Conference Paper

Microwave Pre-processing Effect on Pectin Yield from Citrus Raw Material

Gennady Alekseev, Olga Egorova, and Aleksey Egorov

ITMO University, Saint-Petersburg, Russia

Abstract

The article describes a more environmentally friendly method to produce pectin compared to the classical acid scheme, which requires the use of strong mineral acids and toxic solvents. This method of obtaining pectin, like other analogs of the classical method, causes a decrease in the yield of the final product. This study aims to find ways of eliminating these barriers and increase the yield of pectin. The paper investigates the possibility to increase the yield of pectin obtained by acid hydrolysis applying citric acid through the use of preliminary microwave exposure to citrus raw materials. The work compares pectin quality indicators, such as the degree of esterification, molecular weight and gelation, for raw materials dried by the convective method and the combined method consisting of microwave pretreatment and blowing dry air. Curves of comparable pre-drying methods are presented. The rate of pectin yield at the stages of hydrolysis depending on the drying methods is analyzed. Optimal power modes for preliminary microwave drying of citrus raw materials are selected. The data obtained are valuable for both development and improvement of industrial technology of pectin production using environmental methods of extraction without the use of strong mineral acids to increase the yield and quality of pectin.

Keywords: pectin, environmentally friendly method, microwave, convective drying, citric acid, drying curve

Corresponding Author:
Olga Egorova
jeerol@list.ru

Received: 24 December 2019
Accepted: 9 January 2020
Published: 15 January 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the BRDEM-2019 Conference Committee.

1. Introduction

Currently, there are serious problems associated with increased environmentally negative load on the environment. Much attention is paid to waste processing. This is especially true for the food industry, where waste can potentially be converted into more valuable products or raw materials for other industries.

40-60% of orange is considered to be waste during the industrial production of orange juice [1]. This waste can be a raw material to produce essential oils, flavonoids, pectin and other important products [2].

It is convective drying that is used for storage and preparation for the processing of secondary food raw materials. In the process of drying there is a chemical transformation of the components of pectin-containing raw material [3.4]. It is subjected to enzymatic, biochemical and microbiological changes leading to rapid deterioration during storage. Thus, the extraction of raw materials is a necessary production step. Although convective drying does not always have a good effect on the quality of pectin produced, at present, this way remains essential to preserve pectin-containing raw materials due to its simplicity and economy.

Since the beginning of the XXI century, microwave drying has been studied by Russian and foreign scientists, as this type of drying takes a much shorter time for pectin-containing raw materials compared to the convective one [5]. However, microwave drying is not only less time consuming, but it also uses another way of supplying heat to the material, which presumably can affect the quality and quantity of the final product.

On the other hand, the production of pectin is associated with the use of harmful and dangerous components such as strong acids, alkalis and toxic solvents such as acetone, methanol, etc. Not every company can afford the classic technology of pectin production, because there is a large amount of dangerous waste [6]. Recently, a trend towards the design of environmentally friendly production methods has become obvious in the development of pectin production technology [7-10].

This work does not use strong mineral acids, which are supposed to cause a decrease in the yield of the final product, but attempts have been made to find methods that eliminate these obstacles and increase the yield of pectin.

The purpose of this study is to evaluate the effect of pre-processing of raw materials due to microwave exposure on the yield of pectin and select the parameters of that impact.

2. Methods and Equipment

For the purpose of the study, orange of varieties "Valencia" was used. This variety is the world leader in the number of uses in the production of juice products. Since it is advisable to consider the possibility of using industrial waste to produce pectin, orange peel varieties "Valencia" is considered the most relevant raw material.

Flavedo and albedo of fruits were peeled by hand and crushed. Raw materials were analyzed for moisture content by the gravimetric method. For this, three samples

DOI 10.18502/kls.v5i1.6015

were taken from mixed raw materials. The moisture content of the raw material was determined by the formula:

$$\omega = \frac{m_1 - m_2}{m_1} \cdot 100\%, \quad (1)$$

where m_1 is the mass of the sample before drying (g), m_2 is the mass of the sample after drying (g).

Three samples of equal mass for microwave drying and three samples for convection drying were taken from the total mass. The weight of each sample was 100 g. Part of the fresh raw materials were dried using convection drying, the another was processed using microwave drying, and a combined method was applied to the third part.

Drying was conducted till the final moisture content of the product was 10%. The moisture content of the dry product was determined by the gravimetric method, as described above.

Convective drying was done in a drying oven at temperature 70 °C.

