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Optimization of starch sulfation process with a deep eutectic solvent-mixture of sulfamic acid:urea

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Abstract. The process of sulphation of potato starch with a deep eutectic solvent, a mixture of sulfamic acid: urea, was optimized. The influence of varying factors was established - the ratio of sulfamic acid: urea (SAA: U), the ratio of starch: sulfating complex (St: SC) and the duration of the process on the sulfur content (wt.%) in the obtained starch sulfate. The data of analysis of variance for the obtained mathematical models indicate good prognostic properties. The optimal conditions for starch sulfation, which provide water-soluble sulfated starch with a high (up to 11.2% wt.) sulfur content, have been established. The optimal conditions for the process of sulfation of potato starch are the ratio SAA: U 1: 2.0-1: 2.2, the ratio St: SC 1: 3.5-1: 4.0 and the duration of the process is 118-120 minutes.

1. Introduction

In recent years, interest in the study of the chemical transformations of renewable plant biomass has sharply increased, which is due to the need to improve the technology of its processing into popular chemicals [1]. The annual growth of plant biomass far exceeds the annual needs of mankind in chemical products [2]. In principle, from the components of plant biomass - polysaccharides, lignin, extractive substances, you can get the whole range of products of modern organic synthesis [3].

Polysaccharides are present in both plants, animals and microorganisms. Polysaccharides are long chain polymers of mono-, di, and oligosaccharides [4,5]. Modification of polysaccharides by sulfate groups can give them anticoagulant, antioxidant, antiviral and anti-inflammatory activity [6-8].

Among the many polysaccharides, starch is widely used [9]. The introduction of a sulfate group in the structure of starch can enhance its biological activity, giving it, among other things, anticoagulant, hypolipidemic and antiviral properties [10-12].

Sulfated starches have a wide range of applications, which has led to several methods for their preparation [13]. Traditionally, starch sulfates are obtained using highly hydrolytic sulfating agents, such as sulfuric acid, chlorosulfonic acid, and sulfur trioxide [13–16]; however, the use of these chemical agents can lead to partial hydrolysis of high molecular weight starch chains. To reduce the hydrolytic effect, various organic solvents were used as the reaction medium, such as pyridine, dimethyl sulfoxide, triethylamine, toluene, or ethylene dichloride [17, 18].

The aim of this work was to optimize the process of sulfation of potato starch with a deep eutectic solvent - a mixture of sulfamic acid/urea.



2. Experimental part

As the source of raw materials are used potato starch (LLC "Nsk-st").

Sulfation of starch was carried out by the sulfamic acid-urea complex according to a modified procedure [19, 20].

The numerical optimization of the starch sulfation process with sulfamic acid was carried out using the Statgraphics Centurion XVI software [21].

3. Results and discussion

In the study of starch sulfation by sulfamic acid the time and temperature of the process were varied. Data on the sulfur content in starch sulfate obtained under these experimental conditions is shown in table 1.

Table 1. Data of starch sulfation process by sulfamic acid-urea complex.

№	SAA:U ratio (X ₁)	St:SC ratio (X ₂)	Time, min (X ₃)	Sulfur content, mas. % (Y ₁)
1	1: 1	1: 2	30	1.5
2	1: 1	1: 2	60	2.4
3	1: 1	1: 2	120	3.6
4	1: 1	1: 3	30	3.4
5	1: 1	1: 3	60	4.4
6	1: 1	1: 3	120	6.9
7	1: 1	1: 4	30	4.5
8	1: 1	1: 4	60	5.6
9	1: 1	1: 4	120	8.3
10	1: 2	1: 2	30	3.9
11	1: 2	1: 2	60	5.4
12	1: 2	1: 2	120	8.2
13	1: 2	1: 3	30	5.7
14	1: 2	1: 3	60	7.2
15	1: 2	1: 3	120	10.6
16	1: 2	1: 4	30	6.7
17	1: 2	1: 4	60	8.4
18	1: 2	1: 4	120	11.3
19	1: 3	1: 2	30	2.7
20	1: 3	1: 2	60	4.3
21	1: 3	1: 2	120	6.3
22	1: 3	1: 3	30	4.8
23	1: 3	1: 3	60	6.4
24	1: 3	1: 3	120	8.9
25	1: 3	1: 4	30	5.8
26	1: 3	1: 4	60	7.7
27	1: 3	1: 4	120	9.7

The dependences of the sulfur content in sulfated starch on variables of the sulfation process are approximated by the regression equation:

$$Y_1 = -18.05 + 12.9917X_1 + 7.91667X_2 - 2.75X_1^2 - 0.325X_1X_2 - 0.9X_2^2 \quad (1)$$

High prognostic properties of the mathematical model are also observed if it is implemented using the sulfur content in the sulfated starch sample as an output parameter (Table 2).

Table 2. Analysis of variance for Y_1 depending on X_1 and X_2 .

