- Kinetics of pectin extraction after thermomechanical D.I.C. preprocessing:** The first part of this work consisted in determining the kinetics of extraction for all the samples resulting from the experimental design

In figure 4, we gathered the various kinetics of pectin acid hydrolysis according to the processing pressures applied during the D.I.C. pre-treatment. Fig. 4A displays the kinetics of the experiments for which the processing pressure varied between 100 kPa and 400 kPa while fig. 4B shows the kinetics of pectin extraction for the samples preprocessed at steam pressures between 400 and 700 kPa. It is clear that the quantity of pectin extracted from the preprocessed samples was always higher than that obtained for the control sample in the first fifty minutes of acid hydrolysis extraction for processing pressures higher than 400 kPa



**Figure 4. Kinetics of pectin extraction after D.I.C. thermomechanical preprocessing compared to control sample, according to two processing pressure domains.**

For processing pressures lower than 400 kPa, the quantity of extracted pectin is lower than that of control sample until 5 min of acid extraction. Beyond this value, the quantity of pectin extracted is higher in the majority of the cases. Fig. 5 displays the kinetics obtained for the eight repetitions performed in the central point of the experimental design (400 kPa, W=35 % and 2 min). It can be also seen that in the first minutes of extraction the quantity of pectin extracted was higher for the preprocessed samples. To model the quantity of pectin extraction for the mean values of the repetitions, we used a simple model of solid-liquid extraction (Mafart and Béliard, 1992) because this is of practical interest to find out at what moment of time the quantity of pectin extracted reaches its maximum value. The variation of pectin concentration versus the variation of time can be expressed by:

$$dC = - K (C - C') dt \quad [4]$$

Where:  $dC$  the gradient of concentration;  $C$  and  $C'$ : concentrations (w/w) of pectin respectively in solid and acid media phases.

and K: coefficient which take into account the global coefficient of heat transfer and the surface exchange.

The integration of eq. 4 allowed obtaining eq. 5.

$$C' = C'_{\infty} \left(1 - e^{-\lambda t}\right) \quad [5]$$

where :  $C'_{\infty}$  : mass concentration of pectin for a long extraction time

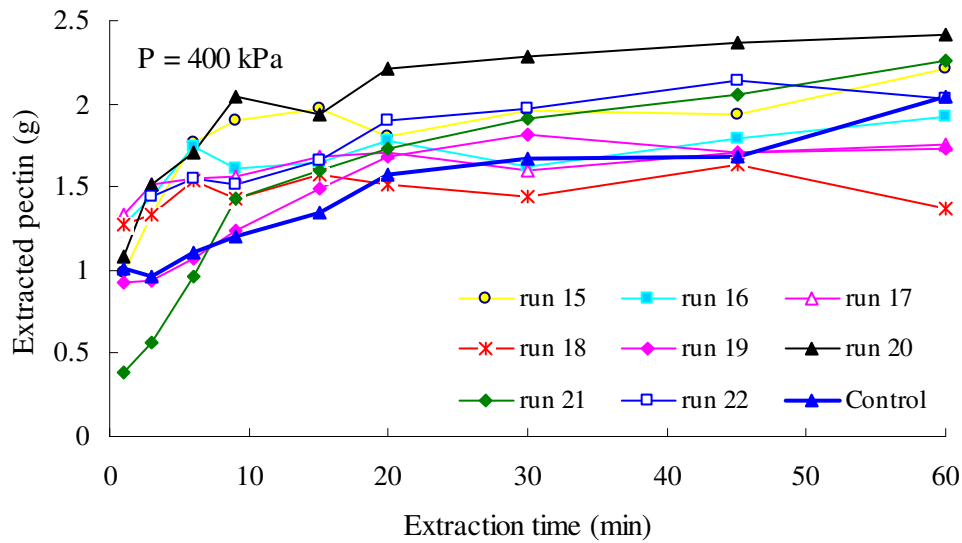
$$\text{and } \lambda = -\frac{K}{(1-S)} \quad [6]$$

S : mass of solid phase on the total mass of the suspension.