Microwave drying was done in a household microwave oven at different powers.

Combined drying was an alternation of microwave exposure for 5 minutes with a 5-minute period of dry air blowing.

The samples weighing 15 g were separately taken from each type of dry raw material and sent for hydrolysis.

The raw material was washed in cold water (10 °C) to remove water-soluble impurities.

Grinding was conducted in a screw grinder, providing a particle size less than 1 mm. Raw materials were mixed.

The acid method was used to produce pectin. Hydrolysis was performed using citric acid to achieve pH=2.5, at temperature of 70 °C, hydromodule 1:10. Hydrolysis was done in three stages, each stage lasted 60 minutes [11]. The total hydrolysis time was 180 minutes.

Pectin evaporation was performed on a rotary evaporator with continuous mixing, t = 70 °C, P = 60 mbar.

Precipitation was done with 96% ethyl alcohol. The precipitate was separated by filtration with a Buchner funnel and washed with alcohol.

The pectin obtained was dried in an oven at 50 °C.

Pectin is classified as highly esterified, low esterified and low esterified amidated. Each type of pectin is used for its own purposes under different conditions. The highest degree of gelation has pectin with the high esterification degree of more than 50%.

The degree of esterification of the pectin obtained was determined by the titrometric method according to GOST 29186-91. Pectin. Technical conditions.

Molecular weight was determined by viscometric method using a capillary glass viscometer VPG-1.

The molecular weight was found according to the formula Kuhn-Mark-Houwink:

$$[\eta] = k \cdot M^{a}, \quad (2)$$

where [η] is intrinsic viscosity, M is molecular weight, k and a are parameters depending on temperature and polymer-solvent system, here we take k=1.1 $\cdot 10^{-5}$, a = 1.22 [4].

Gel formation was determined organoleptically. For this analysis, jellies were prepared according to GOST 29186-91. Pectin. Technical conditions.

3. Results

Moisture of fresh raw materials before drying was 77%.

Raw materials were crushed and dried in charges of 100 g on a silicone surface. The average particle size was 7x5x2 mm. For uniform heating it is necessary that the linear dimension of a particle does not exceed 2-5 mm in one direction at least, this is especially important for microwave exposure [12].

Selecting the powers we considered other authors' recommendations on the critical effect of high temperatures on the quality of pectin during drying of raw materials. The temperature of the raw material increased to 94 °C in the case of drying by the microwave method without interruptions for the blowing, which influences negatively on the properties of the final product. Many authors report that the temperature should not exceed 70-80 °C [4].

There is a study describing the method of combined drying which alternates five-minute microwave exposure and five-minute air blowing [13, 14]. This method does not consider the change in product moisture during drying. The temperature increases at the beginning of the heating of raw materials and decreases with moisture reduction.

The optimal value of power was determined for microwave drying and equals 300 watts. At higher power (450 W or more), the product began to burn, at lower value (180 W or less) unnecessarily lengthening the drying time.

Drying was performed with alternating microwave and air blowing. A single cycle consisted of 2-4-minute exposure to microwave processing and a 4-minute blowing of air. This method makes it possible to fully use the main advantage of microwave heating -- high rate. Moreover, it allows to avoid uneven heating of some parts of the processed

Table 1: Scheme of the combined method of drying with alternation of energy microwave supply and air-flow.

Cycle number	Drying time, minutes	Duration, minutes	Processing	Average temperature, °C
1	1-4	4	SHF	60
	5-8	4	Blowing	50
2	9-12	4	SHF	68
	13-16	4	Blowing	45
3	17-20	4	SHF	70
	21-24	4	Blowing	43
4	25-28	4	SHF	71
	29-32	4	Blowing	42
5	33-34	2	SHF	75
	35-38	4	Blowing	44
6	39-40	2	SHF	74
	41-44	4	Blowing	44
7	45-46	2	SHF	73
	47-50	4	Blowing	45
8	51-52	2	SHF	71
	53-56	4	Blowing	46
9	57-59	3	SHF	70
	60-63	4	Blowing	43
10	64-66	3	SHF	66
	67-70	4	Blowing	44
11	71-73	3	SHF	66

raw materials, since cyclic heating provides the possibility of temperature redistribution by thermal conductivity of the material. Table 1 shows the average surface temperature of raw materials, measured at five points eight times in each cycle. At the beginning of drying, with a large amount of free moisture, the energy of the microwave field is spent mainly on evaporation of moisture and partially on compensation of heat loss to the environment. Then the bound moisture begins to evaporate, as well as endothermic processes associated with the chemical transformation of proteins, carbohydrates and destruction of raw tissue occur.

