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Mathematical modeling of protopectin decomposition under high temperatures and pressures

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Abstract. On the basis of experimental data on the influence of the parameters of the process of hydrolysis-extraction of plant raw materials under the influence of high temperature and pressure, a full-factor mathematical protopectin decomposition model connecting the input (type of source of raw materials, process and parameters of the hydrolysis-extraction process) and output (output and physico-chemical parameters of each decomposition product of the PP) parameters. As a model of the effect of any hydrolysis-extraction parameter, a polynomial of the form is chosen: $y = \sum_{k=0}^{5}(\sum_{m=0}^{5}(\sum_{n=0}^{5}p_{mn}^kT_i^m)P^n)T^k$. To determine the coefficients, systems of linear algebraic equations are applied. For each pair of variables by the least squares method, using the accuracy functions, a number of coefficients were found, the total number of which was 385. This mathematical model formed the basis for the software "PEKTINI", which allows to identify optimal conditions for hydrolysis-extraction of protopectin at the design stage and direct the process of obtaining pectic polysaccharides in the direction of increasing yield and optimizing the quality.

1. Formulation of the Problem

In general, hydrolysis-extraction is a key stage determining the yield and quality of pectin. At the same time, the theoretical foundations of this process have not been adequately studied at present. There is no integrated model of the process, taking into account both the characteristics of plant raw materials, and the possibility of controlled extraction. In order to assess the influence of various factors on the individual stages of the hydrolysis-extraction process and their combined effect as a whole, it is necessary to express these relationships using mathematical models that will allow us to calculate the parameters of the process and find the optimal regimes for its.

A study of the extraction process in the solid-liquid system in the food industry is devoted to the work of many researchers. The main drawback of these works is that many of them are empirical and experimental, they consider separately hydrodynamic, thermal and mass-exchange processes and do not take into account external effects [1-6].

The more general computational, theoretical and model methods for investigating of interaction processes in multicomponent systems of different nature [7-13] don’t allow to solve this problem too – because of the complexity of account (for modeling) of all the main processes, lack of parameters (thermodynamic, kinetic and other characteristics) required for the application of these methods.
Therefore, it is necessary to solve a complex problem, allowing to take into account all the processes and factors that are operating.

2. Methodology
The basis of the mathematical model is the results of experimental studies of the decomposition of protopectin from various sources of raw materials. Hydrolysis-extraction was carried out by the developed method under the influence of high temperature and pressure. The duration of the process varied from 3 to 10 minutes, pressure from 1.5 to 3.0 atm., Temperature from 100 to 140°C [14-18]. The hydrolyzate solutions were separated from the cellulose, the extract obtained was divided into three fractions, conventionally named: microgel, pectin substances and oligosaccharides [19, 20]. For the input parameters were taken: the type of raw materials, the degree of maturity, the parameters of the hydrolysis-extraction process (pressure, temperature, hydromodule, hydrolyzing agent pH, duration of hydrolysis-extraction). Over the weekend, the yield of the target products, the content of galacturonic acid units in them, the molecular weight parameters, and the degree of esterification.

3. Results and Discussion
The effectiveness of the hydrolysis-extraction method developed depends on the temperature, pressure, and duration of the process. On the basis of experimental data, a full-factor model "PECTIN" was constructed [21, 22]. As a model of any hydrolysis parameter, a polynomial of the form is chosen:

\[ y = \sum_{k=0}^{5} \left( \sum_{m=0}^{5} \left( \sum_{n=0}^{5} \beta_{mn} T^n \right) P^m \right) t^k, \]

where \( m = \overline{0, 5} \).

To determine the coefficients \( \{\beta_{mn}\} \) applied, the procedure described below.

1. At the first stage, we represent the parameter \( y \) in the form:

\[ y_{ij} = \sum_{k=0}^{5} a_{jk}^{(i)} t^k, \]

where: \( i = \overline{1, 4} \) – temperature option number, \( T = \{100, 120, 130, 140\} \);
\( j = \overline{1, 3} \) - pressure variant number, \( P = \{1.5; 2; 3\} \);
\( k = \overline{0, 5} \) - indices of the model coefficients (1);
the variable \( t \) – is the duration of the hydrolysis process, takes values from a given set options - \( t \in \{3, 5, 7, 10\} \).

