Evaluation of the Effectiveness of the Preliminary Chemical Treatment of Grape Cake and Environmental Aspects of the Chemical Hydrolysis Process

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ABSTRACT

During operation, grape cake is pretreated with nitric acid before preparation for the process of enzymatic hydrolysis. When producing biofuels of the second generation, agricultural waste, industrial and forestry waste containing lignin cellulose are mainly used. Chemical processing of raw materials ensures fast and efficient flow of the enzymatic hydrolysis process. In order to avoid harm to the environment and ecology during chemical treatment, the solution used is repeatedly used and at the end of the experiment is neutralized with ammonia.

Keywords: grape cake, hydrolysis, temperature, nitric acid, lignin, cellulose, hemicellulose, filtration

The main raw material in the work is grape cake. Its chemical composition has been investigated [1-3]. The main polysaccharide is cellulose, in addition, the cake contains an almost comparable amount of lignin and pentosans. These components do not allow for effective enzymatic hydrolysis. According to the literature, the main method of their removal from lignin-cellulosic raw materials is chemical treatment with acids and alkalis. The task is achieved by preparing a suspension by pretreatment with a solution of nitric acid with a concentration of 1-4%. In the implementation of the process, the technique is used [4, 5]. The temperature of the procedure is 90-95 ° C, the duration is 2-6 hours, the ratio of acid to raw materials is 1:20.

In laboratory conditions, in order to swell the fibers of grape cake, we grind them to 1-2 mm and keep them in distilled water for 30 minutes to a degree of humidity of 60-65%. Further, for pre-treatment, the grape cake is treated with 1% nitric acid for 2 hours, thereby the molecules of lignin, hemicellulose and crystalline cellulose in the raw grape cake are separated from each other. In the next cycle, the concentration of nitric acid in the solution is increased to 4%, and the grape cake is treated with acid for 4 hours After extracting lignin from the raw material using nitric acid contained in grape cake, crystalline cellulose passes into an amorphous state. The spent acid solution used in the pretreatment process is reused. After 18-25 cycles of reuse, the spent solution is neutralized with ammonia to obtain an ammonium nitrate solution. Further, ammonium nitrate can be used as a fertilizer. A product treated with nitric acid is called POA. The results of the pre-treatment are shown in Table 1

Table 1 - Results of determining the chemical composition of the initial grape pomace and its chemical treatment products (n = 3)

Quantity	Object of study, % by weight		
	Grape cake	Substrates	
		PAO	PSCHO
Polysaccharides, incl. α-cellulose	43,0±1,0	76,8±0,1	78,6±0,1
Ligno-like substances	37,0±0,1	6,2±0,1	6,5±0,1
Pentosans	15,9±0,1	13,0±0,1	12,2±0,1
Nitrogen substances	1,5±0,1	1,8±0,1	1,7±0,1
Ash residue	2,6±0,1	1,8±0,1	1,0±0,1
Yield of raw materials, %	100	46,3±0,1	44,7±0,1

In order to conduct a comparative analysis of the effectiveness of nitrate treatment, grape pomace was treated with sodium hydroxide. At this stage, pre-crushed grape pomace fibers of 1-2 mm and swollen in distilled water are treated for 2 hours with 1% nitric acid in a ratio of 1:20. The acid solution is drained and the grape pomace suspension is kept for 5 hours in a 4% solution of sodium hydroxide in a ratio of 1:20. The resulting product is neutralized with a solution of 1% nitric acid and distilled water. A product treated with sodium hydroxide is called an alkaline treatment product. Subsequently, the resulting substrate is filtered on a vacuum funnel, squeezed and washed with distilled water to a neutral state. Then the substrate with a moisture content of 60-65% is sent to the process of enzymatic hydrolysis. The change in the concentration of reducing sugars that accumulate in the reaction mass when using pre-treated raw materials in the process of enzymatic hydrolysis can be traced in Table 2.

