



## Valuable Raw Materials For Producing Furfural

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### ABSTRACT

The article investigates the composition of the properties of various kinds of pentosan-containing raw materials germinating in the Republic of Uzbekistan. More than 15 types of plant raw materials germinating in Uzbekistan have been selected. Their composition was analyzed and their suitability as raw materials for the hydrolysis industry was determined. The yield of furfural and other products from the corresponding raw materials has been determined. It is shown that Uzbekistan has huge reserves of PSS, which are renewed annually on the territory of the Republic of Uzbekistan.

### KEYWORDS

Furfural, pentosans-containing raw materials, xylitol, polysaccharides, hydrolysis, analysis, pentosans, reactor.

### INTRODUCTION

In the hydrolysis and microbiological industry for the production of furfural, feed yeast, carbohydrate feed for animals, xylitol, and other products, pentosan-containing raw materials are used, which is a waste of plant origin. Uzbekistan has a huge stock of pentosan-containing raw materials, which is

renewed every year. Only in the Republic of Karakalpakstan, more than 1 million are grown annually. tons of rice (grain) and the same amount of rice straw, more than 500 thousand tons of rice husk are accumulated annually from rice. The purpose of this work was to study the chemical composition of

pentosan-containing raw materials formed in Uzbekistan. At present, the plants of the hydrolysis and microbiological industries use an improved technology for the hydrolysis of plant raw materials in one apparatus for the hydrolysis and dehydration of pentosans. [1,2] The continuously increasing demand of numerous consumers for furfural requires an accelerated development of the production of this scarce product. One of the key problems determining the possibility of the fastest and most efficient increase in the production of furfural is to increase its yield from raw materials. At the current level of furfural production at specialized plants, a relative increase in its output of only 10% will be equivalent to the construction of a new large enterprise, which provides annual savings of

hundreds of thousands of tons of raw materials. The yield of furfural depends on a number of factors, including the quality, granulometric composition of raw materials, conditions of its preparation, compliance of the technological regime with the requirement of directed conversion of pentosans into furfural, taking into account the preservation of cellulose. The potential content of furfural in the feed was determined using an improved method. The content of the bark was determined by the gravimetric method after separating it from the chips. Physicochemical characteristics of wood chips from tree and shrub vegetation, to with. in % is given below.

Polysaccharides:

Highly hydrolysable . . . . .	19-24
Difficult to hydrolyze . . . . .	28-30
Pentosans . . . . .	18,8-24
Potential furfural. . . . .	10-13
Bark . . . . .	17,3-23
Ash content . . . . .	3-3,3
Humidity . . . . .	50

The tests were carried out on an installation consisting of an autoclave and a flow-through reactor, which ensures uniform passage of vapors through the layers of raw materials. Along with sulfuric acid, ammonium chloride and monocalcium phosphate were also used as a catalyst. The use of various salt catalysts, in particular, water-soluble salts of chromium and ammonium, salts of chloride metals and a number of others.

In Uzbekistan, pentosan-containing raw materials are generated annually in the form of plant waste: sawdust and garden scraps, corn stalk, cotton husk, rice husk, sunflower husk, guza-paya, sunflower stalks, hemp fire, flax fire, grapevine, winter crop scraps wheat, peat, tobacco stalk, sugar industry waste (cane), paper industry waste, reed stalks, wood-shrub industry chips, rice straw, annual plants, sunflower stalk, peanut shells (peanuts), etc.

Of the above types of raw materials, the industry mainly uses cotton husks, rice husks, sunflower husks, sawdust, corn cobs and others. From the above list of raw materials, garden scraps, hemp and flax bonfires, grapevines and guza paya are used as fuel. Other types of raw materials can be used as pentosan-containing raw materials for the hydrolysis industry to obtain furfural. The rate of the reaction of hydrolysis of pentosan is several times higher than the rate of the

reaction of their dehydration (formation of furfural).

7% is obtained from cotton husk, 7% of winter straw, 8.5% of tobacco stalks, 8.5% of corn stalks, and 8.1% of furfural sawdust. Table 1 shows the chemical composition of some types of pentosan-containing raw materials in absolutely dry raw materials, in% formed in Uzbekistan.