Figure 1 shows the rise in temperature when the microwave energy is supplied and the decrease when the microwave energy is turned off. The ambient temperature was 27 °C. The average temperature inside the chamber at the time of microwave exposure was 46 °C. The average temperature on the surface of the sample at first rises and then slowly falls. The average value shows that the maximum temperature is in the sixth cycle.

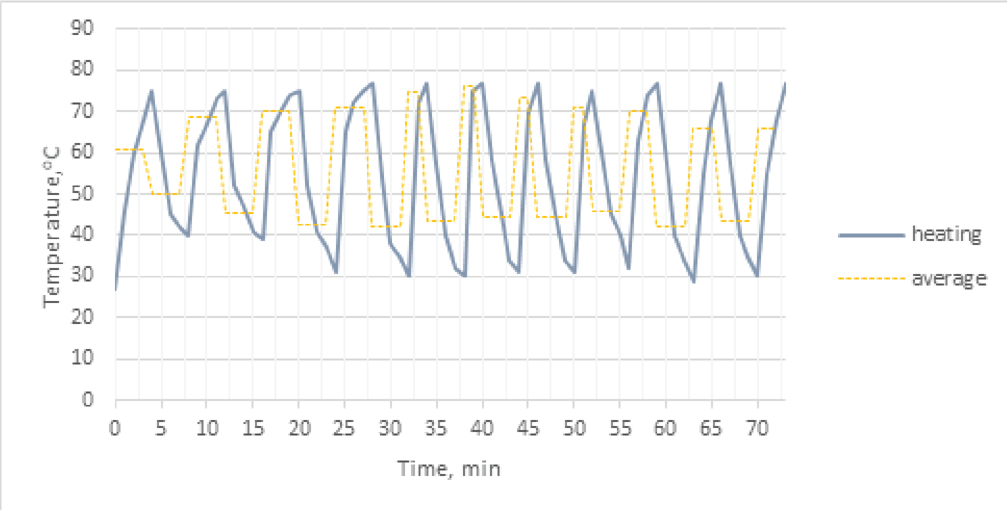

Figure 1: Temperature change in the dryer chamber with the combined method of drying citrus raw materials.

After the fourth cycle, the temperature on the surface of the raw material increases to the limit value of 77 °C, so it is necessary to reduce the time of exposure to microwave processing before the fifth cycle. The peak point of the fourth cycle corresponds to moisture content of 40%. The peak point of the sixth cycle corresponds to moisture value of 33%, which, as can be seen from the microwave drying curve (Figure 3), corresponds to the point of critical moisture content. To the point of critical moisture content, mostly free moisture is removed, the effect of microwave radiation also affects the bound moisture, and therefore results in the temperature rise. After this point, the drying rate decreases, the moisture content of the product reduces as well. During this period, the bound moisture is removed, and the gradual decrease in the drying rate is explained by the increase in the binding energy of moisture with the material. Here, the process of removing moisture depends on the moisture content, the nature of the association of moisture with the material, and the physicochemical properties of the material. When the moisture content of the product reduces, the average temperature decreases. It is assumed that due to the temperature distribution in the center of the sample, the temperature constantly increases during the drying time.

Applying the method described the temperature exceeded at the point above 70 °C. However, the time of high temperatures was small (no more than 7 minutes), and this did not significantly affect the quality of the pectin obtained. The temperatures distribution for the whole drying time is shown in Figure 2.

Analysis of the diagram shows that microwave processing significantly reduces the drying time.

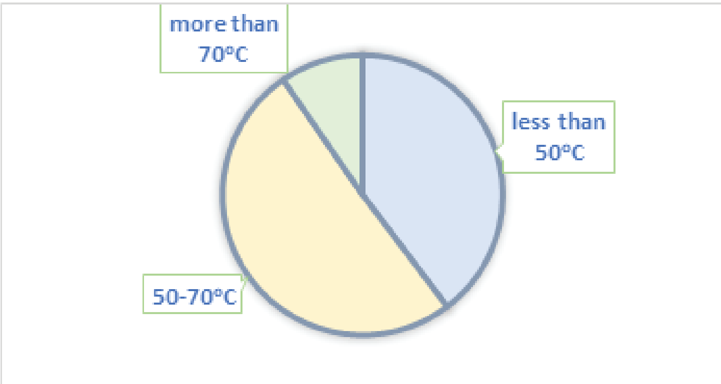

Figure 2: Analysis of the temperature regime.

