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# Spray drying of pectin obtained from *Citrus Sinensis* waste

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## ABSTRACT
Polysaccharides are high molecular weight polymers that have functional groups, which can be used as sites to derivate or bind specific ligands. Pectin is a polysaccharide that is obtained from plant resources mainly from citrus plants. It is a widely used product in the food and in the pharmaceutical industry for its thickener, stabilizing and gelling properties. The objective of this work was to establish a pectin drying process obtained by acid hydrolysis from citrus waste by spray dry. An acid extraction process with the dry and ground plant material was used. The influence of the inlet and outlet temperatures on the yield and drying speed was evaluated by an experimental design $3^2$ replicated at the central point. With the best variant, five batches were developed at laboratory scale and one batch at bank scale, evaluating the obtained material by infrared spectroscopy and scanning electron microscopy. The results of experimental design showed that the temperature does not influence significantly the yield, but it does affect the speed of the drying. An input-output temperature ratio of 200/80 ºC was established as the best drying variant. The batches prepared on a laboratory scale showed a yield higher than 85.0% and a drying speed higher than 0.7 L / h. The yield of the batch on a bank scale was 90%. The degree of esterification was 63.5%, indicative of a high degree of methoxylation pectins. The results show that the drying process is adequate to obtain pharmaceutical grade pectin.

**Keywords:** *Pectin; Acid extraction process; Degree of esterification; Spray dry; Infrared Spectroscopy; Electron Microscopy.*

## 1. INTRODUCTION

Polysaccharides are high molecular weight polymers that have functional groups, which can be used, as sites to derivate or bind specific ligands. Pectin is a polysaccharide that is obtained from plant resources mainly from citrus plant. It is a widely used product in the food and pharmaceutical industry for its thickener, stabilizing and gelling properties [1, 2]. The main source of extraction of pectin is the apple pulp and the peel of citrus fruits (by-product of the juice manufacturing industry). It has been reported that the extractable pectin content of citrus fruits is between 30 and 35% [3].

Pectins are classified according to the degree of esterification or methoxylation. Pectins with a degree of methoxylation higher than 50% are called high methoxyl pectins (HMP), and pectins with a degree of methoxylation less than 50% are called low methoxyl pectins (LMP) [3, 4]. In both cases, the remaining carboxyl groups are present as a mixture in the form of free acids (-COOH) and salts (-COO-$Na^+$). The degrees of methoxylation strongly influence the functional properties, such as solubility and gelling capacity of the pectins [5-7].

The process of producing pectin from citrus residues basically consists of three stages: Extraction, purification of the extract and separation of pectin. Various studies on the process of obtaining have been reported in the literature [8-13]. One of the methods used for the extraction of the pectin from the peel of the orange is the extraction by acid hydrolysis with subsequent precipitation with ethanol [4, 14, 15]. The pectin was recovered by filtration and subsequently was dried. The commonly used drying methodology is heat drying in ovens [12].

Drying is one of the most complex unit operations in chemical engineering. It simultaneously involves heat and mass transfer, as well as the physical and chemical transformations that can occur in the material. This operation is an essential stage in several processes of different industries. At present, one of the used techniques in the drying of the extract is the spray dry due to the operational flexibility and affordable cost. Spray dried powder has high stability being easy handling and storage [16-18]. The objective of this work was to establish a pectin drying process obtained by acid hydrolysis from citrus waste by spray dry.

## 2. MATERIALS AND METHODS

### 2.1. Vegetal material.

***Citrus sinensis*** (residual peel and skins) from Citrus Company Victoria de Girón (Jaguey Grande, Matanzas Province, Cuba) was collected. Herbarium specimens voucher ROIG 4633; have been deposited in herbaria of the Experimental Station of Medicinal Plants Dr Juan Tomas Roig (Artemisa province, Cuba). The material collected was washed with water. Later disinfested with 2% solution of sodium hypochlorite. Dried in an oven at 80 °C and milled (MANESTY equipment, Italia). To the material obtained the residual moisture content, total ash content and particle size (sieves of 600, 250, 150 y 63 µm) were determined. The powder material was stored in polyethylene bags until use.

### 2.2. Extraction process of pectin by acid hydrolysis.

A process of extraction by acid hydrolysis was applied (ratio drug/extraction solvent 1:20, agitation speed 200 rpm: reflux time 2h; volume 5 L). As an extraction solvent, HCL solution (0.2 M) was used. Stainless steel reactor (stirred tank type) 10 L capacity, marine propeller stirrer and heating system and gas

extraction were used. Subsequently, the extract was filtered under vacuum and the plant material was discarded. To the residual liquid, ethanol in a 1:1 ratio was added. The solution was mixed for 30 min and allowed to stand for 24 hours. The obtained gel was vacuum filtered using as a filter medium cotton (XX, 2 mm, Filtronic, Brazil), washed with ethanol and dried by spray dry. Before performing the experimental design experiments, the moisture content of the gel was determined by the Karl-Fischer method. The results showed a moisture content of 57.7 ± 1.04%.