For each pair \((i, j)\) by the method of least squares coefficients \( \{a_{jk}^{(i)}\} \), using the accuracy functional:

\[ J_{ij} = \sum_{q=1}^{4} \left( y_{ij}^{(q)*} - \sum_{k=0}^{5} a_{jk}^{(i)} t^k \right)^2 \rightarrow \min \] by coefficients \( a_{jk}^{(i)} \).

where the index \( q \) – is the number of the variant of the duration of hydrolysis \( q = \overline{1, 4} \).

Coefficients \( \{a_{jk}^{(i)}\} \) are determined from the solution \( i \cdot j = 12 \) systems of linear algebraic equations (SLAE), resulting in the following set of coefficients (Table 1):

|   | \( P_1 \) | \( P_1 \) | \( P_1 \) | Coefficients \( a_{jk}^{(i)} \) |
|---|---|---|---|---|
| \( T_1 \) | \( y_{11} \) | \( y_{12} \) | \( y_{13} \) | \( \{a_{1k}^{(1)}\} \) |
| \( T_2 \) | \( y_{21} \) | \( y_{22} \) | \( y_{23} \) | \( \{a_{2k}^{(2)}\} \) |
| \( T_3 \) | \( y_{31} \) | \( y_{32} \) | \( y_{33} \) | \( \{a_{3k}^{(3)}\} \) |
| \( T_4 \) | \( y_{41} \) | \( y_{42} \) | \( y_{43} \) | \( \{a_{4k}^{(4)}\} \) |
For each pair \((i, j)\) SLAE (1) are obtained by equating the partial derivative of the functional (3) with respect to \(a_{jk}^{(i)}\) to zero:

\[
\begin{align*}
\frac{\partial I_{ij}}{\partial a_{j0}^{(i)}} &= \sum_{q=1}^{4} F_{iq} \cdot \frac{\partial F_{q}}{\partial a_{j0}^{(i)}} = \sum_{q=1}^{4} F_{q} = 0 \\
\frac{\partial I_{ij}}{\partial a_{j1}^{(i)}} &= \sum_{q=1}^{4} F_{iq} \cdot \frac{\partial F_{q}}{\partial a_{j1}^{(i)}} = \sum_{q=1}^{4} F_{q} \cdot t_{q} = 0 \\
\frac{\partial I_{ij}}{\partial a_{j2}^{(i)}} &= \sum_{q=1}^{4} F_{iq} \cdot \frac{\partial F_{q}}{\partial a_{j2}^{(i)}} = \sum_{q=1}^{4} F_{q} \cdot t_{q}^2 = 0 \\
\frac{\partial I_{ij}}{\partial a_{j5}^{(i)}} &= \sum_{q=1}^{4} F_{iq} \cdot \frac{\partial F_{q}}{\partial a_{j5}^{(i)}} = \sum_{q=1}^{4} F_{q} \cdot t_{q}^5 = 0
\end{align*}
\]

where  \(F_{q} = \left(y_{j}^{(i)*} - \sum_{k=0}^{5} a_{jk}^{(i)} t_{q}^k \right)\).

Solving system (4) alternately, the values of the coefficients \(\{a_{jk}^{(i)}\}\) were defined, the total number of which is 72.

2. The next step is the build procedure for each \(T_{i}\) dependence on \(a_{k}^{(i)} = a_{k}^{(i)}(P)\). This problem is solved by a method similar to that described in A.1. For this, the coefficients are expressed by the dependence:

\[
a_{k}^{(i)} = \sum_{m=0}^{5} \alpha_{km}^{(i)} p_{m}^{(i)}
\]

Using the accuracy functional:

\[
J_{ik} = \sum_{j=1}^{3} \left( a_{km}^{(i)} - \sum_{m=0}^{5} \alpha_{km}^{(i)} p_{m}^{(i)} \right)^2 \rightarrow \min \text{by coefficients } \alpha_{km}^{(i)}.
\]

Denoting the expression in the parentheses of the accuracy functional as:

\[
F_{j} = \left(a_{k}^{(i)*} - \sum_{m=0}^{5} \alpha_{km}^{(i)} p_{m}^{(i)} \right)^2.
\]

For each pair \((i, k)\), differentiating \(J_{ik}\) with respect to the variables \(a_{km}^{(i)}\) and, equating these partial derivatives to zero, are obtained \(i \cdot k = 24\) SLAE, from the solution of which a set of coefficients of the relation (5) (Table 2):