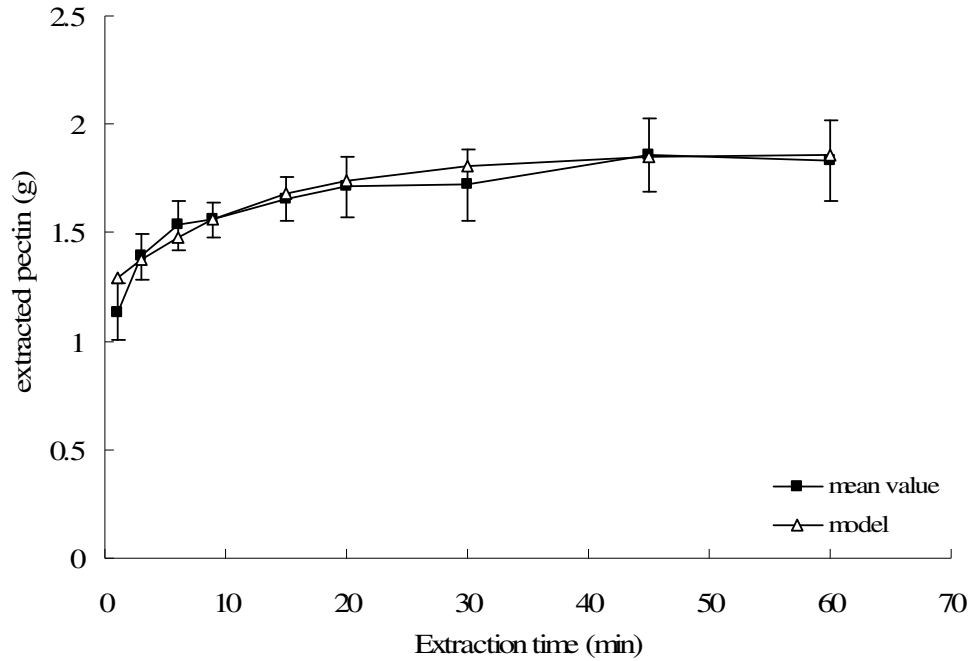
The obtained equation is as follows:

$$\text{extracted pectin(g)} = 0.620 \times (1 - \exp(-0.081 \times t)) + 1.242 \quad [7]$$

The constant 1.242 was added because pectin is considered to be dissolved as soon as the hydrochloric acid was added in the solution.



**Figure 5. Kinetics of pectin extraction after D.I.C.thermomechanical preprocessing for the replications points of the experimental design (P=400 kPa, W=35% and t = 2 min), compared to control sample.**



**Figure 6.** Comparison between the kinetics of the mean values of extracted pectin for the replications in the experimental design with the results of the theoretical model.

**3.2- Fitting the model:** A regression analysis (table 3) was carried out to fit mathematical models to the experimental data aiming at an optimal region for the studied response. The predicted model can be described by the following equation in terms of coded values.

$$\eta = 16.31 + 2.72x_1 + 0.41x_2 + 0.83x_3 - 0.46x_1^2 - 3.51x_1x_2 - 0.02x_1x_3 - 0.94x_2^2 + 1.83x_2x_3 - 0.53x_3^2 \quad [8]$$

Where  $x_1$ ,  $x_2$  and  $x_3$  are the coded values for processing pressure, moisture content of peels before D.I.C. preprocessing and processing time respectively.

**Table 3.** Estimated regression model of relationship between response variable (pectin yield) and independent variables ( $x_1, x_2, x_3$ )

Variables	DF	SS	MS	F-value	p-value
$x_1$	1	25.402	25.402	51.90	0.0002
$x_2$	1	0.580	0.580	1.19	0.3123
$x_3$	1	2.392	2.392	4.89	0.0451
$x_1^2$	1	0.820	0.820	1.68	0.2366
$x_2^2$	1	3.426	3.426	7.00	0.0331
$x_3^2$	1	1.099	1.099	2.25	0.1775
$x_1 x_2$	1	24.655	24.655	50.37	0.0002
$x_2 x_3$	1	6.704	6.704	13.70	0.0076
$x_1 x_3$	1	0.001	0.001	0.00	0.9653

The significance of each coefficient was determined using Fisher-test (F-value) and the probability p (p-value). The corresponding variables would be more significant if the F-value becomes greater and p-value becomes smaller (Lorezen and Anderson, 1993). It can be seen that the variables with the largest effect were the linear terms of the processing pressure and processing time and the quadratic term of the moisture content of orange peels before the thermomechanical preprocessing, followed by two interaction effects; that of processing pressure and moisture content and that of processing time and moisture content.