**2.3. Technological development process.**

**2.3.1. Establishment of drying parameters.**

Experimental design $3^2$ replicated at the central point was performed (Statgraphics plus 5.1, USA). The influence of inlet air temperature (X1) (160; 180 and 200) and outlet air temperature (X2) (80; 90 and 100) on yield (%) and the drying speed (L/h) was evaluated. [19]. The concentrated aqueous extracts were drying in a Buchi B 191 model spray dryer (Switzerland). Inter and outlet air temperatures were carried out according to the experimental design. The product was fed into the spray dryer at room temperature 600 L/h; the rate was varied to regulated exit air temperature at the desired value. Gel solutions in water containing 10% total solids were prepared from the moisture content of the gel. The efficiency of drying (yield) was evaluated by determining the total content of powder obtained in the process and comparing it with the theoretical powder content that should be obtained [20]. The drying speed was calculated from the ratio of the evaporated water mass (estimated by a mass balance) and the time for each experimental drying test [16].

**2.3.2. Scale process.**

Established the technological parameters of drying, five batches at laboratory scale (0.5 L) were elaborated. Drying efficiency was determined by determining the total powder content obtained in the process and comparing it with the theoretical powder content that can be obtained The results were compared statistically. Finally, a lot on a bank scale (5 L) was prepared.

**2.3.3. FTIR spectroscopy.**

FTIR spectra of the samples were measured on a FTIR - VERTEX 70 / BRUKER spectrometer (Germany). 64 cumulative scans were taken, with a resolution of 4 $cm^{-1}$, in the frequency range of 4000 to 400 $cm^{-1}$, in transmission mode.

The degree of esterification was determined according to the methodology described by Monsoor *et al*., [21]. It consists in determining the area of the bands in the region of 1740 $cm^{-1}$ which is characteristic of axial deformation of carbonyl group, C = O, of methyl ester (esterified carboxylic groups) and 1632 $cm^{-1}$ which represents axial deformation of the carboxylate, $COO^-$ (carboxylic groups not esterified) and apply the following equation: **DE = (APest/APNest + APest) 100** where: APest = Peak area of the esterified carboxylic groups; APNest = Area peaks of the non-esterified carboxylic groups.

**2.3.4. Scanning Electron Microscopy.**

Scanning electron microscopy (SEM) imaging of crystalline cellulose was carried out using a FEG-MEV; JEOL 7500F scanning electron microscope (Germany). The equipment was operated at an acceleration voltage of 2 kV. For each sample, different parts of the grid were used to determine both average shape and size distributions. The samples were coated with a carbon layer with a thickness of 15 nm.

**2.3.5. Statistical analysis.**

Experimental design, data analysis and optimization procedure were performed using Statgraphic plus 5.1 (USA). Results were considered significant when $p < 0.05$ [19, 22].

## 3. RESULTS

Prior to the pectin extraction process, a process of selection and preparation of plant material was performed. This process is of great importance due to the quality of the final product that depends on the selection, washing and disinfection of the plant material and influences the characteristics of the pectin to be obtained [15].

In this process of preparation of the plant material, drying prior to the extraction has been recommended, mainly because the dry material better guarantees its quality and facilitates the milling process. It has been shown that pectin degrades at temperatures above 200 °C [23], so that it is possible to dry the plant material without affecting it. On the other hand, several authors recommend a drying below 110 °C to avoid darkening the material and reduce the risk of fermentation or spontaneous combustion of the material. With this temperature, material moisture values below 12% are guaranteed [24].

Finally, the plant material must be brought to a suitable granulometry in order to guarantee a greater surface area, which guarantees a greater contact between the material and the solvent to be used in the extraction process. In general, the quality and yield of pectins vary according to the citrus species used as raw material and their previous preparation. The thermal treatment carried out on the material before the extraction process favors the performance of the extracted pectin due to the weakening of the primary cell walls [3].

The results of the control analysis carried out on the plant material after drying and grinding showed that the moisture content of the sample was 13.79 ± 0.01% and the total ash content was 3.8 ± 0.20%. The particle size was mostly between 600 and 250 microns (72%), while the rest was less than 250 microns.

In this study the plant material was dried at 80 °C, reaching a moisture value of 13.79 ± 0.01%. The result obtained complies with the parameters established by NRSP 309 [25], which demonstrates the efficiency of drying. On the other hand, the values are similar to those reported by other authors in studies conducted in countries with similar climatic characteristics to those of Cuba [26].

