Kinetics of hydrolysis-extraction of pectin substances from the potato raw materials

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Abstract

Introduction. Hydrolysis-extraction of pectin substances from plant raw materials is one of the most difficult and the most important processes of pectin obtaining technology. Therefore, the study of the technological parameters influence on the kinetics of this process is relevant.

Materials and methods. The subject of the study was the process of hydrolysis-extraction of pectin from the potato pulp using hydrochloric acid. Pectin yield was determined in the percentage by weight of dry matter. Kinetic constants were calculated by the first-order equation. The processing of experimental data, equations selection, calculation and refinement of coefficients of these equations were performed by means of the least squares method.

Results and discussion. On the basis of experimental studies kinetic curves of the process of hydrolysis-extraction of pectin from the potato pulp are built, depending on temperature and pH. PH of the surrounding has the greatest influence on the rate of hydrolysis protopectin. For low acid content as a catalyst for the process, the reaction rate is not significant even at high temperatures. Protopectin hydrolysis is accompanied by a number of adverse reactions connected with the destruction of pectin, which makes it difficult to determine the reaction rate constant. Through experiment planning and statistical processing of experimental data the optimal parameters of hydrolysis-extraction of potato pectin are determined: temperature of 75ºC, pH of hydrolysis weight is 1.6; hydrolysis duration is 72 minutes.

Conclusions. Application of results of researches during pectin production provides maximum extraction of pectin without damaging its structure.

Introduction

Hydrolysis-extraction of pectin from plant from raw materials is one of the most difficult and the most important processes of pectin obtaining technology.

Pectin in the cell walls is found in two basic forms: soluble pectin (pectin) and insoluble pectin (protopectin), which is a complex of cellulose with pectin. During hydrolytic processing of raw materials in the presence of catalysts, protopectin is more subjected to destruction, hemicellulose is less subjected to destruction, and cellulose undergoes minor destructive influence [2].

Protopectin hydrolysis is carried out by means of catalysts of various types: alkali (sodium hydroxide and potassium), mineral acids (sulfuric, hydrochloric, nitric, phosphoric), organic acids (oxalic, lemon), their different combinations and concentrations [2, 3], enzymes (cellulases, matserases, pectinases). Extraction of insoluble pectin from plant raw materials is held in two stages. During the first stage – under aqueous solutions of mineral and organic acids or other hydrolyzing reagents protopectin is hydrolyzed in pectin soluble form. During the second stage – soluble pectin molecules are diffused into the solution of the raw materials, i.e. extraction. Usually during the hydrolysis of plant raw materials in the presence of acid, these processes take place simultaneously. It should be noted that along with the basic protopectin hydrolysis reaction there is a number of adverse reactions related to the partial hydrolysis of the most polymer pectin chains with the formation of hydrolysis products of different molecular weight.

Traditional technology of pectin, regardless of the type of raw materials, is based on protopectin acid hydrolysis at raised temperature [3]. A number of factors, except the nature of hydrolyzing agent, influence the process of pectin hydrolysis-extraction: temperature, pH of the surrounding, duration of the process. Therefore, the study of kinetics of pectin hydrolysis-extraction from plant raw is relevant.

The purpose of the research was to investigate the kinetic regularities of hydrolysis-extraction process and establish optimal technological conditions of potato pectin extraction, bring mathematical dependence that will optimize the process of raw materials hydrolysis.

Materials and methods

During the study we used potato pulp (72% moisture), previously rinsed from starch.

Pectin extraction was carried through successive stages: acid-thermal hydrolysis-extraction using hydrochloric acid, separation of the liquid phase from the solid one, neutralization of pectin extract, pectin precipitation by ethanol, drying and milling of the ready pectin.

Number of hydrochloric acid solution, as hydrolytic factor, was added according to the set pH of hydrolysis mixture and taking into account hydrological module of hydrolysis. Hydrological module of hydrolysis (q), which is defined by the ratio of weight of the acid solution to the mass taken for hydrolysis of raw potato, was set equal to 2. Yield of the target product (%) was calculated relative to the mass of dry matter (DM).