Chemical composition of some types of pentosan-containing raw materials in absolutely dry raw materials, %

Таблица 1

№	Indicators, %	Bun	Bonfire flax	Sawdust	Rice husk	Rice straw	Winter straw	Tobacco stalks
1.	Humidity	7,02	9,06	10	10	11	11	11
2.	Resin and waxes	2,04	4,84	2	2	1	2	2
3.	Nitrogen	1,03	1,25	1	1	8	8	7
4.	Ash	2,13	1,96	2	2	2	2	1
5.	Cellulose	40	34	40	43	42	27	28
6.	Lignin	27,40	32,80	20	25	22	25	24
7.	Uronic acids	5,80	5,40	4,0	5,0	5,0	5	4
8.	Polysaccharides:							
		16,63	19,08	20	22	21	26	24,7
	Readily hydrolysable	42,30	34,40	40	43	42	32	37,1
	Difficult to hydrolyze							
9.	Pentosan	22,1	21,0	22	23	22	27	20

The use of tree and shrub vegetation, growing on lands subject to reclamation, can also, to a certain extent, penalties to expand the raw material base of the hydrolysis industry. At present it is practically not used at present, although its resources are very significant. Mastering raw materials and processing them from with the help of a complex of machines, it will make it possible to obtain technological chips suitable for processing by hydrolysis

methods. To determine the possibility of using the described raw materials in the production of furfural by vapor-phase methods were carried out tests in office conditions. Potential fur content furol in raw materials was determined using an improved method. Soder barking was determined by the gravimetric method after separating it from chips. Physicochemical characteristics of wood chips

from shrubs vegetation,% to a.w., is given below.

Chips from woody shrub vegetation obtained on an MRT-18 chipper, moistened with 10% sulfuric acid in a falling stream or mixed with an appropriate salt, were loaded into a preheated reactor. After the reactor was sealed, steam superheated to 220 ° C was fed into its lower part under a pressure of 0.8–1 MPa. The heating of the raw material lasted 15

minutes, after which the selection of furfural-containing vapors began, which were cooled in a refrigerator. The distillation of furfural lasted 105-120 min. Condensate samples for analysis were taken at 15-minute intervals. Quantitative analysis of furfural in condensate was carried out by the GLC method (table 2). The furfural yield was 55-60% of the potential content

**Table 2. Modes of processing raw materials from trees and shrubs and the main indicators of the process**

catalyst	Amount of catalyst % to absolute dry raw material	Cooking mode			Furfural yield, % to absolute dry raw material	Furfural yield, % potential content in raw materials	Condensate acidity %		content of difficult-to-hydrolyzable polysaccharides in cellulignin6 % to absolute dry raw material
		Time min	Pressure, MPa	Reactor temperature, °C			mineral	organic	
10 % H <sub>2</sub> SO <sub>4</sub>	0,03 by monohydrate	105	0,9	174	6,06	60,6	0,164	0,430	19,4
NH <sub>4</sub> Cl	2,7	105	0,9	174	4,02	40,2	0,09	0,342	25,4
Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	2,7	105	0,9	174	4,33	43,3	0,146	0,178	27,3
NH <sub>4</sub> Cl	4	105	0,9	174	5,30	53,0	0,144	0,217	22,7
Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	4	105	0,9	174	4,36	43,6	0,09	0,189	25,1
ACID-FREE	—	105	1,1	184	3,14	31,4	—	0,293	28,3
10 % H <sub>2</sub> SO <sub>4</sub>	0,03 by monohydrate	105	1,1	184	6,04	60,4	0,280	0,388	16,6
NH <sub>4</sub> Cl	4	105	1,1	184	5,70	57,0	0,172	0,310	24,9
Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	2,7	120	1,1	184	6,06	60,6	0,170	0,185	26,2
Ca (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	2	120	1,1	184	5,52	55,2	0,149	0,202	26,0

Note. Cooking was carried out at a constant temperature of fresh steam equal to 220 °C in the raw material. At the same time, a change in temperature by 10 °C and a pressure by 0.3 MPa practically does not affect the yield of furfural with a catalyst such as sulfuric acid, and noticeably change it at salt catalysts. [3-7]

Cellulignin analysis showed that the content of difficult to hydrolyzate polysaccharides in it with salt catalysts is almost 1.5 times higher, than with sulfuric acid, which increases its value as a source obtaining monosaccharides by percolation hydrolysis. Percola-hydrolysis of raw materials prepared from woody-shrub vegetation, was produced at the Andijan

hydrolysis plant in a hydrolysis apparatus with a capacity of 18 m<sup>3</sup>. The apparatus was loaded with 6.5 t natural raw materials or 3.25 tons of absolutely dry. Cooking was carried out according to the experimental mode, slightly different from the mode, when changeable at the plant when processing traditional raw materials, consisting from a mixture of wood chips and sawdust. In the course of increase of the whole cooking hydrolyzate dispensing was not limited, pressure drop did not exceed 0.15-0.25 MPa. Cooking control was carried out by control parameters, as well as analysis of hydrolyzate samples, sampled at 20 minute intervals. Was also analyzed average sample of lignin taken after the shot (table 3.)

