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CHEMICAL PROCESSING OF AGRICULTURE WASTES INTO VANILLIN, PULP AND GLUCOSE[*]

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Agrotechnical wastes from processing herbaceous plants consist of lignin and polysaccharides, which can be processed into monomers – phenols and carbohydrates. The prospects of chemical processing of several agrotechnical waste types with a high lignin content (flax shives, sunflower seed husks and buckwheat husks) into vanillin, pulp, and glucose by oxidation and acid hydrolysis were studied. It has been shown that despite the distant phylogenetic relationship of the studied plants, their lignins have a similar structure: they contain a similar amount of methoxyl groups (10–13 wt.% per lignin) and give close yields of aromatic aldehydes upon oxidation with nitrobenzene (17–19%) and oxygen (14–16%). In general, the suitability of agrotechnical wastes for oxidation to aromatic aldehydes determines by the lignin content. Among the studied wastes, flax shives are the most promising feedstock for chemical processing into vanillin and glucose. Cellulose-containing solid residues of oxidation process are more easily hydrolyzed compared to the initial lignocellulosic biomass. The inversion of glucose oligomers during the hydrolysis of cellulose with H_2SO_4 is limited by the hydrolysis of the tetra- and octamers.

Keywords: flax shives; *Linum usitatissimum;* sunflower seed husks; *Helianthus annuus;* buckwheat husks; *Fagopyrum esculentum;* lignin; oxidation; vanillin; hydrolysis.

Introduction

Plant biomass is a promising renewable raw material that can replace fossil hydrocarbons in the processes of large-scale and fine chemical synthesis in a future [1–3]. Consisting of three polymers, lignin, cellulose and hemicelluloses, it can be converted into their monomers – phenols and carbohydrates, which are bio-based platform molecules for the synthesis of various valuable products.

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Existing industrial chemical methods to process lignocellulosic biomass produce cellulose mainly. The resulting technical lignins (lignosulfonates, Kraft lignin, Klason lignin, etc.) have a high degree of condensation and low reactivity, and therefore they are almost never used in production of chemicals. The advantages of native lignins for the production of monomeric aromatic compounds compared to technical ones have led to a modern concept, expressed in two words: "Lignin first" [4, 5]. That is, processing the lignocellulosic raw

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materials should begin from the conversion of lignin into valuable and in-demand products. Unlike condensed technical lignins, agricultural and timber harvesting wastes are products of plant feedstock mechanical treatment, as a rule. Processing such essentially native lignins can give high yields of monomeric phenolic products. In this way, large-scale agricultural wastes combine the advantages of technical and native lignins: low price and a possibility to obtain monomeric chemicals with high yields. High lignin content was found in flax (23–31%) [6], sunflower (23–35%) [7, 8] and buckwheat (23–33%) [9–11].

The currently developing method of lignin valorization is catalytic oxidation by molecular oxygen (OMO) to obtain hydroxy aldehydes, mainly vanillin and syringaldehyde. They are valuable feedstock for the pharmaceutical, food and perfume industries [12, 13]. The oxidative processing of native lignins to obtain aromatic aldehydes, primarily vanillin, has the obvious advantage of a high yield compared to technical, condensed lignins [14]. One of the products of oxidation of lignocellulosic biomass is a solid cellulosic residue, pulp, suitable for acid hydrolysis into glucose.

Hardwood lignins is well known to consist mainly of syringylpropane structures, and its oxidation yields more aromatic aldehydes compared to softwood lignins [15]. This is due to the greater tendency of guaiacylpropane structures to condensate at position 5 of the aromatic ring of the phenylpropane unit (PPU). Lignins of herbaceous plants, in contrast to woody ones, contain a significant amount of non-methoxylated PPU, for which condensation is possible at the third and fifth positions of the aromatic ring. This can lead to a decrease in the yields of aromatic aldehydes in the oxidation processes during the transition from wood feedstock to herbaceous one [16]. Indeed, lignins of herbaceous plants give smaller amounts of aromatic aldehydes in the oxidation processes [6] in comparison with softwood and moreover hardwood lignins.

The purpose of this work is to study the oxidation of several agrotechnical wastes contained a high lignin content according to [5–10] (flax shives, sunflower and buckwheat husks) into vanillin and pulp followed by an acid hydrolysis of cellulose into glucose.