According to literature data, reaction of hydrolysis-extraction of pectin substances from plant tissues occurs according to kinetic first-order equation. Kinetics equation used to describe hydrolysis [2, 5]:

$$\frac{dx}{d\tau} = K\left(\grave{a} - x\right) \tag{1}$$

where x – amount of substance reacted to a given point in time; a – original amount of substance; τ – time of hydrolysis; K – reaction rate constant.

The rate constant for this reaction is determined by the formula:

$$K = \frac{1}{\tau}\ln\frac{a}{a-x} \tag{2}$$

Unlike the reaction rate (υ), reaction rate constant K does not depend on concentration for this reaction at a given temperature and may characterize this reaction.

Results and discussion

By means of experiment planning a series of studies on the extraction of pectin from potato pulp through acid-thermal hydrolysis have been previously held, their results were analysed and taken into account, statistical processing of experimental data have been conducted that made it possible to determine the optimal parameters of the process [1].

With the aim to study the kinetics of the process of hydrolysis-extraction of pectin from the potato pulp a series of experiments for pectin extraction at different pH values (0,6; 1,6; 2) and at the temperature of 60, 70 80 i 90ºC are held. Ratio of liquid and solid phases during the process is as 2:1. Selection of parameters is conditioned by previous studies. During hydrolysis every 20 min samples were analyzed for ethanolprecipitated content of pectin in % by weight of dry matter. For this purpose, the liquid phase was separated, neutralized to pH 3.5 and precipitated pectin by ethanol if added in a ratio, respectively: 1:2. Pectin was dehydrated, dried to a constant weight and weighed. Based on the data received, kinetic curves of hydrolysis-extraction of pectin from the potato raw materials at different temperatures and pH were built (Fig.1).

Kinetic curves of hydrolysis-extraction of pectin from the potato raw materials are built according to yield index of ethanolprecipitated pectin (%) at each time and characterize protopectin hydrolysis of plant raw materials and the transition of soluble pectin into the extract. However, in the strict conditions of hydrolysis there are simultaneous and undesirable reactions connected with subsequent hydrolytic cleavage of pectin macromolecules. Reducing the molecular weight of pectin as a result of destruction leads to minimization of pectin yield which is precipitated by ethanol. That is why, if pH of the surrounding is 0.6 (Fig. 1 a) at the beginning of hydrolysis process, the yield of ethanolprecipitated pectin substance increases. The reaction of rate hydrolytic cleavage of protopectin is the largest. When the temperature increases the rate of all reactions increases, therefore at a temperature of 80° C and 90° C pectin yield reaches 40-50% by weight of dry matters. With the increase of duration of the process pectin yield decreases sharply, whereas reactions of depolymerization, deetherification and deacetylation of pectin macromolecules accelerate simultaneously [3], i.e. pectin destruction and therefore further reduction of the amount of ethanolprecipitated pectin substances [4].

