

Environmentally friendly guar gum sulfation with a sulfamic acid-urea mixture

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Abstract. The guar gum was sulfated for the first time with a deep eutectic solvent, a sulfamic acid / urea mixture at a ratio of (1:1). The optimal conditions of the process are shown to ensure the production of guar gum sulfate with a maximum sulfur content (16.1% wt.). The introduction of a sulfate group into a guar gum molecule is proved by elemental analysis. A mathematical model of the process of sulfation of guar gum is calculated. It is shown that the resulting model has high predictive properties. The developed method is environmentally safer due to the fact that it eliminates the use of toxic solvents.

1. Introduction

In recent years, plant polysaccharides are increasingly used as therapeutic and prophylactic agents, possessing immunomodulating, prebiotic, lipid-lowering, mitogenic, antimutagenic, hepatoprotective, gastroprotective membranes [1]. They are also characterized by a complex of other extremely valuable properties (low toxicity, good solubility in water, the ability to bind fat and retain moisture, dispersing properties). The combination of these properties opens up broad prospects for the use of polysaccharides in medicine, veterinary medicine, food and cosmetic industries [2].

It is known [3-4] that they are promising carriers of drugs and biogenic metals, while they themselves exhibit physiologically active properties. It is believed that the biological activity of polysaccharides is directly related to their structural features: the length and structure of the main and side carbohydrate chains, as well as the molecular weight and ability to form intermolecular associates [5,6].

Sulfated polysaccharides (fucans, dextransulfates, heparin, carrageenans, sulfated chitosans, synthetic polyvinyl and polyethylene sulphates), as well as algae extracts, have varying degrees of antiviral activity against various viruses (flavi-, toga-, arena-, rhabdo -, orthopoxviruses, as well as the family of herpes viruses) [7]. Among sulfated polysaccharides, special attention is drawn to compounds that inhibit the reproduction of retroviruses [8].

Guar gum is a galactomannan polysaccharide extracted from guar beans, which has thickening and stabilizing properties, useful in food, feed and industrial fields [10]. Guar gum sulfates have antioxidant, anticoagulant, and biodegradable properties [11-14]. Despite the wide field of application of sulfated polysaccharides, there are currently several methods for the synthesis of guar gum sulfates based on the use of toxic agents [11,12].

The aim of this work was to synthesize guar gum sulfates in an environmentally friendly way - by sulfating with a mixture of sulfamic acid with urea.

2. Experimental part

As the source of raw materials are used guar gum (LLC "Mast-sl").

Sulfation of guar gum was carried out by the sulfamic acid-urea complex according to a modified procedure [15]. To do this, the sulfating complex (SC) and guar gum were triturated to obtain a homogeneous mass. Sulphating complex was obtained by preliminary mixing 7.2 g of sulfamic acid (75 mmol) and 4.5 g of urea (75 mmol). The ratio of guar gum and sulfating complex was 1: 3 (mol / mol). The resulting reaction mixture was thermostated with constant stirring and at temperatures of 70, 80, 90°C, with a process duration of 30, 60 and 120 minutes. In this temperature range, the reaction mass melted.

At the end of the thermostating process, the melt was cooled to room temperature, the formed solid product was dissolved in 50 ml of water, the unreacted sulfamic acid was neutralized with a 10% aqueous sodium hydroxide solution to pH 7-8. The resulting solution was evaporated to a volume of 10-15 ml in vacuum of a water-jet pump.

Purification of the sodium salt of sulfated guar gum was carried out by dialysis on cellophane against distilled water. The product was dialyzed for 10 hours, changing the water at intervals of 1-2 hours.

Elemental analysis of sulfated guar gum was performed on a FlashEA-1112 elemental analyzer (ThermoQuest, Italia).

The numerical optimization of the guar gum sulfation process with sulfamic acid was carried out using the Statgraphics Centurion XVI software, according to the procedure described in [16].

3. Results and discussion

Guar gum sulfation reaction with sulfamic acid-urea complex and the subsequent isolation of guar gum sulfate was carried out according to the scheme (figure 1).

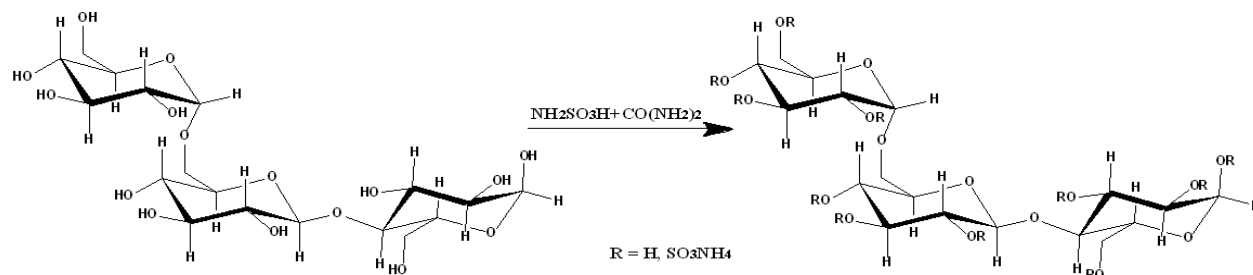


Figure 1. Scheme of guar gum sulfation reaction.