Variance source	Sum of squares	Number degrees of freedom	F-Ratio	P-Value
A: X_1	6.20167	1	61.17	0.0044
B: X_2	20.9067	1	206.20	0.0007
AA	15.125	1	149.18	0.0012
AB	0.4225	1	4.17	0.1339
BB	1.62	1	15.98	0.0281

Analysis of variance showed that, within the limits of the accepted experimental conditions, a significant contribution to the total dispersion is made by the factor X_2 . This is indicated by high values of the dispersion ratios F, also called influence efficiencies. The influence of the dispersion source on the output parameter is considered statistically significant if the significance level is $P < 0.05$, corresponding to a confidence level of 95%. According to the above model, the optimal conditions for starch sulfation with a duration of 120 minutes are the ratio SAA: U 1: 2,1 and the ratio St: SC 1: 4.

The values of the output parameter Y_1 obtained in the experiment are compared with the values predicted by equation (1) (figure 1). The straight line corresponds to the calculated values of Y_1 . The proximity of most “experimental points” to the line indicates good prognostic properties of the regression equations.

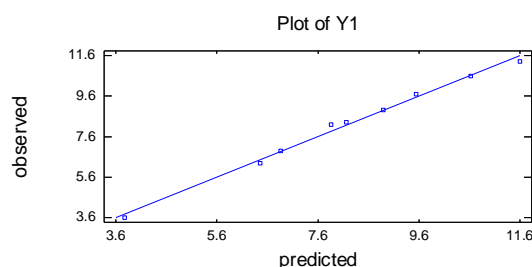


Figure 1. Comparison of experimental and calculated values of sulfur content in sulfated starch during sulfation with varying ratios of SAA: U and St: SC.

A graphical representation of the dependence of the output parameter on the sulfur content (% wt.) (Y_1) on variable factors of the ratio SAA: U (X_1), ratio St: SC (X_2), using mathematical models, is presented in the form of response surfaces in figure 2.

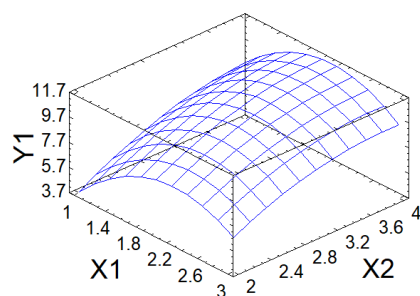


Figure 2. The response surface of the output parameter sulfur content wt.% Y_1 from variable factors - the ratio of SAA:U X_1 , the ratio of St:SC X_2 , with a duration of 120 minutes.

The influence of the ratio SAA:U (X_1) and the duration of the process of sulfation of starch (X_3) on the sulfur content (Y_1) in sulfated starch is described by the regression equation:

$$Y_1 = -3.9722 + 8.2917X_1 + 0.062937X_3 - 1.8667X_1^2 - 0.00035714X_1X_3 - 0.000111X_3^2 \quad (2)$$

The analysis of variance was performed for the output parameter - sulfur content in sulfated starch (Y_1) depending on variable parameters - the ratio SAA:U (X_1) and the duration of the process (X_3) (table 3).

Table 3. Analysis of variance for Y_1 depending on X_1 and X_3 .

Variance source	Sum of squares	Number degrees of freedom	F-Ratio	P-Value
A: X_1	3.75581	1	28.89	0.0126
B: X_3	25.215	1	193.94	0.0008
AA	6.96889	1	53.60	0.0053
AB	0.00107143	1	0.01	0.9334
BB	0.0771429	1	0.59	0.4972

Analysis of variance (table 3) indicates good prognostic properties of the models: high efficiency of all components of the regression equation, high determination coefficient (98.4%), low significance levels. The optimal conditions for this model of starch sulfation at a ratio of St: SC 1:4 are the ratio of SAA: U 1:2.2 and the duration of the process is 118 minutes.

Good agreement between the values calculated for equation (2) and the measured values of the output parameters presented in figure 3, talks about the adequacy of the regression equation to the observation results and allows you to use it as a mathematical model of the process under study.

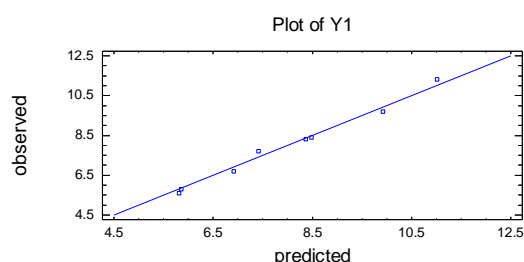


Figure 3. Comparison of experimental and calculated values of sulfur content in sulfated starch during sulfation with varying SAA: U ratio and process duration.

Figure 4 shows the response surface of the output parameter sulfur content (Y_1) from the ratio SAA: U (X_1) and the duration of the process (X_3) with the ratio St:SC 1:4.