Table 2 – Results of enzymatic hydrolysis

Substrates	Concentration of RS, g/l			Yield of RF from the mass of the substrate, %		
	FP-1 "CelloLux-A"	FP-2 «Ultraflo Core»	FP-3 «BrewZyme BGX»	FP-1	FP-2	FP-3
Grape cake	7,2±0,1	7,5±0,1	4,4±0,1	21,6±0,2	22,5±0,2	13,2±0,2
POE	23,1±0,2	24,1±0,2	14,2±0,2	69,3±0,3	72,3±0,3	42,6±0,3
PSCHO	20,8±0,2	21,6±0,1	13,5±0,1	62,4±0,2	64,8±0,2	40,5±0,3

In the course of experimental work, the POA substrate is used in the process of enzymatic hydrolysis. This is expressed in the removal of non-hydrolyzable lignin from the raw material with the help of nitric acid and an increase in the concentration of cellulose for a better course of the enzymatic hydrolysis process. In addition, delignification using sodium hydroxide has a number of disadvantages, one of which is the formation of sodium ions in the reaction mass. Firstly, sodium ions are difficult to purify, and secondly, they adversely affect the bioconversion process. Based on the results given in Table 1, when grape cake is exposed to 1-4% nitric acid in the raw material, the content of lignin and other components that do not contain cellulose decreases, along with this, the proportion of cellulose in the product increases.

The use of nitric acid for pre-treatment of lignocellulosic raw materials in order to obtain bioethanol has been little studied and environmental issues occupy an important place. Pretreatment with nitric acid is fundamentally different from pretreatment with other acids: at the first stage, in addition to breaking the chemical bonds between cellulose, hemicelluloses and lignin, hemicelluloses are hydrolyzed to form soluble xylose and its precursors, and at the second stage, partial hydrolysis of cellulose and conversion of sugars into simple organic acids and carbon dioxide, oxidative nitration of lignin occurs [6]. Given the chemistry of the process, stainless steel equipment and piping should be used in nitrate treatment to avoid corrosion. At the processing stage, a 4% solution (w/v) was used at a module of 1:20 (w/v), so the question of disposal of the spent nitric acid solution immediately arises.

In laboratory conditions, it has been established that 18-25 times the use of the spent solution is possible. Pre-treatment with nitric acid is carried out in hermetically sealed equipment with a reverse refrigerator, which eliminates the ingress of nitrogen oxides into the atmosphere, so the process is environmentally friendly. Spent solutions of nitric acid are neutralized with ammonia to obtain combined lignohumic fertilizers. Both nitric acid and organic acids and carbon dioxide formed during the processing of raw materials are neutralized. Mineral nitrogen is represented by both ammonium and nitrate components.

Another environmental issue is the washing of the resulting palp from the spent solution of nitric acid. Optimization to reduce the volume of wash water in the framework of this work was not carried out due to the impossibility of implementing the task in the conditions of pilot production. There is no doubt that this task can be successfully solved, relying on the experience of existing pulp and paper mills.

References:

1. Derevenko V.V., Sidorenko A.V., Kovalev V.A., Volodko N.G. Main technological parameters of convective drying of Cabernet grape pomace. Food technology. – 2011. – № 5-6. – P. 103-105.
2. Derevenko V.V., Sidorenko A.V., Kovalev V.A., Volodko N.G. Patterns of convective drying of white grape pomace. Food technology. – 2011. – №4. – S. 88-89.
3. Liobera, Antonia. Dietary fibre content and antioxidant activity of Manto Negro red grape (Vitis nivifera): pomace and stem / Antonia Liobera, Jaime Canellas // Food Chemistry. – 2007. – Vol. 101, № 2. – P. 659-666.
4. Kurschner, K. Cellulose and cellulose derivative / K. Kurschner, A. Hoffer // Fresenius Journal of Analytical Chemistry. – 1993. – Vol. 92, № 3. – P. 145–154.
5. Skiba, E.A. Problems of fermentation of hydrolysates from non-traditional cellulose-containing raw materials / E.A. Skiba // Technologies and equipment of chemical, biotechnological and food industries. – 2012. – Part 1. – P. 287-291.
6. Skiba, E.A. Biotechnological transformation of easily renewable cellulose-containing raw materials into valuable products. Doctor of Technical Sciences: 1.5.6. / Skiba Ekaterina Anatolyevna. – M., 2022. – 212 p.