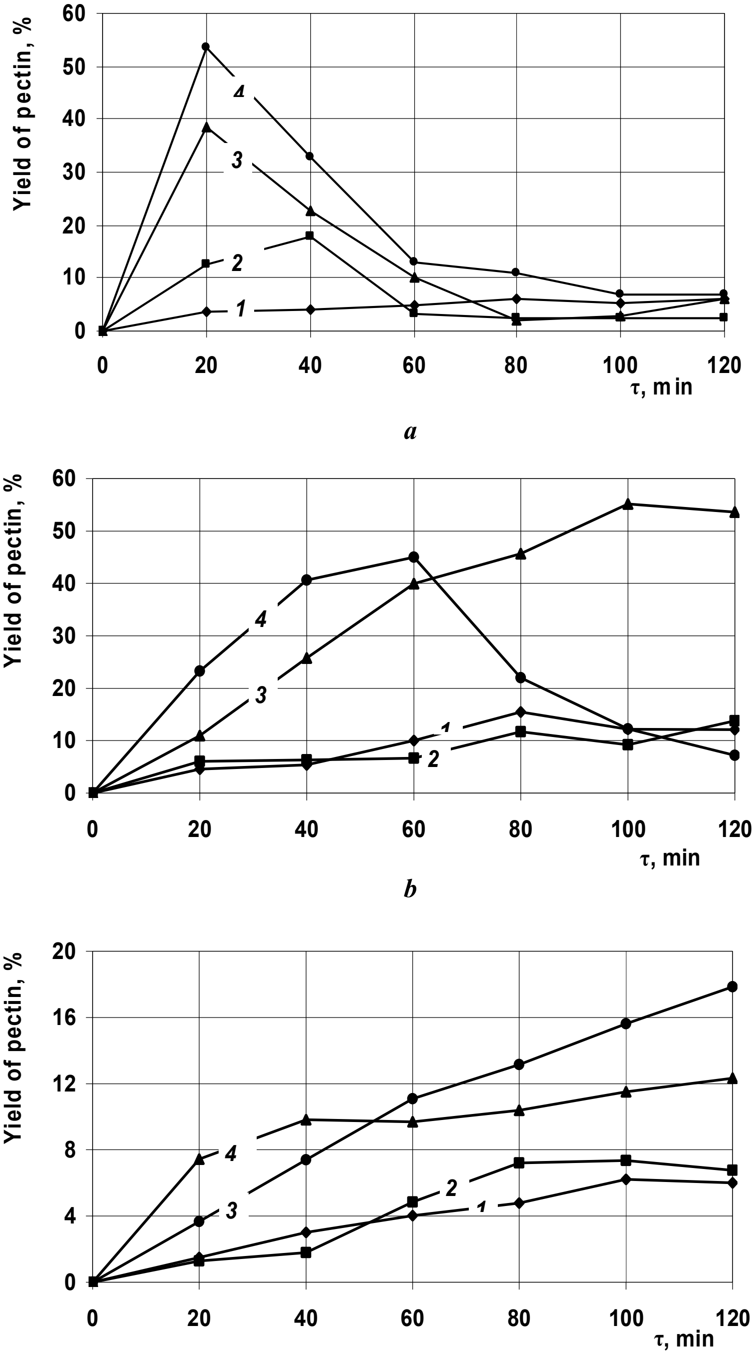

Fig.1. Kinetic curves of hydrolysis-extraction of pectin from the potato raw materials at different temperatures and pH:
a **– pH 0,6;** ***b*** **– pH 1,6;** ***c*** **– pH 2.** ***1*** **- 60°C;** ***2*** **- 70°C;** ***3*** **- 80°C;** ***4*** **- 90°C.**

At larger pH of the surrounding (pH 1,6) (Fig.1, b) the largest pectin yield at the temperature of 80° C and duration of the process 100 min. Reaction of insoluble protopectin hydrolysis also slows down at the temperatures of 60 and 70° C pectin yield increases slightly. At high temperature (90° C) destructive processes prevail and pectin yield at duration of the process over 60 minutes reduces. Increasing of the pH of the surrounding to 2 significantly reduces the rate of protopectin hydrolysis reaction (Fig. 1, c). With the increase of duration of the process to 120 min. the increase of pectin yield is only to 18%. Thus, it is not effective for hydrolysis of this raw material to conduct a process at pH 2.

Reaction rate constant is a constant at a given temperature and may characterize this reaction. The largest reaction rate constant of protopectin hydrolysis is while using hydrochloric acid, and the lowest – while using lemon acid. Furthermore, the kinetic constant is different for different raw materials [2]. For a more complete understanding of the reaction rate of protopectin hydrolysis of potato raw materials at different temperatures and pH we have calculated value of the reaction rate constant in each period by the formula 2.