The results suggested that the change of pressure level during the D.I.C. thermomechanical preprocessing had highly significant effect on pectin yield after its chemical extraction ( $p=0.0002$ ), and the processing time of the D.I.C. preprocessing for pectin extraction had also a considerable effect on pectin yield ( $p= 0.0451$ ). Analysis of variance (ANOVA) for the model was given in table 4. The coefficient of determination ( $R^2$ ) of the predicted model was 0.92, suggesting a good fit; the predicted model seemed to reasonably represent the observed values. Thus, the pectin yield was sufficiently explained by the model.

**Table 4:** Analysis of variance showing the effect of independent variables ( $x_1, x_2, x_3$ ) as a linear term, quadratic term and interactions (cross product) on the response (pectin yield).

Source	Degrees of freedom	Sum of square	Mean square	F-ratio
Model	9	65.082	7.231	15.127 <sup>a</sup>
Linear	3	28.374	9.458	19.787 <sup>a</sup>
Quadratic	3	5.346	1.782	3.728 <sup>a</sup>
Interactions	3	31.362	10.454	21.870 <sup>a</sup>
Residual	12	5.738	0.478	-
Lack of fit	5	2.312	0.462	0.966
Pure error	7	3.426	0.489	-
$R^2$				0.92

a : p-value<0.05

In order to make it more directly express the effects of the processing parameters, we took the three expressions of eq.3 i.e. eqs (9-11):

$$x_1 = \frac{2(X_1 - 400)}{360} \quad [9]$$

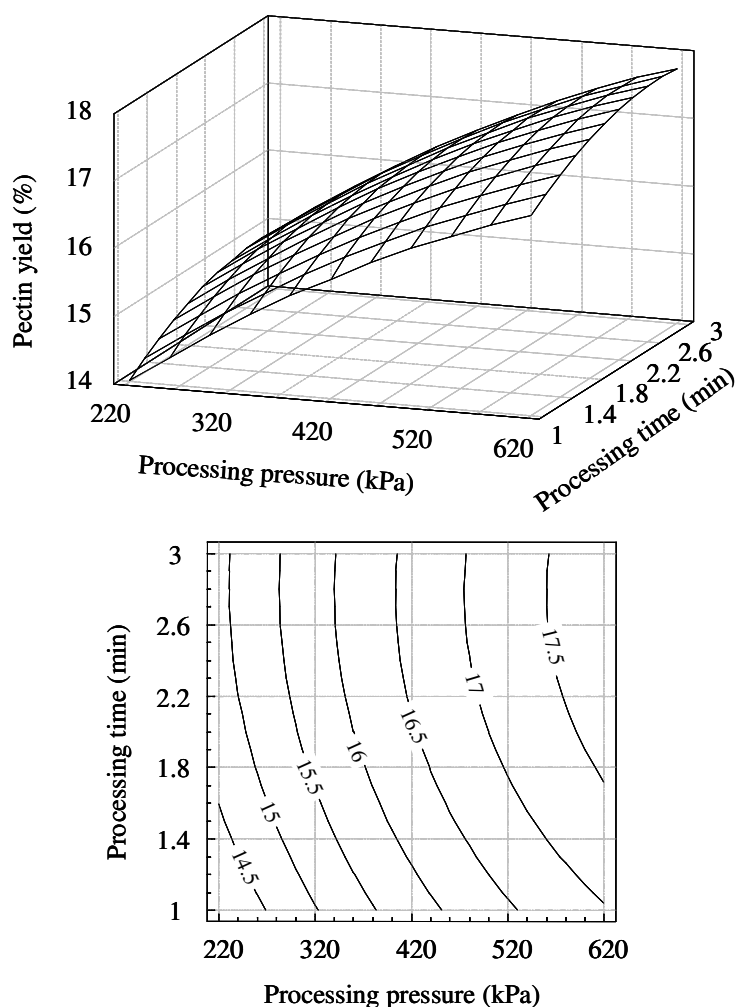
$$x_2 = \frac{2(X_2 - 35)}{30} \quad [10]$$

$$x_3 = (X_3 - 2) \quad [11]$$

into eq. (8) to obtain eq. (12)

$$\begin{aligned} \eta = & 2.3206 + 0.0361X_1 + 0.2980X_2 + 0.6269X_3 \\ & - 0.7101 \cdot 10^{-4} X_1^2 - 0.0007X_1X_2 - 0.6223 \times 10^{-3} X_1X_3 \\ & - 0.0210X_2^2 + 0.0610X_2X_3 - 0.2664X_3^2 \end{aligned} \quad [12]$$

**3.3- Analysis of response surfaces:** The regression model issued from eq.12 allowed the prediction effect of the three parameters of D.I.C. preprocessing on pectin extraction. The relationship between independent and dependant variables is illustrated in three dimensional representations of the response surfaces and two dimensional contours plots generated by the model (fig 7-9). In each figure, the third variable was kept constant at its “0” level.