**Table 3. Composition of hydrolyzate by percolation periods**

Frequency of selection samples from the beginning of percolation, min	Content of RV,%	Acidity,%
5	3,06	0,49/0,44
25	2,87	0,61/0,37
45	2,24	0,44/0,32
65	1,78	0,44/0,29
85 (flushing)	1,78	0,39/0,37
105 (spinning)	2,24	0,37/0,17
avarage	2,36	0,45/0,32

Note. The numerator is mineral acidity, the denominator is organic acidity.

The content of furfural in the average sample of the hydrolyzate was 0.038%. Inversion of the hydrolyzate with 3% sulfuric acid did not give a significant increase in RS. With the actual selection of hydrolyzate from cooking 34.8 m<sup>3</sup>, the yield of radioactive substances was 821 kg. In the analysis of lignin, the content of

difficult-to-hydrolyzable polysaccharides was 37%, unwashed RS was 1.7%, and the acidity was 0.31%.

The chemical composition of white alder, aspen and birch growing in Lithuania, given in (table 4)

**Table 4. Chemical composition of wood**

components	Content , % in completely dry wood		
	aspen	birch	white alder
Cellulose	42,5	37,4	38,1
Lignin	18,0	18,3	20,1
Pentosans (without uronic acids)	20,3	22,7	19,3
Polysaccharides: readily hydrolyzable	22,0	25,9	21,2
difficult to hydrolyze	46,0	40,2	42,5
Potential furfural: in wood	13,8	15,8	15,8
in the bark	8,4	8,3	11,5

The content of potential furfural in white alder wood is the same as in birch, and in bark it is much higher than in aspen and birch. Odubin, which is a waste obtained after the extraction of tannins from oak wood, also serves as a full-fledged raw material for obtaining furfural. It has been established that in a growing oak tree the share of its main parts is, %: trunk 50-75, roots 15-20, branches 10-20 Assortments with a diameter of 5 cm and more belong to the extract raw materials. The roots and branches of trees can also be used as raw materials, while in the roots from there is an increased content of tannides. Compared to other types of wood, oak has the largest share of roots and branches. Consequently, the use of these parts of wood will increase the raw material base for the production of both tannins and furfural. To increase the rate of hydrolysis of polysaccharides and the yield of monosaccharides, wood is preliminarily subjected to freezing. The authors believe that after freezing wood chips at a temperature of -30 to -40 ° C with

subsequent hydrolysis, it is possible to achieve an RS yield comparable to that from sawdust. Some polysaccharides, in particular xylan isolated from wood, which had a degree of polymerization of 100, completely dissolved after freezing in an aqueous medium at a temperature of -25 ° C for 12 hours. One of the important properties of plant raw materials is its flux flotation in the liquid phase. Air and water occupy 50% of wood volume, and the air content is inversely proportional to the moisture content of the wood. When wood is impregnated, air is displaced by solutions and is reduced in the cell cavities. The pressure created by the air interferes with the impregnation, slowing it down. Simulating the conditions of vapor-phase hydrolysis, it was determined that chips from aspen wood at a saturation degree of 190% are completely saturated with water and become submerged in it. Conditions for displacing products of thermocatalytic processing of raw materials largely depend on its fractional composition. This is of particular importance in the

processing of wood raw materials. The presence of a large amount of small, dusty fractions, sawdust not only sharply reduces the rate of hydrolyzate dispensing during percolation hydrolysis, but also negatively affects the rate of evacuation of furfural and other products of the vapor phase process from the reaction space. GOST 1832-78 provides a method for determining tests for the content of a dust-like fraction with a diameter of up to 1 mm; this figure should not exceed 10%. However, when determining the content of fine fractions according to this method, contradictory data can be obtained, since GOST 1832-78 does not regulate the moisture content of sawdust analyzed for the content of fine fractions. In particular, when determining fine fractions (up to 1 mm in diameter) sawdust of natural moisture (numerator) and dried to an air-dry state (denominator) in identical samples, the results,%, presented below, were obtained.

Samples:

1.....	7.50 / 18.80
2.....	5.00 / 22.60
3.....	1.50 / 14.84
4.....	7.50 / 28.87
5.....	4.75 / 19.15
6.....	4.92 / 13.19
7.....	10.00 / 19.83
8.....	2.03 / 18.66
9.....	6.10 / 20.33
10.....	3.30 / 12.96
11.....	2, 15 / 16.10
12.....	4.65 / 23.97
13.....	2.65 / 11.07
14.....	3.82 / 27.10
15.....	2.50 / 23.50
16.....	5.30 / 20.17

17.....	5.40 / 16.10
18.....	4.45 / 17.50
19.....	1.60 / 26.49
20.....	5.63 / 27.44
Average value .....	4.53 / 19.92

Thus, the actual presence of fine fractions in dried sawdust exceeds this indicator in wet ones by 4-5 times.

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