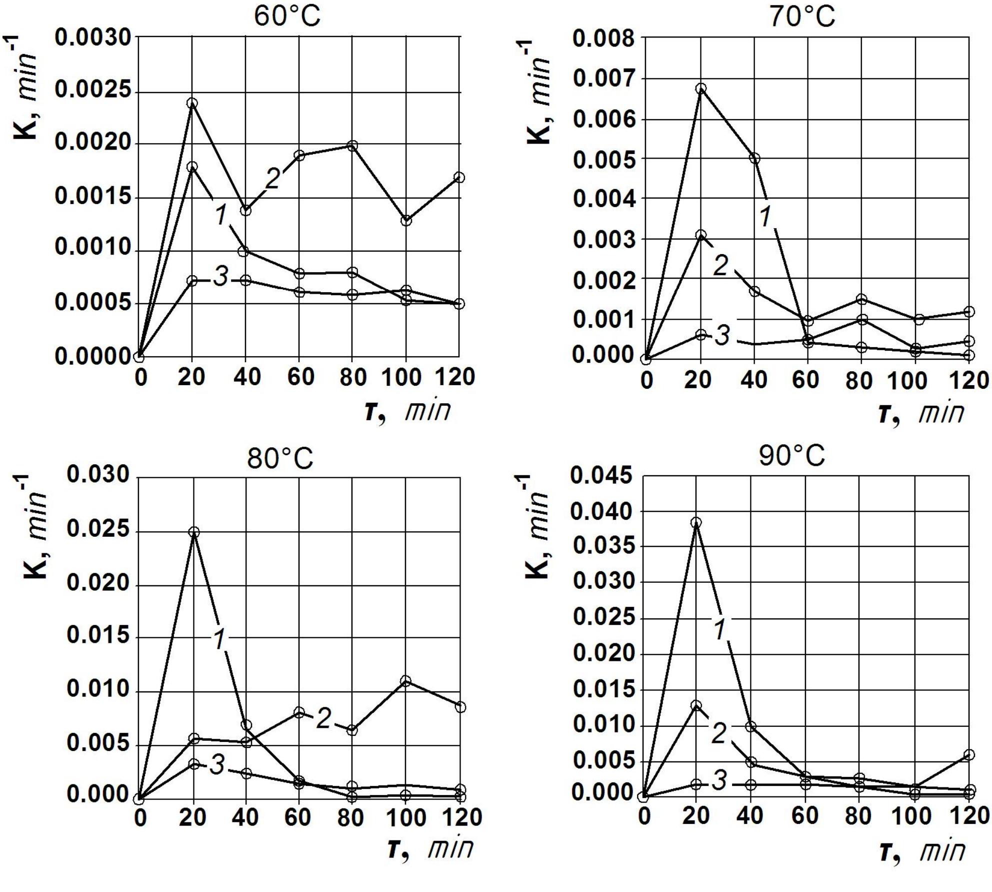

Fig.2 Dependence of the rate constant of hydrolysis-extraction of pectin substances of potato raw materials on temperature.
1 – pH 0.6; *2* – pH 1.6; *3* – pH 2.0

As we can from the Fig. 2 at increasing temperature of process to 80° C value of the reaction rate constant increases, however, at further temperature increase to 90° C (excluding pH 0,6) a decrease in the hydrolysis rate constant because of the increasing of destructive processes takes place. Such fluctuations in the values of kinetic constants indicate a course of parallel reactions that significantly affect the course of the main reaction reducing yield and quality of pectin. When reducing pH from 2 to 0.6 the rate of hydrolysis increases. However, this affects the quality of pectin indices. Because of the acid activity increasing and pH lowering, the hydrolysis rate of protopectin and other compounds (starch, protein, hemicellulose, cellulose) increases [4]. Macromolecular hydrolysis products of these substances are co-precipitated with pectin, thus increasing the overall yield, but the pectin purity (uronid component) decreases. Thus, pH of the surrounding has the greatest impact on reaction rate of protopectin hydrolysis. For low acid content as the process catalyst, even at high temperatures, the reaction rate is not significant. Experimental data processing, selection of equations, calculation and refinement of coefficients of these equations were implemented by means of the method of least squares. As a result, the following equations of local optimization criteria were obtained for each value of pH: 1 – for pH 0,6; 2– for pH 1,6; 3 – for pH 2,0.

