

KINETIC FEATURES OF THE HYDROLYSIS OF THE
HEMICELLULOSES OF SUNFLOWER SEED HUSKS

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A kinetic analysis has been made of the hydrolysis reactions of sunflower seed husks. The presence of six kinetically homogeneous fractions in the hemicellulose complex has been shown. The kinetic characteristics and the amounts of each fraction have been determined.

The basic possibility has been shown in [1] of the use of a mathematical-graphical method for the kinetic analysis of a polycomponent system of hemicelluloses (HCs), which represents the hydrolysis of the hemicellulose complex as a system of n parallel irreversible first-order reactions with a common product, $P_i \xrightarrow{k} G$. In contrast to known and widely used methods for the kinetic analysis of HCs with the arbitrary division of the curve $\ln P = f(t)$ (where P is the amount of unhydrolyzed polysaccharides (PSs) at time t) into 2-3 sections considered to a first approximation as linear [2], the proposed method is based on the assumption that even when only two kinetically significant fractions of HCs are present in the system the kinetic curve $\ln P = f(t)$ assumes a linear nature only after the completion of the hydrolysis of the most reactive fraction. On the combined hydrolysis of the fractions, the relationship has the form of a curve, which does not permit an adequately based determination of the effective hydrolysis rate constants and the other kinetic characteristics of the process.

The essence of the method used in the present work consists in the successive elimination from the semilogarithmic anamorphosis of the kinetic curve in $P = f(t)$ of the contributions of the reactants P_i in the order of increasing values of their hydrolysis rate constants. This enables one to give a strict evaluation of the kinetic homogeneity of the HC complex and a quantitative characterization of the groups (fractions) of polysaccharides with close reactivities.

In the present paper we give a kinetic analysis of the hydrolysis of sunflower seed husk HCs.

Figure 1 shows semilogarithmic anamorphoses of the kinetic curves of the hydrolysis of sunflower seed husk HCs. As can be seen, after the lapse of a certain time the relation $\ln P = f(t)$ assumes a linear nature. By extrapolating the terminal linear part of the kinetic curve to $t = 0$ the initial amount of the last, least reactive, n -th fraction of the HCs ($P_{n,0}$) was obtained. The rate constant of the hydrolysis of the n -th fraction (k_n) was calculated from the slope of the linear section. The amount of the n -th fraction at each experimental point ($P_{n,t}$) was found from the equation

$$P_{n,t} = P_{n,0} \cdot e^{-k_n t} \quad (1)$$

When the values of P are expressed as percentages on the initial amount of polysaccharides in the raw material, a completely definite point (P_k) on the graph of $\ln P = f(t)$, numerically equal to the initial amount of readily hydrolyzable polysaccharides (RHPs), will correspond to the moment of the completion of the hydrolysis of the HCs. Then the magnitude ($P_{n,t}$) will include the n -th fraction of the HCs, continuously decreasing with the time of the reaction, and the residual difficultly hydrolyzable polysaccharides (DHPs) of the raw material that have remained unchanged under the given conditions. The absolute amount of the unhydrolyzed n -th fraction at each experimental point (P_n) can be found as the difference ($P_{n,t} - P_k$). By determining the difference ($P - P_n$) and taking logarithms, values are found for plotting the kinetic curve $\ln (P - P_n) = f(t)$ which describes the hydrolysis of the hemicellulose complex without the least reactive n -th fraction. By analyzing the new kinetic curve similarly and excluding from it the contribution of the penul-

TABLE 1. Rate Constants of the Hydrolysis of the Fractions of Sunflower Seed Husk HCs ($k \cdot 10^{-2}, \text{min}^{-1}$)

$T, ^\circ\text{C}$	k_n	k_{n-1}	k_{n-2}	k_{n-3}	k_{n-4}	k_{n-5}
130	0,44	0,45	0,79	1,68	1,98	5,68
140	0,69	0,91	1,52	2,55	3,17	6,68
150	1,75	1,85	2,89	4,42	4,75	8,25

TABLE 2. Amounts of the Fractions of Sunflower Seed Husks (% $P_{S_{\text{init}}}$)

$T, ^\circ\text{C}$	P_n	P_{n-1}	P_{n-2}	P_{n-3}	P_{n-4}	P_{n-5}
130	29,2	2,5	2,0	2,3	1,5	1,8
140	28,4	2,8	2,6	2,3	2,0	1,1
150	29,3	2,6	2,5	2,4	1,8	1,0
$P, \text{ average}$	29,0	2,6	2,4	2,5	1,8	1,3
$P, \% \text{ RHP}_{S_{\text{init}}}$	73,4	6,6	6,1	6,3	4,6	3,0
$P, \% \text{ a.d.m.}$	15,3	1,4	1,3	1,3	1,0	0,7