The total ash content also complies with the parameters established by NRSP 309 [25]. Various authors for oranges grown in similar climates to Cuba have reported similar values. Rincón *et al*, [26], reported total ash values of 3.2% in ground orange peel, while Piza [27], reported values of 0.29% for orange peels from Costa Rica. In general, the ash values range between 0.2 and 5% depending on the type of soil and cultural treatment given during the harvest of the fruit.

The particle size was mostly between 600 and 250 microns (72%), while the rest was below 250 microns. It is known, that this

parameter influences the process of extracting the bioactive components from the plant material. A small granolumetry of the material favors that the cell walls are more open for the penetration of the extraction solvent by capillarity processes, favoring the extraction of the components of interest. The best results were achieved when the extraction process is done with plant material dry [28]. It is also known that particle sizes smaller than 250 microns have a high content of fine particles that affect the extraction process to form compact cakes when moistened with the extraction solvent, while sizes greater than 600 microns bring the inconvenience of that the volume of plant material is too large for handling [29]. The results obtained in this work show that the granolumetry of the material used in the extraction process was adequate.

Figure 1 shows the Pareto chart for yield and drying speed.

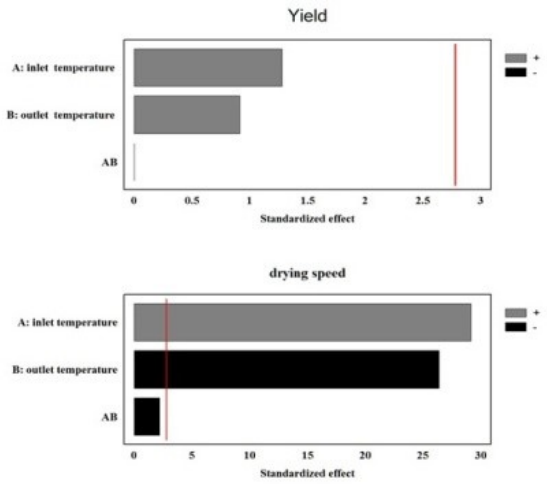


**Figure 1.** Pareto chart. Pareto chart for yield (upper) and Pareto chart for drying rate (lower).

Figure 1 (upper) shows the Pareto chart for yield. No significant influence of temperatures (p = 0.2313 and p = 0.3344 for the inlet air temperature and the outlet air temperature, respectively) was observed. The best yields (90.2 %) at 200 ° C and 100 ° C for the temperature between air and the exit air temperature, respectively were obtained. This behavior was described by the following model equation:

$$\textbf{Yields}\ (\%) = 122{,}8 - 0{,}54X1 - 0{,}83X2\ (R^2 = 0{,}993)$$

On the other hand, Figure 1 (lower) shows the Pareto chart for drying speed. A significant influence of temperatures (p = 0.0001 and p = 0.027 for the inlet air temperature and the outlet air temperature, respectively) was observed. The best drying speed (1,15 L/h) at 200 ° C and 80 ° C for the temperature between air and the exit air temperature, respectively were obtained. This behavior was described by the following model equation:

$$\textbf{Drying speed}\ (L/h) = 0{,}465 + 0{,}01X1 - 0{,}02X2\ (R^2 = 0{,}971)$$

Evaluating the results of the design of experiments as technological parameters for drying the following: Inlet air temperature of 200 °C and outlet air temperature of 80 °C were established.

Studying the influence of input and output temperatures is important due to the need to guarantee a material that is not affected by heat and that is sufficiently dry [30]. During the drying process, a high inlet temperature should be used to allow the rapid formation of a semipermeable membrane on the surface of the drop, but this temperature cannot cause damage to the dried product. Neither can cause excessive growth of bubbles and the alteration of the surface because this phenomenon causes losses during the drying obtaining sticky particles [16].

In the present study, a response surface design (RSM) was applied [19]. This type of design is suitable for studying the main effects and their interactions of the inlet and outlet temperatures on the yield and drying speed.

In general, the results of the experimental design showed that the behavior of the different indicators of the process was not similar. The inlet and outlet temperatures had no statistically significant influence on the yield, however, the inlet temperature showed a strong positive influence on the drying rate, while the exit temperature showed a negative influence. The interaction between both factors was not significant.

This result indicates that the drying speed was directly proportional influenced by the inlet temperature and inversely proportional influenced by the exit temperature. It has been reported that this can be interpreted as the amount of energy available to evaporate the water from the system. Therefore, an increase in the drying speed to achieve at a greater the temperature difference between the inlet and outlet temperatures. There is more energy available to evaporate the water from the solution, which means that the performance of the dryer is increased. If analyzed from the economic point of view, this favors the reduction of the operating costs; therefore, more product can be produced per hour [16].