$$P(t,\tau) = e^{37,217-2,264\cdot t+0,038\cdot t^2-2,64\cdot 10^{-5}\cdot t^3} \cdot \tau^{6,54-0,28\cdot t+5\cdot 10^{-3}\cdot t^2-2,65\cdot 10^{-5}\cdot t^3} \times$$
$$\times e^{(-2,56+0,13\cdot t-2,09\cdot 10^{-3}\cdot t^2+1,062\cdot 10^{-5}\cdot t^3)\cdot\tau+(0,028-1,27\cdot 10^{-3}\cdot t+1,89\cdot 10^{-5}\cdot t^2-9,065\cdot 10^{-8}\cdot t^3)\cdot\tau^2} \quad (1)$$

$$P(t,\tau) = e^{-117,4+4,64\cdot t-0,062\cdot t^2+2,79\cdot 10^{-4}\cdot t^3} \cdot \tau^{-14,632+0,67\cdot t-9\cdot 10^{-3}\cdot t^2+4,028\cdot 10^{-5}\cdot t^3} \times$$
$$\times e^{(9,86-0,4\cdot t+5,428\cdot 10^{-3}\cdot t^2-2,4\cdot 10^{-5}\cdot t^3)+(-0,05+1,86\cdot 10^{-3}\cdot t-2,46\cdot 10^{-5}\cdot t^2+1,06\cdot 10^{7}\cdot t^3)\cdot\tau^2} \quad (2)$$

$$P(t,\tau) = e^{348,96-14,69\cdot t+0,2\cdot t^2-9,01\cdot 10^{-4}\cdot t^3} \cdot \tau^{52,97-2,13\cdot t+0,03\cdot t^2-1,31\cdot 10^{-4}\cdot t^3} \times$$
$$\times e^{(-10,27+0,43\cdot t-0,006\cdot t^2+2,65\cdot 10^{-5}\cdot t^3)\cdot\tau+(0,05-0,002\cdot t+2,96\cdot 10^{-5}\cdot t^2-1,34\cdot 10^{-7}\cdot t^3)\cdot\tau^2} \quad (3)$$

Experimental data processing, selection of equations, calculation and refinement of coefficients of these equations were performed by means of package of applied programs Mathcad Professional 2000 using the method of least squares. Based on the data obtained according to yield of pectin, using the program of process optimization lines of level of generalized optimization criterion were received, which allow finding the optimal parameters values of the process of hydrolysis-extraction of pectin from the potato raw materials (Fig. 3).

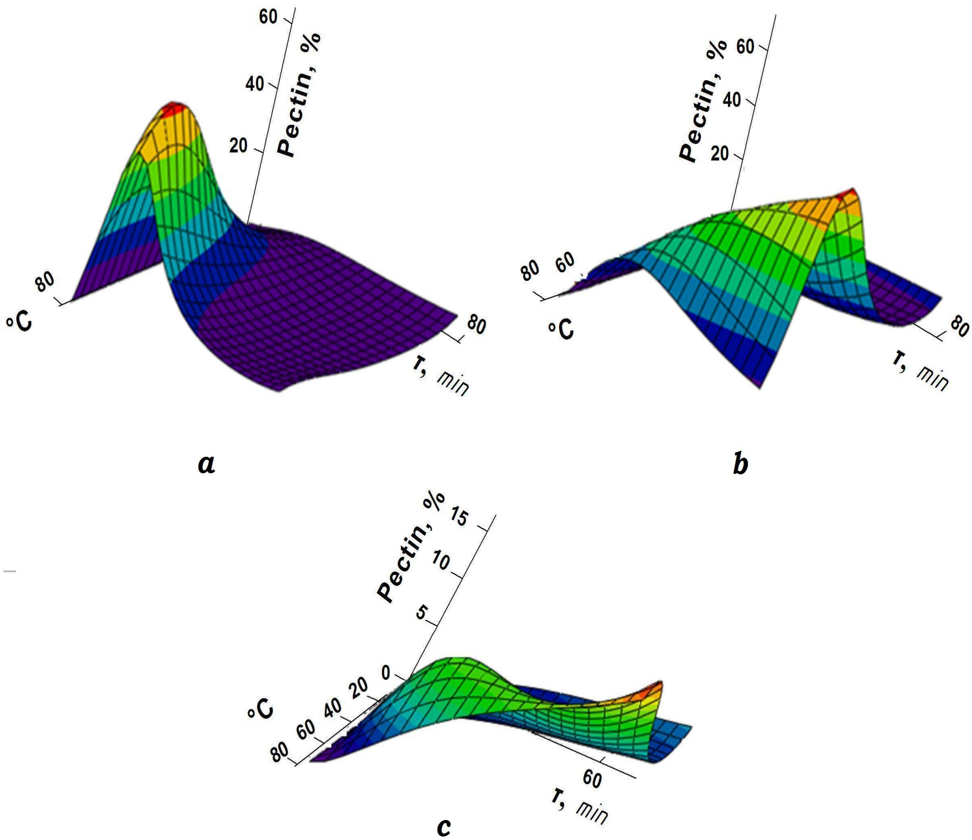

Fig. 3. Response area of optimal parameters of pectin extraction while changing the duration and temperature of the process:
a - pH 0,6; b - pH 1,6; c - pH 2,0