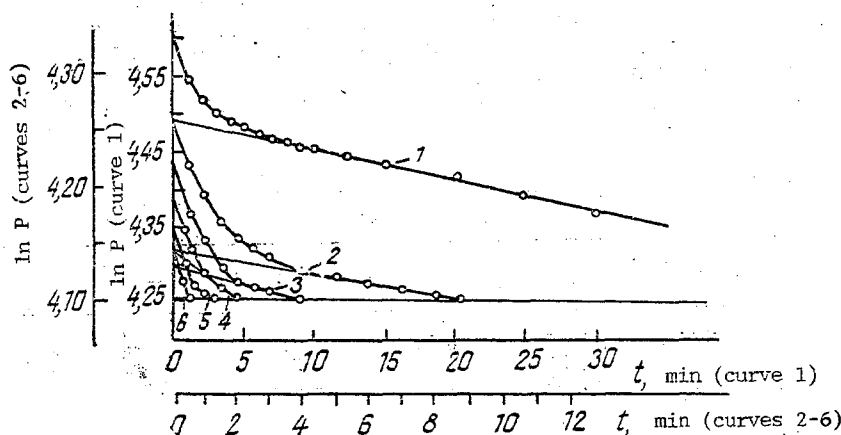


Fig. 1. Semilogarithmic anamorphoses of the kinetic curves of the hydrolysis of sunflower seed husk hemicelluloses: 1) $\ln P = f(t)$; 2) $\ln(P - P_n) = f(t)$; 3) $\ln(P - P_n - P_{n-1}) = f(t)$; 4) $\ln(P - P_n - P_{n-1} - P_{n-2}) = f(t)$; 5) $\ln(P - P_n - P_{n-1} - P_{n-2} - P_{n-3}) = f(t)$; 6) $\ln(P - P_n - P_{n-1} - P_{n-2} - P_{n-3} - P_{n-4}) = f(t)$

timinate, $(n-1)$ -th, fraction of the HCs we obtain the following kinetic curve $\ln(P - P_n - P_{n-1}) = f(t)$, and so on until, in the final account, we obtained a straight line showing the kinetic homogeneity of the sample.

The kinetic analysis carried out in this way enabled us to show the presence of six kinetically homogeneous fractions in the HC complex of sunflower seed husks. Tables 1 and 2 give the hydrolysis rate constants and the relative amounts of the HC fractions. It can be seen from these results that, with a rise in the temperature of the process by each 10°C there was a regular increase in the rate constant for the hydrolysis of each HC fraction in accordance with the Van't Hoff rule, while for the less reactive fractions the increase in the rate of the reaction took place by a higher amount. On passing from the P_n -th to the P_{n-5} -th fraction, the temperature coefficient of the reaction rate, γ , assumed the following respective values: 2.14, 2.04, 1.87, 1.67, 1.51, and 1.31. The decrease in the temperature coefficient is not a consequence of a change in the composition of the fractions with a change in the temperature conditions of treating the sample.

A study of the monosaccharide composition of the HC fractions showed that a change in the temperature regime does not lead to a change in the qualitative composition of the HC

TABLE 3. Determination of the Activation Energies of the Fractions of Sunflower Seed Husk HCs, $\log (k \cdot 10^{39}, \text{min}^{-1})$

$1/T \cdot 10^5, \text{°K}$	k_n	k_{n-1}	k_{n-2}	k_{n-3}	k_{n-4}	k_{n-5}
248	0,64	0,66	0,90	1,22	1,30	1,75
242	0,84	0,96	1,18	1,41	1,50	1,82
236	1,24	1,27	1,46	1,65	1,68	1,92

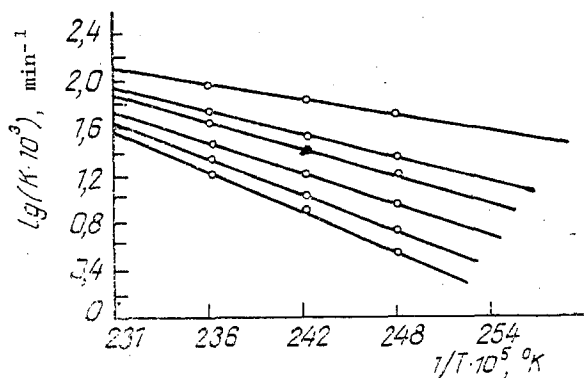


Fig. 2. Graphical method of calculating the activation energies of the fractions of sunflower seed husk HCs.

fractions. The characteristic changes in the temperature coefficients are determined by the reactivities of the polysaccharide macromolecules composing each fraction of the HCs. The initial amount of each HC fraction remained the same at any temperature regime of the treatment of the sample.

A characteristic feature of sunflower seed husk HCs is the considerable predominance of one fraction (P_n), making up 73.4% of the initial amount of RPHs in the husks. In the kinetic respect, this fraction possessed the lowest reactivity (for 130°C, $k_n = 0.0044 \text{ min}^{-1}$; $k_{n-5}/(k_n = 12.9)$). This exhibits a decisive influence on the whole course of the hydrolysis of the HCs; in particular, it determines to a substantial degree the time for the complete hydrolytic dissolution of the HCs, which proved to be fairly long in the case of the sunflower seed husks.