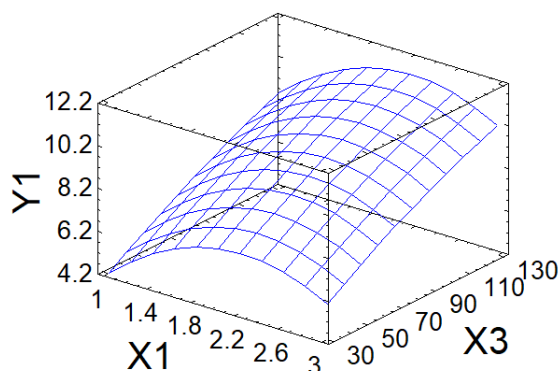


Figure 4. The response surface of the output parameter sulfur content wt.% Y_1 from variable factors - the ratio SAA: U X_1 and the duration of the process X_3 with the ratio SC: St 1:4.

The analysis of the value of the output parameter Y_1 (sulfur content,% wt.) From the ratio of St:SC (X_2) and the duration of the process (X_3) with the ratio of SAA:U 1:2, obtained using the regression equation:

$$Y_1 = -4.59722 + 4.475X_2 + 0.04925X_3 - 0.51667X_2^2 + 0.0015476X_2X_3 - 0.000018519X_3^2 \quad (3)$$

Table 4. Analysis of variance for Y_1 depending on X_2 and X_3 .

Variance source	Sum of squares	Number degrees of freedom	F-Ratio	P-Value
A: X_2	13.1057	1	334.16	0.0004
B: X_3	31.74	1	809.29	0.0001
AA	0.533889	1	13.61	0.0345
AB	0.020119	1	0.51	0.5256
BB	0.00214286	1	0.05	0.8302

According to the analysis of variance (table 4), good predictive properties of the models are shown: high efficiency of all components of the regression equation, high determination coefficient (99.3%), Low significance levels (P - Value). The optimal conditions for this model of starch sulfation at a ratio of SAA: U 1: 2 are ratios SC: St 1: 3.5 and the duration of the process is 118 minutes.

A good agreement between the calculated and calculated values of the output parameters (figure 5) indicates the adequacy of the regression equation to the observation results and allows it to be used as a mathematical model of the process under study.

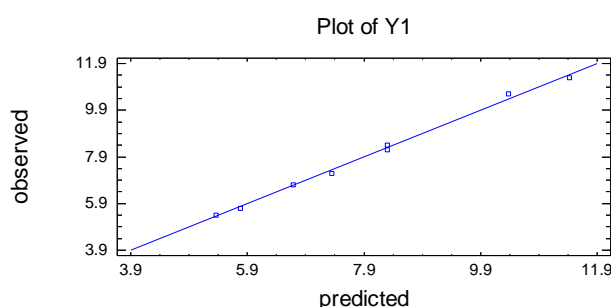


Figure 5. Comparison of experimental and calculated values of sulfur wt% in a sulfated starch sample during sulfation with varying SC: St ratio and process duration.

Figure 6 shows the response surface of the output parameter Y_1 (sulfur content) from the ratio SC: St (X_2) and the duration of the process (X_3) with the ratio SAA: U 1:2, obtained using the regression equation (3).

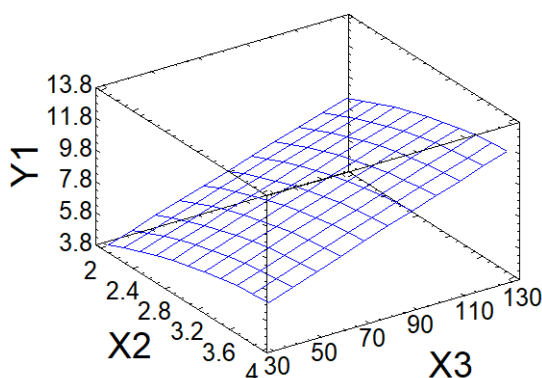


Figure 6. The response surface of the output parameter sulfur content wt.% Y_1 from variable factors - the ratio of St:SC (X_2) and the duration of the process of sulfation of starch (X_3). with a ratio of SAA: U 1: 2.

4. Conclusions

The influence of varying factors was established - the ratio of sulfamic acid: urea (SAA: U), the ratio of starch: sulfating complex (St: SC) and the duration of the process on the sulfur content (wt.%) In the obtained starch sulfate.

Analysis of variance data for the obtained mathematical models indicate good prognostic properties: high efficiency of all components of the regression equation, high determination coefficient (98.4-99.2%), low significance levels and low values of relative error (0.1-2.6 %). Based on the obtained regression equations, the optimal conditions for the process of sulfation of potato starch are the ratio SAA: U 1: 2.0-1: 2.2, the ratio St: SC 1: 3.5-1: 4.0 and the duration of the process is 118- 120 minutes.

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