By means of a mathematical model the parameters of optimal technological regime of pectin extraction from potato pulp are defined: temperature of 75°C, pH of hydrolysis weight – 1,6; hydrolysis duration – 72 min. Under these parameters pectin extraction is maximum without damaging its structure. Also, these data are consistent with the previous researches.

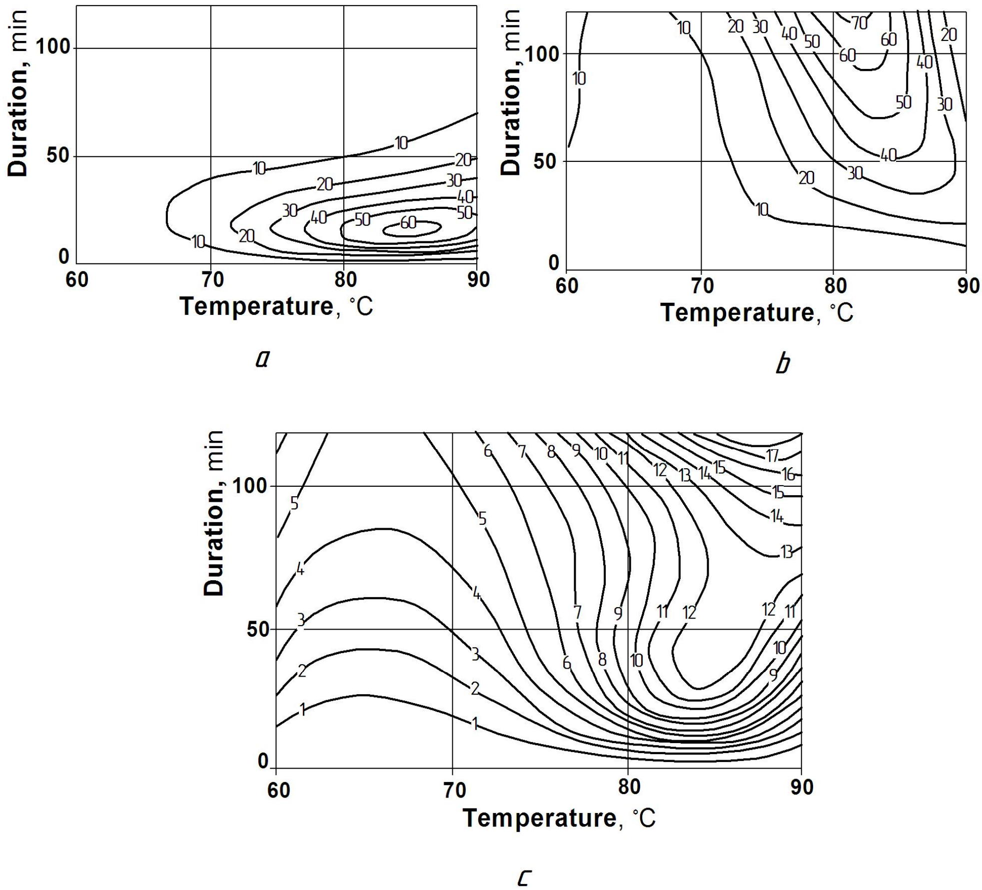

Fig. 4. Lines of optimal parameters level of pectin extraction while changing the duration and temperature of the process:
a - pH 0,6; b - pH 1,6; c - pH 2,0

Conclusion

On the basis of experimental and theoretical studies the optimal parameters of hydrolysis-extraction pectin from potato raw materials are determined: temperature of 75°C, pH of hydrolysis weight – 1,6; hydrolysis duration – 72 min. Mathematical model of this process is elaborated.

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