Materials and methods

Agrotechnical wastes and its treatment. Flax shives (*Linum usitatissimum,* region of growth and collection - Belarus), sunflower seed husks (*Helianthus annuus,* Barnaul halvah factory, Altai Krai, Russia) and buckwheat husks (*Fagopyrum esculentum,* Omsk Oblast, Russia) were used as a substrate. The air-dry lignocellulosic biomass was ground in a VR-2 vibrating mill. A fraction of less than 2 mm was used.

Component analysis of lignocellulosic feedstock. Cellulose content was measured as Kürschner cellulose obtained by refluxing a sample three times for 1 h with a 1 : 4 (v/v) mixture of concentrated nitric acid and ethanol [17]. Lignin content in the studied materials was measured as the Klason lignin remaining after hydrolyzing the carbohydrate components with 72 vol.% sulfuric acid [18]. To remove components of lignocellulosic biomass that can affect the quantitative analysis of lignin, a substrate was poured with 5% NaOH solution, kept for 1 h at room temperature, then filtered and washed with water. The dried residue was placed in a Soxhlet apparatus and extracted with hexane for 8 h after that, and then with an alcohol-benzene mixture (1 : 2) for 8 h [19].

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Quantitative analysis of methoxy groups in lignin. Determination of the methoxy groups content in Klason lignin isolated from raw materials by hydrolysis with 72% sulfuric acid [18], was carried out according to the methods [20–23]. Concentrated sulfuric acid (10.5 ml) was added to a flask with a portion of lignin (150 mg) through a reflux condenser. The flask was heated on a sand bath until SO_3 vapor appeared and kept for 10 min. Then the flask was cooled to 60 °C, 75 ml of water was poured through a reflux condenser, and the condenser was replaced with a direct one with a Wurtz's nozzle. Next, the solution in the flask was distilled and a sample with volume 20 or 40 ml was taken off. The volume of the distillate was transferred into a

25 or 50 ml volumetric flask, a water solution of an internal standard (isopropanol, 1 g/l) was added. The volume of the solution was adjusted to the flask mark and the CH_3OH concentration was determined.

Quantitative analysis of the methanol content was carried out by gas chromatography on a Varian 450 GC instrument with a flame ionization detector using a VF-624 capillary column. Temperature program: initial column temperature 35 °C, isotherm 5 min, rise rate 10 °C/min to 200 °C, isotherm 1 min. Carrier gas (He) flow through column was of 1 cm^3/min. Evaporator temperature was of 270 °C. Calibration was carried out using standard solutions of methanol and isopropanol in water.

Catalytic oxidation of lignocellulosic feedstock. Oxidation with molecular oxygen (OMO) was carried out in an aqueous alkaline medium in an autoclave made of steel 12Kh18N10T (USA analogues 321, S32100, S32109) with a volume of 1 liter. Copper oxide was used as a catalyst. Loading: feedstock – 20 g, sodium hydroxide – 20 g, copper sulfate pentahydrate – 15 g, water – 400 ml. Temperature – 160 °C; O_2 pressure – 2 bar; stirring – 700 rpm. The schemes of the reactor and the oxidation process are presented in details earlier [24]. Nitrobenzene oxidation (NBO) was carried out in the same autoclave. Loading: feedstock – 15 g, sodium hydroxide – 20 g, nitrobenzene – 25 ml, water – 500 ml. Temperature – 160 °C; stirring – 700 rpm; oxidation time – 150 min.

For aromatic aldehydes analysis after oxidation, the reaction mixture samples (10 ml) were taken off from the reactor. Aliquot was acidified by hydrochloric acid to pH 2. The precipitated tars were filtered, and the filtrate was sequentially extracted by three chloroform portions. The products in the extract was then determined by gas–liquid chromatography (Chromos Engineering GH1000 chromatograph, auto sampler DAG-23, column 30 m × 0.32 mm, stationary phase 25% trifluoropropyl polysiloxane). Anthracene was used as internal standard.

The reaction mass unloaded from the reactor was centrifuged and filtered to remove alkali-soluble dark-colored products which contained vanillin and lignin-like products (lignoacids). The solid residue was repeatedly washed with an alkaline solution (0.5–2% NaOH) until complete discoloration. The resulting alkali soluble products were precipitated by acidifying the solution to pH 2, centrifuged several times, washed with distilled water, and then dried at 50 °C.

Solid residue of the oxidation process purified from alkali-soluble products was washed with water and then dispersed in a HCl solution with addition of H_2O_2 to dissolve copper oxides, catalyst, finally washed until a neutral reaction and dried.