**Figure 7. Response surface and contour plots for the effect of processing pressure and processing time at constant initial moisture content of peels on pectin yield in % (g of pectin/100 g dried peels after preprocessing).**

Fig. 7 depicts response surface and contour plots of the effect of two variables, namely processing pressure and processing time during the preprocessing of orange peels before pectin extraction. Both processing pressure and processing time demonstrated a linear increase on pectin extraction with the strongest effect for the processing pressure. This indicate that the severity of the D.I.C preprocessing expressed by the severity of the steam pressure drop have a great influence on further pectin extractibility. At the same conditions of processing time and initial moisture content, the higher the processing pressure the higher the evaporation which leads to a better acid accessibility during the pectin extraction.

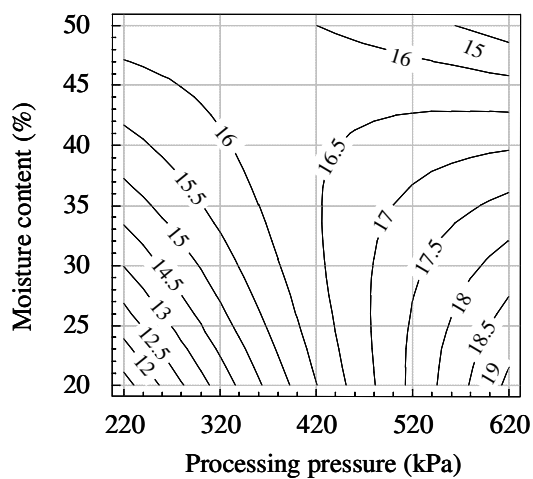
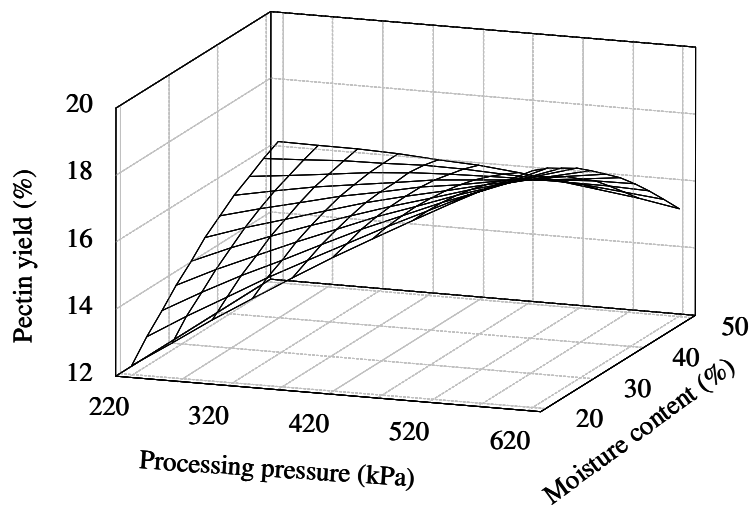
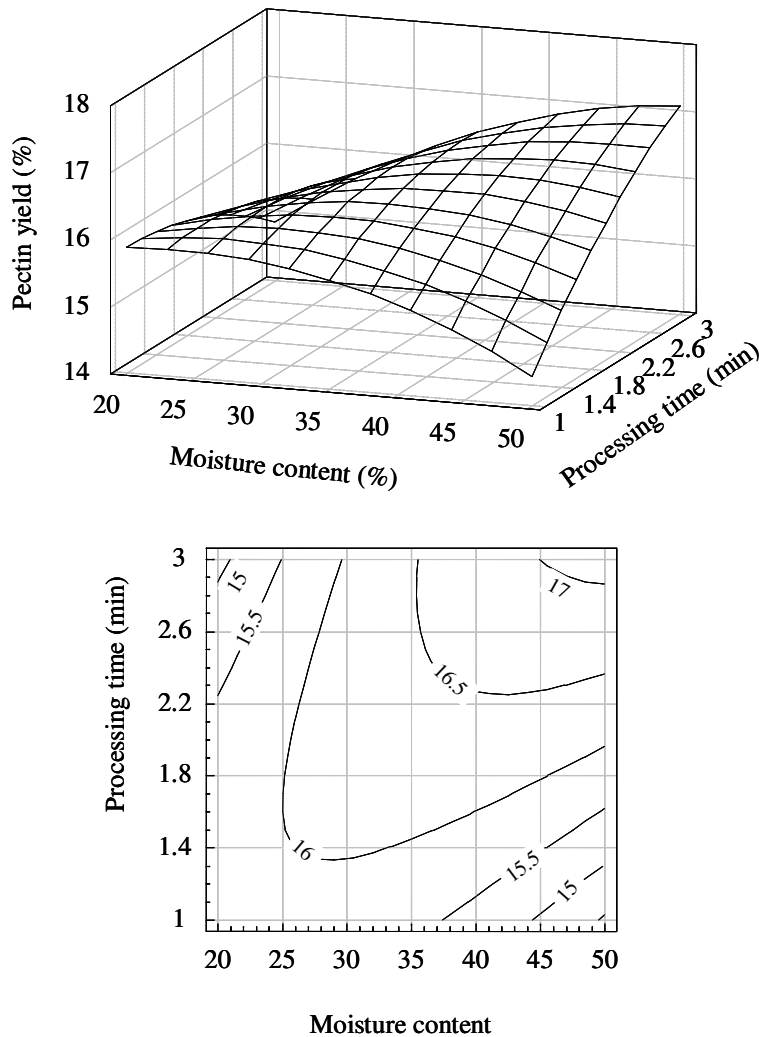