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

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

№	Temperature, °C	Time, min	Sulfur content, mas. %
1	70	30	6.2
2	70	60	8.7
3	70	120	9.6
4	80	30	13.9
5	80	60	16.1

6	80	120	13.8
7	90	30	10.2
8	90	60	8.2
9	90	120	3.9

It was found that the sulfur content in sulfated guar gum can be controlled by varying the temperature and duration of the sulfation process (table 1). The maximum sulfur content was observed at a process temperature of 80°C and the time of process of 60 minutes. With increasing temperature, the sulfur content decreases to 3.9% wt. The observed regularity is consistent with the data presented in [11, 12], and is probably associated with the destruction of the polysaccharide at high temperature.

The aim of optimizing the sulfation process is to search for conditions that provide sulfated guar gum with a maximum sulfur content. The independent variables were used following factors: temperature (X_1) and the duration of sulfation process (X_2). The result of the sulfation process was characterized by the output parameter as the sulfur content in sulfated guar gum (Y_1).

Analysis of variance and mathematical modeling were performed for the output parameter (Y_1) of the guar gum sulfation process.

The influence of factors X_1 and X_2 on the sulfur content (Y_1) in sulfated guar gum is described by the regression equation:

$$Y_1 = -443.84 + 11.0558 * X_1 + 0.523968 * X_2 - 0.06683 * X_1^2 - 0.005536 * X_1 * X_2 - 0.0006296 * X_2^2 \quad (1)$$

The values of the output parameter Y_1 were compared with the values predicted by equation (1) (figure 2). The straight line corresponds to the predicted values of Y_1 . The proximity of most "experimental points" to the straight line indicates that the selected model has good prognostic properties of the regression equations.

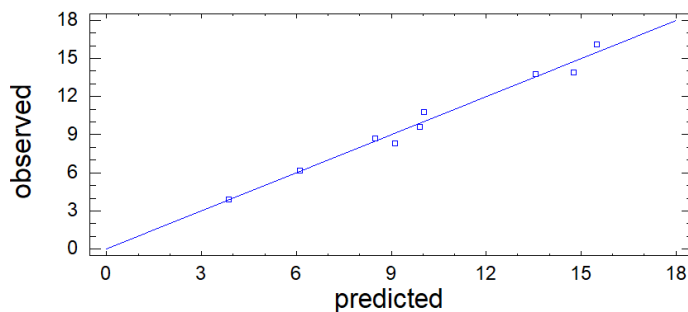


Figure 2. Comparison of experimental and calculated values of sulfur content in sulfated guar gum during sulfation with varying time of process and temperature.

Figure 3 shows the response surface of the output parameter Y_1 (sulfur content) temperature (X_1) and the time of the sulfation process (X_2).

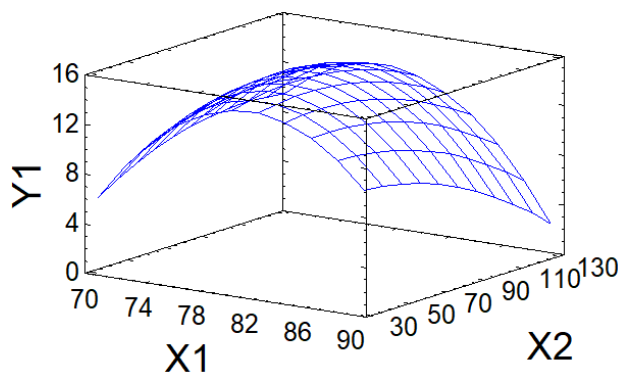


Figure 3. The response surface of the output parameter Y_1 (sulfur content) and variable factors - X_1 and X_2 .

The optimal conditions for the guar gum sulfates obtaining with a maximum sulfur content (15.5% wt) are the process temperature of 80°C and a duration of 64 minutes.

4. Conclusions

A new method for sulfation of guar gum with a mixture of sulfamic acid/urea is developed. This method is environmentally friendly, since it eliminates the use of toxic solvents.

The introduction of sulfate groups into the guar gum molecule were proved by elemental analysis. A numerical simulation of the process of sulfation of guar gum with a mixture of sulfamic acid-urea was carried out. It is shown that the regression equation to a high degree describes the sulfation process. The optimal conditions for producing guar gum sulfates are a temperature of 80°C and time of process of 60-65 minutes.

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