Study of lignoacids obtained in the oxidation process by NMR. Alkali-soluble products of catalytic oxidation were dissolved in DMSO-d6 (for ^{13}C and HSQC NMR) or in a $Pyr/CDCl_3$ mixture (for ^{31}P NMR). The dissolved lignin substances were separated from the insoluble white precipitate, hemicelluloses, by centrifugation. To carry out a quantitative analysis, the mass of the sample was corrected taking into account the mass of hemicelluloses insoluble fraction. To determine the content of hydroxyl groups, the sample was phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) followed by registration ^{31}P NMR spectra [25, 26]. NMR spectra were registered using the Bruker AVANCE III 600 NMR spectrometer at 298 K. The sample preparation details and conditions of spectra registration are provided in the Electronic Supplementary Information. The experiments were carried out in two repetitions.

Acid hydrolysis of the carbohydrates component of lignocellulosic biomass. Hydrolysis of lignocellulose under autoclave conditions was carried out at 180 °C within 3 hours in pure water and with a solid acid catalyst Amberlyst-15 (Acros organics). The hydrolysis was carried out in a rotating autoclave batch reactor with a Teflon insert (ICCT SB RAS, Russia). Rotation speed 5 rpm. The inner volume is 30 ml. The reactor was loaded with 0.75 g of the substrate, 15 ml of distilled water, and 0.25 g of the Amberlyst-15 catalyst.

Two-stage hydrolysis with sulfuric acid was performed according to [27, 28]. One g of the substrate was poured into a test-tube, 8 ml of 80% sulfuric acid solution was added, the tube was closed and vigorously shaken during 60 min at 25 °C. After that, the reaction mixture was diluted with cooled distilled water (120 g) and transferred to a flask. Inversion by diluted acid was carried out under reflux. The hydrolyzate was filtered and analyzed, the solid residue was washed and dried.

Soluble carbohydrate and by-product analysis was performed on an Agilent 1260 Infinity II HPLC complex. Chromatographic column: Rezex HPLC RPM-Monosaccharide Pb^{2+}, refractometric and UV detection, temperature 70 °C, eluent - deionized water, 0.6 ml/min. The samples were filtered through a 0.45 µm PTFE membrane filter.

To study the molecular weight distribution of hydrolysis products, an Agilent 1260 Infinity II Multi-Detector GPC/SEC System with a refractometric detector and two Agilent PL aquagel-OH columns was used. The eluent was

0.1 M NaNO$_3$ with the addition of 0.25 g/L NaN$_3$, 1 mL/min, with an injection volume of 100 µL [29]. Sulfuric acid was precipitated by adding CaO and filtered through a 0.45 µm PTFE membrane filter.

Results of the research and discussion

Study of the component and functional composition of lignocellulose biomass. It was reported previously that flax, sunflower and buckwheat processing wastes have a high lignin content [10, 12, 30]. Therefore, they are promising substrates for processing into aromatic monomers. Indeed, direct determination of lignin in unextracted initial sunflower and buckwheat husks formally gives values of more than 23%. However, after the removal of extractives and, and most importantly, substances extractable with aqueous alkali, the lignin content in terms of the initial substrates decreases down to 17 wt. % (Table 1). The content of extractable by aqueous alkali components is 25–35 wt.% of the feedstock. The color of the alkaline extract of flax shives is light yellow and transparent. When the extract is acidified to pH 2, a white amorphous hemicelluloses precipitates. Alkaline extracts of sunflower and buckwheat husks are dark brown and opaque. This means that most of the extractives from sunflower and buckwheat husks under the conditions (5% NaOH, 1 hour) are polyphenols, and not hemicelluloses. These polyphenols, flavonoids, tannins and others do not dissolve upon analysis of lignin content and are defined as lignin, although they are not.

Table 1 also shows the obtained content of methoxyl groups in the studied substrates. The obtained results show that the hydrolysis lignins of all substrates contain 10–13 wt.% methoxyl groups. In nature, lignin is synthesized by the oxidative condensation of synaptic, coniferyl, and coumaric alcohols. The content of methoxyl groups in synapic and coniferyl alcohols is 30.1 and 17.2 wt.%, respectively; 4-hydroxyphenylpropane structures do not contain methoxyl groups. Therefore, all of these lignins contain less than one methoxyl per phenylpropane structural unit (PPU) in average. Simple stoichiometric estimates, neglecting the presence of syringyl PPUs, show that the part of nonmethoxylated PPUs for flax, sunflower and buckwheat lignins is of 24–43%, and the presence of syringyl PPUs increases this value.