Figure 8. Response surface and contour plots for the effect of processing pressure and initial moisture content of peels at constant processing time on pectin yield in % (g of pectin/100 g dried peels after preprocessing).

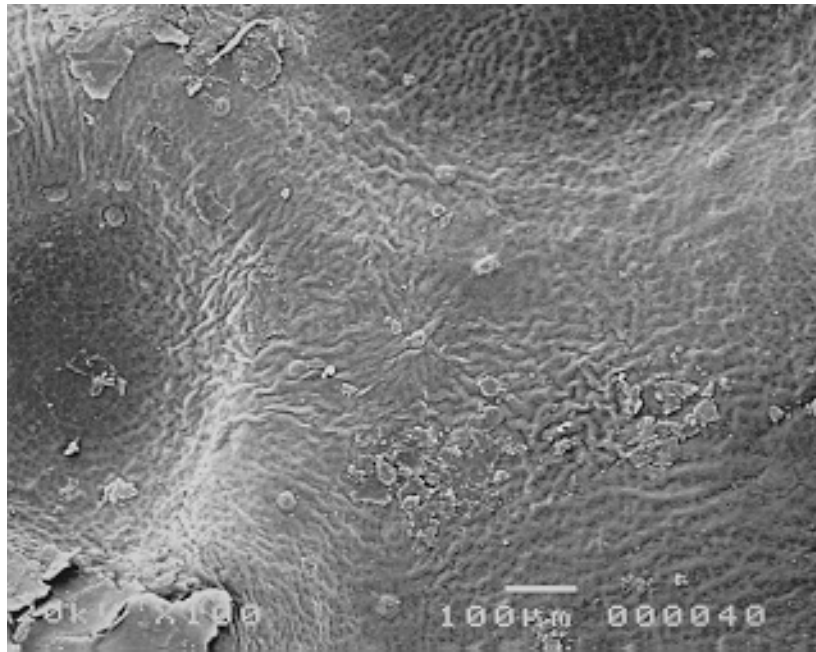


**Figure 9. Response surface and contour plots for the effect of initial moisture content of peels and processing time at constant processing pressure on pectin yield in % (g of pectin/100 g dried peels after preprocessing).**

These observations are close to that of Zhondong et al. (2006) who confirmed that the pectin release from orange peel using microwave pre-treatment is a rapid disintegration process and that there is a swelling effect on the cells of orange peels under microwave radiations. Kratchanova et al. (2004) established that the pre-treatment of the orange peels by microwave heating led to a considerable increase in the yield and quality of pectin. They argued that the damage to the orange peel tissue increased with the rise in the intensity of the microwave field, which was expressed in increase of the intercellular spaces. In the proposed pretreatment, increasing of the heat induced by the saturated steam probably results in intensive vapour formation in the capillary porous structure of the plant material and the subsequent release of the pressure to vacuum allows fixing the structure.