An input-output temperature ratio of 200/80 ºC was established as the best drying variant. Under these conditions, five batches were elaborated on a laboratory scale obtaining yield values above 88% and drying speeds higher than 0.7 L/h. It was statistically verified that there were no significant differences between batches, so it can be said that there are reproducibility and homogeneity in the proposed technological process. The batch obtained on a bank scale confirmed that the established technological parameters were suitable for drying pectin by spray dry.

**Table 1.** Results of the batches at laboratory scale (similar letter no significant for p <0.05)

| Batch | Yield (%) | Drying speed (L/h) |
|---|---|---|
| **1** | 89,6 a | 0,97 |
| **2** | 97,6 a | 0,91 |
| **3** | 89,8 a | 1,00 |
| **4** | 88,5 a | 0,70 |
| **5** | 95,9 a | 0,89 |

Table I shows the results of the batches elaborated at laboratory scale. The yield was above 88%, while the drying rate was between 0.7 and 1.0 L / h. The results showed that among the yield values obtained, there were no significant differences. This result indicates reproducibility between batches at the work scale

used. In the case of the drying speed, although a variability between the lots was observed, it is considered that values higher than 0.7 L / h are adequate in this scale of work.

In the bank lot, when carrying out the gel precipitation process, a yellow material was obtained in the form of a gel, with a characteristic odor and a moisture content of 57.2%. Later, when carrying out the dry-spray drying process, a fine white powder was obtained, with moisture content below 7%. The yield of the process was 90%, which is considered adequate for the scale of work.

Figure 2 shows the FTIR spectrum of the spray-dried pectin sample. Bands at 3316 $cm^{-1}$ and 2923 $cm^{-1}$ attributed to the stretching of the CH groups and the CH3 groups, at 1733 $cm^{-1}$ characteristic of axial deformation of the carbonyl group, C = O of the methyl ester (carboxyl groups esterified by methanol, $COOCH_3$) and 1632 $cm^{-1}$ characteristic of axial deformation of the carboxylate $COO^-$, (non-esterified carboxylic groups) were observed [31]. These two main bands were used to determine the degree of esterification [32].

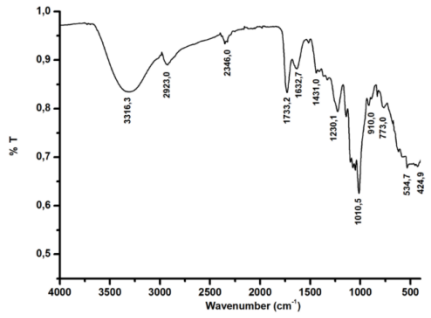


**Figure 2.** FTIR spectrum of spray dried pectin

The bands located in the region of 500-1500 cm -1 are related to the neutral sugars present in the pectin molecule. Bands between 1100 and 1200 $cm^{-1}$ comprise ether (C-O-C) and carbon (C-C) connections in the aromatic galacturonic acid ring of the pectin molecule. The absorption bands in the 800-1300 $cm^{-1}$ range are known as the "pectin footprint" region, considered a complex interpretation region [31]. The result of this determination of degree of esterification by infrared by Fourier transform (FTIR) was 63,5 %. This result allows classifying as pectin high degree of methoxylation (DE greater than 50%). This result is important, because a parameter that characterizes the pectin chains and, therefore, gives an idea of its quality is the degree of esterification. This parameter is directly related to the firmness and cohesion of the tissues of the plants, and strongly influences the solubility and the capacity of formation of the gel, conditions that are required for gelation.

SEM analysis showed the formation of nearly spherical granules, hollow pore characteristic of spray drying (Figure 3).

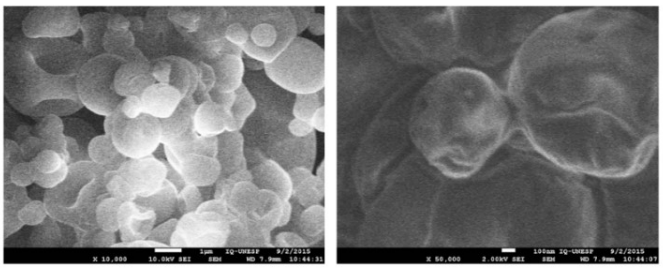

**Figure 3.** Results of analysis by Scanning Electron Microscopy

## 4. CONCLUSIONS

The application of the statistical design used in this work allowed to establishing the parameters of inlet temperature and outlet temperature to dry pectin obtained from Cuban citrus waste. It was found that both temperatures only have a significant influence on the drying speed. A technological process was developed to dry, establishing as an input temperature 200 C and as output temperature 80 C. In these conditions, a high degree of methoxylation pectin was obtained.

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