Catalytic oxidation of lignocellulosic feedstock. The process of catalytic oxidation of flax shives, sunflower seed husks and buckwheat husks with molecular oxygen (OMO) to obtain vanillin, syringaldehyde, and pulp, delignified cellulosic material proceeds for 20-60 minutes (Figure 1).

The yields of vanillin per lignin and the rate of its accumulation during oxidation vary slightly depending on the feedstock (11–14%). However, flax shives is the best choice in the term of the maximum yield of vanillin, based on the loaded feedstock, since it contains 1.5 times more lignin compared to sunflower and buckwheat husks (Table 1).

In addition to vanillin, syringaldehyde is formed, the yields of which are several times less than those of vanillin. Nitrobenzene oxidation (NBO), which is the reference method for lignin oxidation in terms of the maximum possible yields of aromatic aldehydes [14], is more efficient than OMO (Table 2).

Table 1.   Component composition of substrates

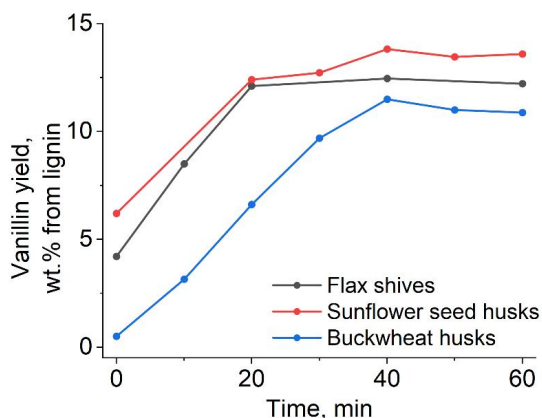| Substrate	Lignin, mas.%	Cellulose, mas.%	Extractable with aqueous alkali, mas.%	Extractives, mas.%	CH$_3$O group content, mas.% per lignin
Flax shives	24.5±0.7	39.6±0.4	24.7	0.96	12.6±1.2
Sunflower seed husks	16.7±0.5	34.0±0.4	36.4	11.4	12.1±2.1
Buckwheat husks	17.1±0.5	36.0±0.5	26.0	7.5	9.5±0.8

Figure 1. Kinetics of vanillin accumulation in the oxidation with molecular oxygen. Feedstock – 20 g, sodium hydroxide – 20 g, copper sulfate pentahydrate – 15 g, water – 400 ml, 160 °C; O$_2$ pressure – 2 bars; stirring – 700 rpm

Table 2. Yields of aromatic aldehydes during the oxidation of agricultural waste and the part of methoxyl groups transferred from lignin to aldehydes.

Substrate	Vanillin yield, wt.% from lignin (CH₃O in vanillin, wt.% for lignin)		Yield of syringaldehyde, wt.% from lignin (CH₃O in syringaldehyde, wt.% for lignin)		Part of methoxyl groups converted from lignin to aldehydes	
	OMO	NBO	OMO	NBO	OMO	NBO
Flax shives	12.14 (2.47)	15.14 (2,98)	2.33 (0.77)	4.20 (1.38)	0.25	0.34
Sunflower seed husks	13.8 (2.81)	14.37 (2,83)	2.63 (0.86)	3.35 (1.10)	0.29	0.32
Buckwheat husks	11.5 (2.27)	14.21 (2.80)	2.34 (0.77)	2.98 (0.98)	0.32	0.40

The results of Tables 1 and 2 make it possible to carry out stoichiometric calculations and estimate the part of methoxyl groups of lignin that pass into vanillin and syringaldehyde during the oxidation. In all the experiments, this part is about ¼ to ⅓ and does not depend on the nature of the herbaceous feedstock. In the process of nitrobenzene oxidation, 35±3% of the methoxyl groups of lignin pass into aldehydes, and during oxidation with oxygen, this part is of 29±2%. The slight difference between these two values is explained by the higher yields of aldehydes during NBO compared to OMO process.

The considered biological species have a very distant phylogenetic relationship, they are united in the clade of the core eudicots, their common taxonomic unit is the class Dicotyledonous (*Magnoliopsida*). Closed yields of aromatic aldehydes from such phylogenetically distant herbaceous plants suggest that the structures of lignins in most herbaceous plants are close to each other. Therefore, for the chemical processing of lignins of herbaceous feedstock into aromatic aldehydes, it is advisable to use substrates with maximum lignin content, and it should be determined taking into account a content of another polyphenols in a feedstock.