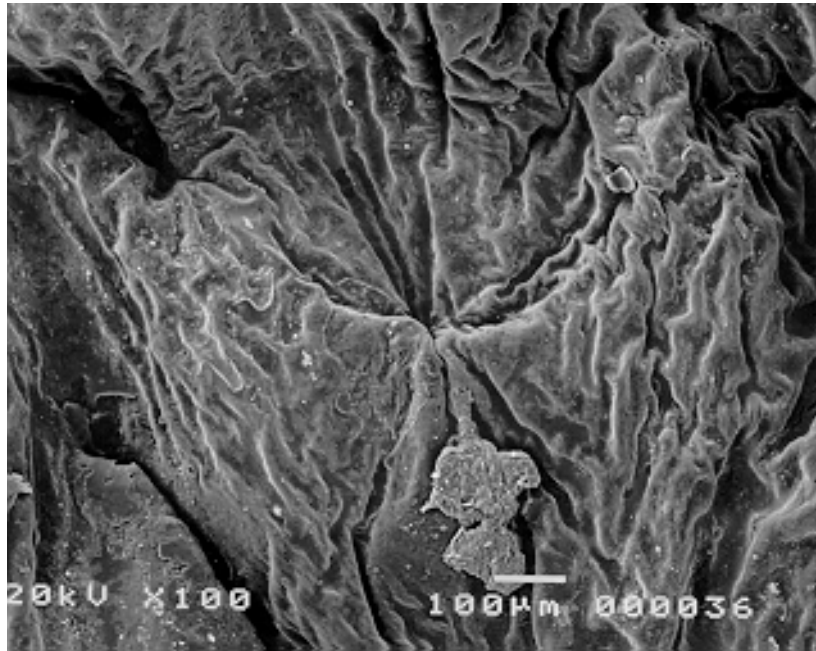
From fig.7 it can be seen a linear effect of the preprocessing time which might due to the short time-contact (3 min. max) of the plant with heat thus avoiding any degradation of pectin molecule. Fishman et al. (2006) stated that molecules of pectin became less compact with increasing of microwave heating time and this leads to an undesirable loss of viscosity of pectin solutions. The distortion of the surface in fig. 8 showed the interaction effects of processing pressure during the D.I.C. thermomechanical pretreatment and the initial moisture content of peels, indicating that greater processing pressure led to higher yield of pectin when initial moisture content of peels was about 20 %. For a central value of processing time (2

min.), the yield of extracted pectin varied from 12.2 to 18.5 % for lower initial moisture content, while for the higher one we observed a decreasing of pectin yield from 16.2 to 15.3 % which makes this interaction very significant.



**Figure 10. Electron micrograph of an untreated orange peel (flavedo side)**

It can be also seen from fig.8 that the initial moisture content displayed a positive linear effect for the low processing pressures (between 220 and 420 kPa) indicating that the flash evaporation of the moisture induced by the pressure drop allowed to create an important microporosity. The higher this microporosity the higher the “wetting” of the microstructure by the reagents during extraction of pectin. The presence of microporosity is clear in fig.11 compared to fig. 10 on which one can see a smooth structure. These results are in accordance with those of Fan et al. (1994) who proposed a model describing dynamics of bubble growth in starchy extrudates. The authors reported that there is no bubble collapse when the moisture content is lower than 30 %, improving the capillary water diffusion.



**Figure 11. Electron micrograph of flavedo side after D.I.C preprocessing at 5.8 bar, 50 % initial moisture content and a processing time of 3 minutes.**

In our study, a quadratic effect of initial moisture content is observed for processing pressure higher than 420 kPa and the decreasing of the pectin yield was generally observed beyond 35 % of initial moisture content. The cooling induced by the rapid decompression, varying between 97 and 580 kPa and 5 kPa, implies that the orange peels is in a region near to the glass transition temperature ( $T_g$ ). Moreover, it is well known (Mitchell and Hartey, 1996) that the addition of water plasticizes the biopolymers, reducing  $T_g$ . At low values of initial moisture content ( $< 35\%$ ), the product is in a zone close to  $T_g$  but does not reach it, generating more amorphous zones and then better wetting of acid during the pectin extraction. In contrast, at higher initial moisture content, the  $T_g$  is crossed and the product is probably in glassy state with reduced molecular mobility and diffusion. The distortion of the surface in fig.9 shows the interaction between the processing time and initial moisture content of peels before the thermomechanical preprocessing. For low moisture contents, the yield of pectin is stable between 1 and 1.8 min and diminishes beyond this value. This is probably due to the insufficiency of water to create microporosity during the flash evaporation. Moreover, one can observe that a prolonged staying of orange peel at high temperature (the “0” level in fig.9 is of 400 kPa corresponding to 143 °C) may induce, in absence of water, to a degradation of pectin molecule. On the other hand, for the highest initial moisture content of orange peels, the decreasing of the pectin yield is not observed, the higher the processing time, the higher the pectin yield.