The activation energies of the HC fractions were determined graphically by plotting the dependence of $\log k$ on $1/T$. It can be seen from Fig. 2, plotted from the figures of Table 3, that for each HC fraction this relationship had the form of a straight line, which shows that the hydrolysis reaction took place in accordance with the Arrhenius equation. Consequently, the activation energy of each fraction of the HCs can be calculated from the equation [3]

$$E = 2.3 \cdot R \cdot \text{tg} \alpha \cdot n, \quad (2)$$

where R is the gas constant;

$\text{tg} \alpha$ is the tangent of the angle of slope α ; and

n is the ratio of the scales on the axes of abscissas and of ordinates.

The activation energies of the fractions of the sunflower seed husk HCs arranged in order of increasing reactivity were, respectively (J/mole): $E_n = 97,531$; $E_{n-1} = 91,945$; $E_{n-2} = 82,681$; $E_{n-3} = 62,884$; $E_{n-4} = 51,790$; $E_{n-5} = 38,365$.

In order to check the correspondence of the proposed kinetic description to the real process of hydrolyzing sunflower seed husk HCs, we calculated the amount of the polysaccharides of the HCs that had passed into solution at each experimental point ($T = 130^\circ\text{C}$) from the equation

$$P_x = P_{n,0} \cdot (1 - e^{-k_n \cdot t}) + P_{n-1,0} \cdot (1 - e^{-k_{n-1} \cdot t}) + \dots + P_{n-5,0} \cdot (1 - e^{-k_{n-5} \cdot t}), \quad (3)$$

TABLE 4. Comparisons of Calculated and Experimental Values for the Hydrolysis of Sunflower Seed Husk HCs (sol. RHPs, % of the RHPs_{init})

Values	Time, min							
	,5	1,0	1,5	2,0	2,5	3,0	4,0	5,0
Calc.	8,8	14,0	17,5	20,3	22,4	23,9	26,8	28,4
Exptl.	9,5	14,3	17,9	20,7	22,5	24,1	26,6	28,4
Difference	0,7	0,3	0,4	0,4	0,1	0,2	0,2	0,0

Values	Time, min									
	6,0	7,0	8,0	9,0	10,0	12,0	15,0	18,0	25,0	30,0
Calc.	30,1	31,8	33,4	34,9	35,9	37,8	40,6	45,2	49,7	54,1
Exptl.	30,2	32,0	33,3	34,8	35,3	37,7	40,4	45,3	49,6	54,0
Difference	0,1	0,2	0,1	0,1	0,6	0,1	0,2	0,1	0,1	0,1

where $P_{n,0}$, $P_{n-1,0}$... $P_{n-5,0}$ are the initial amounts of the n-th, (n-1)-th ... (n-5)-th fractions of the HC polysaccharides; and k_n , k_{n-1} , ..., k_{n-5} are the hydrolysis rate constants of the n-th, (n-1)-th ... (n-5)-th fractions of the HC polysaccharides.

The results of a comparison of the experimental results on the amount of HC polysaccharides that had dissolved with the calculated values (from Eq. (3)) are given in Table 4. This shows a fairly high degree of agreement, the mean square deviation ($S_{\bar{x}}$) being 0.0679, which is considerably lower than the analogous index found from the results obtained previously [4] with the arbitrary division of the hemicellulose complex into two fractions ($S_{\bar{x}} = 1.6921$).

EXPERIMENTAL

Sunflower seed husks, consisting of a mixture of industrial varieties, were ground in a laboratory mill to a particle size of 0.25-0.50 mm. Hydrolysis was conducted in a titanium autoclave with a capacity of 40 cm³ placed in a glycerol thermostat. The catalyst was 0.5% sulfuric acid in a liquor ratio (LR) of ten. The LR selected enabled the influence of diffusional factors on the impregnation of the raw material with the catalyst solution to be excluded and the neutralizing effect of the active ash content of the husks on the acid to be decreased. Hydrolysis was carried out at 130-150°C until the HCs had been completely eliminated. The kinetics of the hydrolysis of the sunflower seed husk HCs was studied from the change in the amount of readily hydrolyzable polysaccharides in the unhydrolyzed residue.

In the performance of hydrolysis the time of reaching the given reaction temperature was determined accurately, which permitted a correction to be introduced into the subsequent kinetic calculations for the nonisothermal conditions in the periods of heating and cooling the material being treated. The correction was obtained from the results of a control experiment which consisted in heating the reaction mixture to the required temperature and then rapidly cooling it, and it was allowed for in the calculation of the hydrolysis rate constant [5]:

$$k = \frac{1}{t_u} \cdot \ln \frac{P_0}{P}, \quad (4)$$

where t_u is the time of hydrolysis in the isothermal regime;

P_0 is the amount of unhydrolyzed polysaccharide after heating and cooling ($t_u = 0$); and P is the amount of unhydrolyzed polysaccharide at the end of the experiment.

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