One of the by-products of the catalytic oxidation of plant biomass to vanillin is the solid residue. The yield of solid residues and its properties are presented in Table 3. These results are typical for oxidation of native lignins [31]. In contrast, both lignin and cellulose of buckwheat hulls are much more destroyed during the oxidation then flax shives and sunflower husks.

Another fraction of the products are alkali-soluble substances, including hemicelluloses, oxidized lignin (lignoacids) and the target product - aromatic aldehydes. Yield of these oxidation products are 18.8 wt.% per the substrate for flax shives, 12.3 for sunflower seed husks and 19.3 for buckwheat husks. Delignification is of 92–97%, and an aldehyde yield is about 16–17 wt.% in the OMO process. Thus, 75 wt.% of lignin are condensed in a native form or become such during oxidation and do not produce the aromatic aldehydes.

This residual alkali-soluble lignin (lignoacids) was studied by nuclear magnetic resonance spectroscopy (NMR). ³¹P NMR spectroscopy (Fig. 1S) was used for the analysis of free hydroxyl groups belonging to various structural units in lignin (Table 4). Along with the signals corresponding to aliphatic and phenolic OH groups, there is a strong signal corresponding to carboxyl OH groups, 23–36% of the total OH content. These values exceed the carboxyl OH groups in different dioxane lignins (3–4%) [15] by a factor of 7–9 due to deep oxidation of the lignins in the process.

In the region of phenolic OH groups in the ³¹P NMR spectra (Fig. 1S) a strong overlap of signals is observed, and this is due to the contribution of a large number of condensed structures (4-O-5' and 5-5'). Additionally, a semiquantitative analysis was carried out by HSQC NMR spectroscopy. It has been established that the structures of β-aryl ethers are almost completely destroyed. The structures of resinol (β-β') and phenylcoumaran (β-5') are found in trace amounts (0.5-3.5 and 0.9-1.5 per 100 PPUs, respectively).

Table 3. Yields and composition of the solid residue of lignocellulosic mass during the oxidation of agricultural waste

Substrate	Yield of residue, wt.%	The content in the residue of OMO, wt.%		Delignification, wt.%	Cellulose yield*, wt.%
		Lignin	Cellulose		
Flax shives	35.7	5.41±0.35	91.20±1.6	92.2	82.2
Sunflower seed husks	35.4	3.96±0.17	84.88±1.50	91.6	88.4
Buckwheat husks	24.8	2.01±0.13	85.55±0.83	97.1	58.9

*Based on the initial content in the substrate.

Table 4.   The content of structures and functional groups in lignoacids obtained by oxidation

Substrate	Flax shives	Sunflower seed husks	Buckwheat husks
Lignin structures, relative per cent			
S	13.6	20.8	24.3
G	80.2	73.2	72.5
H	6.2	6.0	3.2
S/G	0.17	0.3	0.3
Functional groups, per 100 PPUs			
OMe NMR of lignoacids	91.1	68.2	53.4
OMe in Klason lignin	71.2	67.5	57
Total OH	129.3	96.8	88.6
Aliphatic OH	37.8	15.8	21.9
Phenolic OH	61.3	46.3	43.4
COOH	30.1	34.8	23.3

The content of methoxyl groups in lignoacids (the part of lignin soluble in the oxidation process) determined by NMR is 91, 68 and 57 per 100 PPUs for different substrates (Table 4, Fig. 2S). In Klason lignin (all native lignin, although more condensed), their contents determined by hydrolysis and chromatography are close for flax shives and sunflower husks – 67–71, and less for buckwheat husks - 53 per 100 PPUs, respectively (Table 1). The higher content of methoxyl groups in lignoacids obtained from the flax shives, compared to Klason lignin, indicates a greater reactivity of methoxylated phenylpropane units during oxidation in an alkaline medium. Thus, non-methoxylated structural units (H) are more condensed and less prone for solubilyzation compared to guaiacyl (G) and syringyl (S) PPUs. This conclusion is confirmed also by comparing a content of non-methoxylated structural units (H) in a hydrolysis lignins (24–43%) and lignoacids (H : (H+G+S) = 3-6% (Table 4).

