Kinetics of protopectin in decomposition in vegetable raw material under high temperatures and pressures

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Abstract. The kinetics of the catalytic decomposition of protopectin (PP) of pomace, peach, pumpkin, citrus, rhubarb, sunflower heads (SH) and beet pulp in HCl solution at pH = 2.0 and T = 120 °C and pressure 1.5 atm. The decay products of PP are separated according to the previously developed method into fractions: microgel (MG), pectin substances (PS) and oligosaccharides (OS). The experimental data were processed on the basis of the idea of a parallel and successive irreversible chemical reaction of the first order, the rate constants for the decay of the PP into the corresponding components-MG, PS, and OS, were evaluated, conclusions were made about the advantages and disadvantages of the high-temperature process.

1. Formulation of the problem
The effect of external parameters on the kinetics of chemical reactions in the liquid and solid states is mainly due to the influence of neighboring molecules on the change in the shape and dimensions of the activated complex, which at the macroscopic level leads to the dependence of the reaction rate constant (k) on the pressure and the aggregate state of the substance [1]. We have demonstrated in a number of works, on the example of the catalytic decomposition of protopectin (PP) of various sources, a dramatic increase in the rate of the hydrolysis reaction with increasing pressure and temperature, and, most importantly, simultaneous improvement in the quality of the target product, expressed in an increase in the content of galacturonic acid (GA) residues in pectin macromolecules and an increase in their molecular weight [2-6].

The complexity of raw materials composition and its interactions with reagents significantly complicates the problem about influence of the state parameters (temperature, pressure, composition) on physico-chemical properties of products. The available experimental and computational-model studies [7-13] don’t solve this problem - due to the insufficient complexity of the studied systems, incompleteness of the required physico-chemical parameters, etc.

In connection with this, the purpose of this work was to study the decay of PP of different plant raw materials under the influence of high temperature and pressure, and also to estimate the kinetic parameters of the corresponding process.
2. Methodology

In this paper, squeezes of apples, pumpkins, stems and leaves of rhubarb, peach, beet pulp, mandarin crusts and sunflower heads (SH) were used as raw materials. Hydrolysis-extraction of PP was carried out with steam at a temperature of 120 °C, pH = 2.0, a hydro module of 1:20, varying the pressure from 1.5 to 3.0 atm. and the duration of the process is from 3 to 10 minutes [2-6]. Hydrolyzate solutions were separated from the cellulose (CL), and the extract obtained was divided into three fractions conventionally named: microgel (MG), pectin substances (PS) and oligosaccharides (OS) [14, 15].

The content of the elements of galacturonic acid (GA) in pectin substances and the degree of esterification of carboxyl groups of GA (DE) were determined by the methods described in [16, 17], respectively.

3. Results and Discussion

Figure 1 shows the kinetics of yield of MG for different types of plant raw materials. Attention is drawn to the fact that, at a high temperature (120 °C) and a pressure of 1.5 atm, the extreme kinetics of the yield of MH, which is so characteristic of the hydrolysis-extraction process at atmospheric pressure and temperature of 85 °C (low-temperature process) [14, 15] except for KP and pumpkin squeezes. For them, the regularity of the yield of MH remains similar in form to the low-temperature process, but decreases in magnitude of the yield. Another feature of high-temperature hydrolysis of PP is a sharp decrease in the duration of the process, which terminates in almost 10 minutes (three hours in the low-temperature process), and as the pressure and temperature increase, the process accelerates further.

![Figure 1. The kinetics of the yield of MG at T = 120 °C and P = 1.5 atm. for various raw materials. The output of the MG is calculated with respect to the initial mass of the object under study.](image)

It is also important that the quality of the obtained PS, judging by the content of GA in the composition of the links of PS macromolecules, under chosen reaction conditions for all types of raw materials is sufficiently high [2-6].

The absence of a maximum on the graph of the kinetics of the MG reaction may be due not to the
change in the mechanism of the sequential reaction characteristic of the low-temperature process at high temperature and pressure [14, 15], but with the acceleration of the reaction and the shift of the maximum to the initial region of the yield of MG. Proceeding from this, the data presented in Fig. 1 do not indicate a lack of a maximum in the kinetics of the yield of MG, but, on the contrary, confirm its presence, in the form of its right krill. This means that the rate constant of the successive decay of the MG into the PS and OS at a high temperature and pressure increases sharply, in comparison with the rate of decay of the PP by MG. In addition, the low yield of MH (in the 0-5% range, without taking into account KP and pumpkin) gives reason to consider the decay process of PP, not in the form of a sequential PP-MG-PV reaction, but in the form of a parallel decay reaction of PP to PS and OS.