**Table 2. Coefficients \(\alpha_{km}^{(i)} = \sum_{m=0}^{5} a_{km}^{(i)} p_{m}^{(i)} T_{m}^{(i)}\)**, defined by the SLAE decision

| \(T_{1}\) | \(a_{k}^{(1)}\) | \(a_{k0}^{(1)}\) | \(a_{k1}^{(1)}\) | \(a_{k2}^{(1)}\) | \(a_{k3}^{(1)}\) | \(a_{k4}^{(1)}\) | \(a_{k5}^{(1)}\) |
| --- | --- | --- | --- | --- | --- | --- | --- |
| \(T_{2}\) | \(a_{k}^{2}\) | \(a_{k0}^{(2)}\) | \(a_{k1}^{(2)}\) | \(a_{k2}^{(2)}\) | \(a_{k3}^{(2)}\) | \(a_{k4}^{(2)}\) | \(a_{k5}^{(2)}\) |
| \(T_{3}\) | \(a_{k}^{3}\) | \(a_{k0}^{(3)}\) | \(a_{k1}^{(3)}\) | \(a_{k2}^{(3)}\) | \(a_{k3}^{(3)}\) | \(a_{k4}^{(3)}\) | \(a_{k5}^{(3)}\) |
| \(T_{4}\) | \(a_{k}^{4}\) | \(a_{k0}^{(4)}\) | \(a_{k1}^{(4)}\) | \(a_{k2}^{(4)}\) | \(a_{k3}^{(4)}\) | \(a_{k4}^{(4)}\) | \(a_{k5}^{(4)}\) |

SLAE for finding the set of coefficients \(\{\alpha_{km}^{(i)}\}\) have the form:
\[
\frac{\partial J_{ik}}{\partial \alpha_{k0}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k0}^{(j)}} = \sum_{j=1}^{3} F_j = 0
\]
\[
\frac{\partial J_{ik}}{\partial \alpha_{k1}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k1}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \mathbf{P}_j = 0
\]
\[
\frac{\partial J_{ik}}{\partial \alpha_{k2}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k2}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \mathbf{P}_j^2 = 0
\]
\[
\frac{\partial J_{ik}}{\partial \alpha_{k3}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k3}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \mathbf{P}_j^3 = 0
\]
\[
\frac{\partial J_{ik}}{\partial \alpha_{k4}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k4}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \mathbf{P}_j^4 = 0
\]
\[
\frac{\partial J_{ik}}{\partial \alpha_{k5}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \frac{\partial F_j}{\partial \alpha_{k5}^{(j)}} = \sum_{j=1}^{3} F_j \cdot \mathbf{P}_j^5 = 0
\]

(8)

Total number of coefficients \( \alpha_{km}^{(i)} \) is 144.

3. The next step is the build procedure for each \( \alpha_{km}^{(i)} \) dependence on \( \alpha_{km}^{(i)}(T) \). This problem was solved by a method similar to those described in A.1 and A.2. For this, the coefficients are expressed by:

\[
\alpha_{km} = \sum_{n=0}^{5} \beta_{mn}^{(k)} T^n
\]

(9)

Introducing the accuracy functional:

\[
J_{km} = \sum_{l=1}^{4} \left( \alpha_{km}^{(i)*} - \sum_{n=0}^{5} \beta_{mn}^{(k)} T_i^n \right)^2 \rightarrow \min \text{ (by coefficients } \beta_{mn}^{(k)})
\]

(10)

Denoting the expression in the parentheses of the accuracy functional as:

\[
F_l = \left( \alpha_{km}^{(i)*} - \sum_{n=0}^{5} \beta_{mn}^{(k)} T_i^n \right)^2,
\]

(11)

For each pair \((k, m)\), with the solution of which many coefficients of the relation differentiating \( J_{km} \) on variables \( \beta_{mn}^{(k)} \), and equating these partial derivatives to zero, we obtain \((m + 1) \cdot (k + 1) = 36\) SLAE with the solution of which is the set of coefficients of the relation (9) (Table 3):