Drying the product (weight 100 g, moisture 77%) to a final moisture content of 10% took only 73 minutes by microwave processing, while convective drying took 350 minutes.

Drying curves are shown in Figure 3.

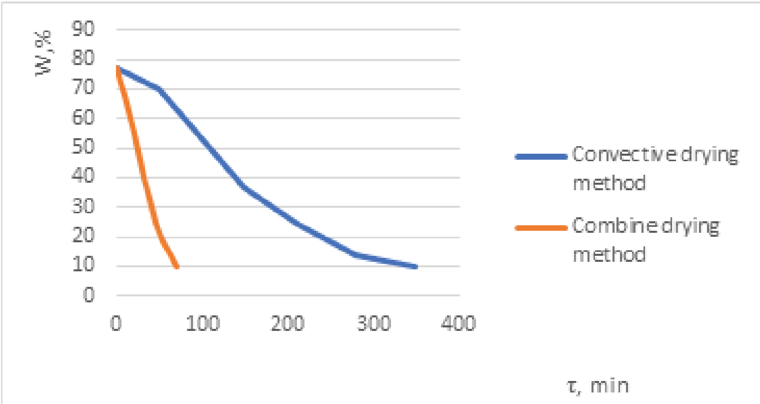

Figure 3: Drying curve.

Organoleptically dried samples did not differ from each other.

Pre-dried raw materials were extracted. The same methods for all samples were used for the extraction of pectin. In this paper, we did not use strong mineral acids, we chose citric acid. The extraction consisted of three stages. After every stage, the aqueous solution was decanted and a new portion of the acidic solution was poured on the raw material. The yield of pectin in stages is shown in Figure 4. It shows that the hydrolysis of raw materials dried by microwave processing is faster. After the second stage, it was possible to obtain 90% of the pectin from the total pectin amount obtained. Raw materials dried convectively after the second stage gave only 60% yield. Thus, to reduce the extraction time as a whole two stages of hydrolysis can be used to obtain pectin by the method described.

The total yield of pectin from raw materials after microwave processing is 2.1 times more than after convection drying.

We assume this can be explained by the effect of microwave processing on the raw material during heating. Orange peel has a capillary-porous structure and it is a complex substance in which the components have different dielectric properties. Water molecules, which are dipoles, play the main role in the process of energy absorption during the dielectric heating of the material. When an electric field is applied to a dipole molecule, its polarization occurs, caused by the attraction of negative and positive charges of molecules in accordance with the direction of the external electric field. Molecules later come into oscillatory motion under the action of an alternating field. Under the influence of an alternating electromagnetic field, the raw material, which is a dielectric material, is heated due to dielectric losses, i.e. the energy of the field is converted into heat.

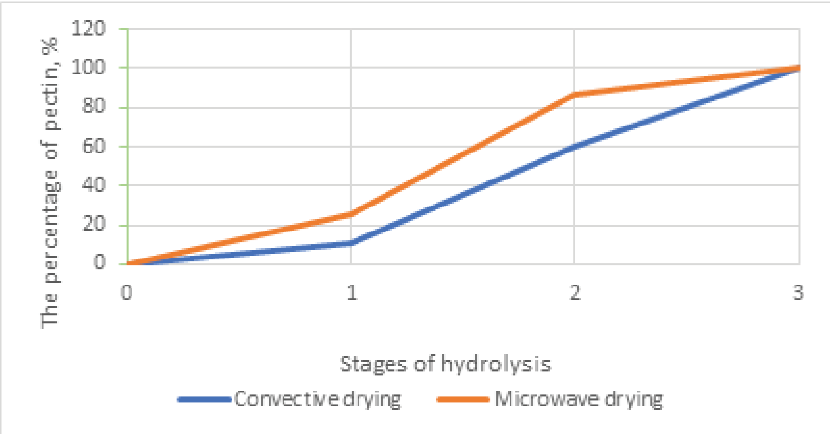

Figure 4: Pectin yield by hydrolysis stages.

Water absorbs most of the radiation, heats up and begins to evaporate due to the high dielectric constant. Water in the raw material is in a closed space so the beginning of its boiling creates overpressure. Increasing internal pressure significantly deforms the structure of the product throughout the volume of the material. Microwave processing allows to achieve a discontinuity of the cell membranes of plant materials before extraction.