## CONCLUSION

The aim of this paper was to demonstrate the feasibility of the D.I.C.process as preprocessing to improve the availability of pectin during its chemical isolation and to determine the optimal experimental conditions. The predicted model for the pectin yield was found to be accurate. The optimum processing pressure was 702 kPa for processing pressure, 9.8 % (g H<sub>2</sub>O/g of dry orange peel) and a processing time of 0.9 min. Under these conditions a high yield of pectin was obtained (21.8 %) close to the predicted yield (22.2 %). These results indicate that it is possible to improve the accessibility of chemical reagents as acids to achieve a high extraction

in short time (6 min in our study). The quantity of pectin extracted was always higher for samples of orange peels preprocessed compared to the quantity extracted from control sample. Nevertheless, a more elaborate study must be performed on the quality of the pectin extracted as viscosity or dissolution rate, on the microporosity of the microstructure and on other parameters of D.I.C. preprocessing as the level of vacuum pressure.

## REFERENCES

- Allaf, K., Rezzoug, S.-A., Cioffi F. and Contento, M.-P. (2000). Thermomechanical treatment method by controlled instant expansion for fruit, juice and citrus peels. French patent n° 2782899 published as European patent under n° WO 00/13532.
- Benoist, D., Tourbier Y. and Germain-Tourbier, S. (1994). Plans d'expériences: construction et analyse. Lavoisier TEC & DOC. Chapter 5, 208-389.
- Bonin, E., Dolo, E., Le Goff, A., Thibault, J.-F. (2002). Characterisation of pectin subunits released by an optimised combinations of enzymes. *Carbohydrate Research*, 337, 1687, 1696.
- Fan, J., Mitchell, J.R. and Blanshard, J.M.V. (1994). A computer simulation of the dynamics of bubble growth and shrinkage during extrudate expansion. *Journal of Food engineering*, 23, 337-356.
- Fishman, M.L., Chau, H.K., Hoagland, P., Ayyad, K. (2000). Characterisation of pectin, flash extracted from orange albedo by microwave heating under pressure. *Carbohydrate Research*, 323, 126-138.
- Fishman, M.L., Chau, H.K., Hoagland, P., Htchkins, A.. (2006). Microwave- assisted extraction of lime pectin. *Food Hydrocolloids*, 20, 1170-1177.
- Giovanni, M. (1983). Response surface methodology and product optimization. *Food technology*, 37, 41-45.
- Hamapitour, M.S., Majidi, S.M., Abdi, M., Farbodnia. (2004) Potentials for industrial utilization of citrus byproducts. CHISA 2004 - 16<sup>th</sup> International Congress of Chemical and Process Engineering, 22-26 August, Prague, Czech Republic, pp. 9263.
- Iglesias, M.T., and Lozano J.E. (2004). Extraction and characterization of sun flower pectin. *Journal of Food Engineering*, 62, 215-223.
- Kalapathy, U. and Proctor., A. (2001). Effect of acid extraction and alcohol precipitation conditions on the yield and purity of soy hull pectin. *Food Chemistry*, 73, 393-396.
- Kar, F. and Arslan, N. (1999) Effect of temperature and concentration on viscosity of orange peel pectin solutions and intrinsic viscosity-molecular weight relationship. *Carbohydrate polymers*, 40, 277-284.
- Kratchanova, M., Panchev, I., Pavlova., Shtereva, L. (1994). Extraction of pectin from fruit materials pretreated in an electromagnetic field or super-high frequency. *Carbohydrate polymes*, 25, 141-144.
- Kratchanova, M., Pavlova, E., Panchev, I. (2004). The effect of microwave heating of fresh orange peels on the fruit tissue and quality of extracted pectin. *Carbohydrate Polymers*, 56, 181-185.
- Kratchanova, M., Pavlova, E., Panchev, I., Kratchanov, C. (1996) Influence of microwave pretreatment of fresh orange peels on pectin extraction. In J. Visser & A.G.J. Voragen (Eds.), *Pectin and pectinases, progress in biotechnology*, Elsevier, vol 14, 941-946.
- Lorezen, J.T. & Anderson, V.L. Design of Experiments. A No-Name Approach. *Marcel Dekker, Inc.* Chapter 3, 53-123 (1993).