Indeed, as can be seen in Fig. 2, the specific rate of decomposition of the propectin of the studied plant materials on the MG (k (MG)) is much smaller than the corresponding decay parameter of the PP on the PS (k (PS)) and the OS (k (OS)). Among the studied objects, the greatest value of k (MH) is observed for a sunflower basket. This is natural, since, due to the high concentration of calcium ions in the composition of MG CL, the pectin chains are more crosslinked than other objects, and the subsequent disintegration of MG SH into the corresponding components becomes difficult.

![Figure 2. Kinetics of the decay of PP into fractions of MG, PS and OS for various types of plant raw materials. (The figure shows successively the value of k and the measurement error Δk, corresponding to the decay of the PP into MG, SH and OS).](image)

Figure 2 also shows that the value of k in the decay of PP to PS (k (PS)) is not the same for different types of plant material. The greatest value of this parameter is achieved with the decay of the peach and PP, followed by pomace, citrus, rhubarb and beet. The value of k (PS) for a pumpkin is practically zero.

Finally, the corresponding objects of investigation differ significantly from each other in terms of the value of the specific rate of decay of the PP on the OS (k(OS)). The greatest value of k (OS) is observed for pumpkin, then, in descending order, beet, peach, citrus, rhubarb, pomace and CL.

Comparing the values of k (MG), k (PS) and k (OS) with each other, it can be concluded that under the conditions of high-temperature hydrolysis of various types of plant raw materials, the most optimal component ratio is achieved for KP (the maximum yield of PV with minimum MG and OS content) and the worst - in the decay of the pumpkin PP (the highest number of OS in the almost complete
absence of fractions of MG and PS).
Proceeding from this, the kinetic parameters of the decay of the PP SH with a change in pressure and a fixed temperature (120 °C) can be analyzed on the basis of the kinetics of the sequential PP-MG-PS reaction, in the manner described by us in [14]. The Table 1 shows the dependence of the constants $k_1$ and $k_2$ on the pressure.

| $P$, °K | $k_1$, мин$^{-1}$ | $k_2$, мин$^{-1}$ |
|---------|-----------------|------------------|
| 1.5     | 0.0534          | 0.4967           |
| 2       | 0.0417          | 0.5385           |
| 3       | 0.0295          | 0.5530           |

The dependence of the rate of the chemical reaction on the pressure in the liquid state, which can be attributed to the particle swells swelling in the water, can be described on the basis of the Evans-Polanyi theory [16], within the framework of the free-volume model as a bulk-activated process. According to this idea, when the activated complex is formed, the initial volume of the molecule $V_0$ varies by the activation volume $\Delta V$.

$$
\frac{\partial (\ln K)}{\partial p} = -\frac{\Delta V \neq}{RT},
$$

where $p$ is the external pressure, $R$ is the universal gas constant.

Based on the data in the table, we calculated the values of $\ln k_1$ and its derivatives from the pressure (Fig. 3), and using the equation (1), the values of $\Delta V \neq$ at different pressures were calculated.

Figure 3 shows that the change in $\ln k_1$ from pressure, contrary to the predictions of the Evans-Polanyi theory (equation (1)), is not linear, but is described by the second-order equation $y = 0.1002x^2 - 0.8475x - 1.8836$, with a correlation coefficient equal to unit. The nonlinearity of this relationship is also found for numerous monomolecular reactions in the liquid and solid state, and the magnitude of the effect itself depends on the nature of the solvent, temperature and pressure [19, 20]. In this case, it is important that the pressure dependence of $d\ln k_1/dP$ is linear and is described by the equation $y =$
0.2004x – 0.8475 with the correlation coefficient equal to unity (Fig. 3). This made it possible to calculate the amount of activation volume (ΔV ≠) equal to -22.34, -19.40 and -13.51 cm³/g-feed at a pressure of 1.5, 2.0 and 3.0 atm, respectively. The values obtained are high and, most likely, indicate the presence of a sufficiently large activation volume during the course of the decomposition reaction of PP in water vapor.

4. Conclusion
Thus, experimental data on protopectin decay of a plant cell at high temperature and pressure indicate a significant acceleration of the reaction velocities, especially in

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