The structure of the raw material obtains a developed phase contact surface, which intensifies mass transfer processes and at the same time ensures uniform hydrolysis of protopectin substances, regardless of its localization in the cell. As a result, the process of hydrolysis of protopectin substances is completed faster than for raw materials obtained by convection drying. The yield of pectin increases.

During the microwave processing of raw materials moisture evaporates faster, which increases the rate of drying, and the cell walls containing pectin heat up less, which improves its quality.

The samples obtained can be classified as highly esterified, since the degree of esterification of all samples was more than 50%.

Molecular weight and gelation do not significantly differ in the samples. Mass of 70 kDa is enough for the formation of jelly 150 ° SAG [15]. All samples have an average molar mass greater than this value.

The results of the experiment are given in table 2.

TABLE 2: Experimental results for different methods of preparing raw materials.

	Convection drying	Combined drying
The yield of pectin to dry matter, %	10.8	21.9
The degree of esterification, %	75.0	76.5
Average molecular weight, kDa	103	96

4. Conclusion

The work describes the method of combined drying with a cyclic supply of microwave energy. The optimum power of microwave exposure was determined and equals 300 watts. The point of critical moisture content was found, based on which the cycle duration was selected. The comparison of microwave drying and drying by the convective method of citrus raw materials to produce pectin was made. Drying curves are given.

Significant differences in the quality of the pectin obtained were not identified. At the same time, microwave drying allowed to reduce the drying time 4.5 times and increase the yield of pectin 2.1 times.

The method of obtaining pectin using the microwave drying simplifies the technology, increases the yield and reduces not only the drying time, but also the duration of hydrolysis.

Conflict of Interest

The authors have no conflict of interest to declare.

References

[1] Licandro, G., Odio, CE. (2002). *Citrus by-products*. London: Taylor & Francis. Citrus.

[2] Rafiq, S., Kaul, R., Sofi S.A., et al. (2018) Citrus peel as a source of functional ingredient: A review. Journal of the Saudi Society of Agricultural Sciences, vol. 4

(17), pp.351-358.

[3] Berk, Z. (2016*).* Citrus Fruit Processing. Academic press.

[4] Donchenko, L.V., Firsov, G. G. (2007). *Pectin: basic properties, production and use*. Moscow: DeLi print.

[5] Markin, V.I., Cheprasova, M. Yu., Bazarnova N.G. (2014). Basic directions of use microwave radiation in the processing of plant raw material (review). *Khimija Rastitel'nogo Syr'ja*, vol. 4, pp. 21-42.

[6] Ciriminna. R., Fidalgo, A., Delisi, R., et al. (2016). Pectin Production and Global Market.. *Agro Food Industry Hi Tech*, vol. 27(5), pp. 17-20.

[7] Cho, E., Jung, H, Lee, B.(2019). Green process development for apple-peel pectin production by organic acid extraction. *Carbohydrate Polymers*, vol 204, pp. 97-103.

[8] Tipsina, N.N. (2007) Changes in the chemical composition of Siberian small apples under the influence of microwave energy. *The Bulletin of KrasGAU*, vol 2, pp. 272-277.

[9] Liew, S.,Chin, N., Yusof, Y. (2014). Extraction and Characterization of Pectin from Passion Fruit Peels. Agriculture and Agricultural Science Procedia, vol 2, pp. 231-236.

[10] Perfilova, O.V. (2018). Biologically active value change of secondary raw materials in microwave heating process. *The Bulletin of KrasGAU*, vol 2 (137), pp. 123-128.

[11] Try, A.V., Miheeva, L.A. (2014) Extraction of pectin substances from different plant materials and effect various factors on this process. *Scientific Bulletin.* Natural Sciences, vol 23(194), pp.123-128.

[12] Rogov, I.A., Nekrutman, S.V. (1976). *Ultra high frequency and infrared heating of food*. Moscow: Food industry.

[13] Ilina, I.A., Zemskova, Z.G., Uvracheva, T.V., Kvasenkov, O.I. (2003). Ru, Pat. No. 2198183 *The method of producing pectin declare*

[14] Kupin, G.A., Komen, N.N., Matvienko, A.N., et al. (2016). Innovative technology for the production of food additives from pumpkin processing secondary resources. *Scientific Journal of KubSAU*, vol.121, pp. 929-940.

[15] Kukin, M.Yu. (2017). Improvement of pectin production technology from apples. *Scientific journal NRU ITMO Series "Processes and Food Production Equipment"*, vol 2(32), pp 9-17.