- Mafart, P and Béliard, E. (1992). *Génie Industriel Alimentaire. Tome 2 : Techniques Séparatives*. Lavoisier Tec & Doc Ed. Paris, 37-43. ISBN 285068087.
- Mitchell, J.R. and Hartley, L. (1996). The influence of water on the mobility, structure and dispersibility of hydrocolloids. In G.O. Philips, P.A. Willams & D.J. Waddock (Eds), *Gums and stabilisers for the food industry*, 8, 3-13. Oxford: Oxford university Press.
- Osterveld, A., Beldman, G., Schols, A., Voragen, A.G.J. (1996). Arabinose and ferulic acid rich pectic polysaccharides extracted from sugar beet pulp. *Carbohydrate Research*, 288, 143-153.
- Pagan, J., Ibarz, A., Llorca, M., Pagan, A., Barbosas-Canovas, G.V. (2001). Extraction and Characterization of pectin from stored peach pomace. *Food Research international*, 34, 605-612.
- Panchev, I., Kirshev, N., Kratchanov, C. (1988). Improving pectin technology: II extraction using ultrasonic treatment. *International Journal of Food Science and Technology*, 23, 331-341.
- Panchev, I., Kirshev, N., Kratchanov, C. (1989). Kinetic model of pectin extraction, *Carbohydrate Polymers*, 11, 193-204.
- Ralet, M.-C., Axelos, M.A.V., Thibault, F. (1994). Gelation properties of extruded lemon cell walls and their water-soluble. *Carbohydrate research*, 260, 271-282.
- Rezzoug, S -A., Boutekedjiret, C., Allaf, K. (2005). Optimization of operating conditions of rosemary essential oil extraction by a fast controlled pressure drop process using response surface methodology. *Journal of Food Engineering*, 71, 9-17.
- Rezzoug, S. A., Maache-Rezzoug, Z., Mazoyer, J, Jeannin, M., Allaf K. (2000a) Effect of instantaneous controlled pressure drop process on hydration capacity of scleroglucan. Optimisation of operating conditions by response surface methodology. *Carbohydrate polymers*, 42 (1), 73-84.
- Rezzoug, S.A., Cioffi, F., K. Allaf. (2000b). Mise au point d'une procédé thermomécanique d'extraction d'huiles essentielles : Application aux peaux d'oranges. *Proceedings of "12<sup>èmes</sup> Rencontres Scientifiques et technologiques des Industries Alimentaires"*. AGORAL. Lavoisier Eds., Paris, 205-210.
- Rezzoug, S.A., Louka, N., Maache-Rezzoug, Z., Nouviaire, A., Allaf, K. ( 1998) présentation du séchage couple a la texturation par détente instantanée contrôlée. application aux produits agro-alimentaires en morceaux. *Proceedings of "10<sup>èmes</sup> Rencontres Scientifiques et technologiques des Industries Alimentaires"*. AGORAL. Lavoisier Eds., Paris, 319-324.
- Schieber, A., Hilt, P., Steker, P., EndreB, H-U., Rentschler, C. (2003). A new process for the combined recovery of pectin and phenolic compounds from apple pomace. *Innovative Food Science and Emerging Technologies*, 4, 99-107.
- Thibault, J.F., Dedreu, R., Geraeds, C.C.J.M., Rombouts, J.M. (1988). Studies on extraction of pectins from citrus peels, apples marks and sugar-beet pulp by arabinase and galactanase. *Carbohydrate Polymers*, 9, 119-131.
- Wang, S., Chen, F., Wu, J., Wang, Z., Liao, X., Hu, X. (2007). Optimization of pectin extraction assisted by microwave from apple pomace using response surface methodology. *Journal of Food Engineering*, 78, 693-700.
- Yapo, B.M., Robert, C., Etienne, I., Wathelet, B., Paquot, M. (2007). Effect of extraction conditions on the yield, purity and surface properties of sugar beet pulp pectin extracts. *Food Chemistry*, 100, 1356-1364.