**Table 3.** Coefficients \( a_{km}^{(i)} = \sum_{n=0}^{5} \alpha_{km}^{(i)} P_{nm} \), defined by the SLAE solution

| \( a_k^{(i)} \) | \( \beta_{00}^{(k)} \) | \( \beta_{01}^{(k)} \) | \( \beta_{02}^{(k)} \) | \( \beta_{03}^{(k)} \) | \( \beta_{04}^{(k)} \) | \( \beta_{05}^{(k)} \) |
| \( a_k^{(1)} \) | \( \beta_{10}^{(k)} \) | \( \beta_{11}^{(k)} \) | \( \beta_{12}^{(k)} \) | \( \beta_{13}^{(k)} \) | \( \beta_{14}^{(k)} \) | \( \beta_{15}^{(k)} \) |
| \( a_k^{(2)} \) | \( \beta_{20}^{(k)} \) | \( \beta_{21}^{(k)} \) | \( \beta_{22}^{(k)} \) | \( \beta_{23}^{(k)} \) | \( \beta_{24}^{(k)} \) | \( \beta_{25}^{(k)} \) |
| \( a_k^{(3)} \) | \( \beta_{30}^{(k)} \) | \( \beta_{31}^{(k)} \) | \( \beta_{32}^{(k)} \) | \( \beta_{33}^{(k)} \) | \( \beta_{34}^{(k)} \) | \( \beta_{35}^{(k)} \) |
| \( a_k^{(4)} \) | \( \beta_{40}^{(k)} \) | \( \beta_{41}^{(k)} \) | \( \beta_{42}^{(k)} \) | \( \beta_{43}^{(k)} \) | \( \beta_{44}^{(k)} \) | \( \beta_{45}^{(k)} \) |
| \( a_k^{(5)} \) | \( \beta_{50}^{(k)} \) | \( \beta_{51}^{(k)} \) | \( \beta_{52}^{(k)} \) | \( \beta_{53}^{(k)} \) | \( \beta_{54}^{(k)} \) | \( \beta_{55}^{(k)} \) |

SLAE for finding the set of coefficients \( \beta_{mn}^{(k)} \) have the form:
\[
\begin{align*}
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m0}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m0}} = \sum_{i=1}^{4} F_i = 0 \\
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m1}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m1}} = \sum_{i=1}^{4} F_i \cdot T_i = 0 \\
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m2}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m2}} = \sum_{i=1}^{4} F_i \cdot T_i^2 = 0 \\
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m3}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m3}} = \sum_{i=1}^{4} F_i \cdot T_i^3 = 0 \\
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m4}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m4}} = \sum_{i=1}^{4} F_i \cdot T_i^4 = 0 \\
\frac{\partial J_{km}}{\partial \beta^{(k)}_{m5}} &= \sum_{i=1}^{4} F_i \cdot \frac{\partial F_i}{\partial \beta^{(k)}_{m5}} = \sum_{i=1}^{4} F_i \cdot T_i^5 = 0
\end{align*}
\]

Total number of coefficients \( \beta_{mn}^{(k)} \) is – 216.
\[
y = \sum_{k=0}^{5} \left( \sum_{m=0}^{4} \left( \sum_{n=0}^{5} \beta_{mn}^{(k)} T_i^n \right) p^m \right) t^k,
\]

where \( m = 0.5 \). As a result of the research, the PEKTINI software was developed, which allows predicting the yield and quality of pectin.

In Figures 1-4, as an example of program operation, a comparison of the experimental values of the yield of pectin with the calculated models obtained as a result of the work.

**Figure 1.** The yield of pectin at \( P = 2.0 \) atm. depending on the temperature and duration of the hydrolysis-extraction process (experimental data); \( T_1 – 100^\circ C, \ T_2 – 120^\circ C, \ T_3 – 130^\circ C, \ T_4 – 140^\circ C \).

**Figure 2.** The yield of pectin at \( P = 2.0 \) atm. depending on the temperature and duration of the hydrolysis-extraction process (calculated data); \( T_1 – 100^\circ C, \ T_2 – 120^\circ C, \ T_3 – 130^\circ C, \ T_4 – 140^\circ C \).
Figure 3. The yield of pectin at 120 °C, depending on the pressure and duration of the hydrolysis-extraction process (experimental data); P₁ – 1.5 atm, P₂ – 2 atm, P₃ – 3 atm

Figure 4. The yield of pectin at 120 °C, depending on the pressure and duration of the hydrolysis-extraction process (calculated data); P₁ – 1.5 atm, P₂ – 2 atm, P₃ – 3 atm

4. Conclusions

Thus, the developed mathematical model of protopectin decomposition under the influence of high temperature and pressure and software allow at the design stage to identify optimal technological conditions, predict the yield and physico-chemical parameters of the target products, and significantly optimize the process of obtaining high-quality pectin.

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