Similar relation is well-known for condensation of guaiacyl and syringyl structures, and it can be traced by the ratio of the aldehyde yields obtained from flax shives (Table 2) and the ratio of structures S and G in lignoacids according to the NMR data. According to the NMR, the ratio S:G = 0.17 for flax, and the S/G ratio in aldehydes obtained in the process of nitrobenzene oxidation, products of complete cleavage of bonds between the PPUs of lignin, S : G = 0.28 (Table 2). Consequently, the syringyl PPUs of flax shives lignin are more easily split, i.e. less condensed compared to guaiacyl ones. Such regularities are not observed in the oxidation products of sunflower seed husks and buckwheat husks. These substrates contains a lot of antioxidants, tannins and flavonoids (Table 1), and they may inhibit lignin oxidation and the aldehydes formation [32, 33].

Acid hydrolysis of the carbohydrate components of lignocellulosic biomass. The solid residues of the catalytic process of lignin oxidation with molecular oxygen enriched in cellulose is expediently processed into glucose. To assess the prospects of such a process, experiments on hydrolysis of the considered agriculture wastes and their oxidation products were performed. Hydrolysis at 180 °C was carried out in autoclave in water with and without solid acid Amberlyst-15 (Table 5).

The catalyst fundamentally increases the yield of glucose during the hydrolysis of the initial husks, and 1.5 times (from 9 to 14%) while hydrolysing the oxidized husks. The process of oxidation of sunflower seed husks has the greatest influence on the yield of glucose in non-catalytic hydrolysis: the initial husks does not give glucose, and 7.7 wt.% of glucose is formed from the oxidized husk. Catalytic hydrolysis of oxidized husks with Amberlyst-15 yields almost twice as much glucose as compared to hydrolysis of cellulose of the initial husk. The obtained results show that the process of sunflower seed husks oxidation to vanillin significantly changes the structure of lignocellulosic biomass. It reduces the content of hemicelluloses in the feedstock and activates the resulting cellulose for acid catalyzed hydrolysis and first of all for hydrolysis without a catalyst. The activation of cellulose in the process of lignin oxidation is known; it is especially effective for low-active catalysts operating under mild conditions, including enzymes [24].

The two-stage method of cellulose hydrolysis with sulfuric acid [34] by dissolving in 80% sulfuric acid at room temperature, followed by dilution and inversion of oligosaccharides during boiling is more efficient. This powerful hydrolysis technique provides yield of 73 wt. % glucose per cellulose from both initial and oxidized feedstock (Table 6).

When using this method of hydrolysis, the above conclusions are generally preserved: the content of hemicelluloses in the solid residue after oxidation, and, consequently, the yield of furfural are decreased. Notably, the large amount of glucose formed increases the yield of 5-HMF. The total yield of furfural and 5-HMF is lower during the hydrolysis of the solid residues after oxidation with molecular oxygen, compared with the initial substrates. The lower concentration of furfural and 5-HMF is known to be favorable for subsequent fermentation of sugars, and the oxidation provides this advantage (Table 6).

Table 5.   Results of hydrolysis of lignocellulose mass under autoclave conditions.

Substrate	Catalyst	Yield wt.% on the substrate				
		Glucose	Xylose	Furfural	5-HMF	Mass loss, %
Initial sunflower seeds husk	w/o cat[a]	0.00[c] 0.00	0.17	2.99	0.30	44.30
	A-15[b]	7.13[c] 2.42	1.03	4.18	0.25	52.04
Solid residue sunflower seeds husks after oxidation	w/o cat[a]	9.04[c] 7.67	0.29	1.53	0.80	55.51
	A-15[b]	13.96[c] 11.85	0.15	1.73	0.73	60.23

[a] without catalyst in pure water; [b] Amberlyst-15, [c] yield wt.% per cellulose. Substrate – 0.75 g, Amberlyst-15 – 0.25 g, water – 15 ml, 180 °C, 3 hours.

Table 6.   Conversion of agricultural waste and their solid residue after the oxidation with molecular oxygen in the process of two-stage hydrolysis by sulfuric acid

Substrate		Yield wt.% on the substrate					Mass loss, %
		Glucose	Xylose	Furfural	5-HMF	Sum of products	
Flax shives	Initial	73.03[b] 28.85	7.33	2.55	0.03	39.29	67.67
	SR OMO	73.28[b] 67.38	3.36	1.44	0.22	72.40	94.59
Sunflower seed husks	Initial	56.42[b] 27.49	5.20	1.16	0.02	36.46	71.94
	SR OMO	82.89[b] 70.36	2.03	0.61	0.30	73.31	96.22
Buckwheat husks	Initial	68.29[b] 24.58	9.70	1.73	0.16	38.27	72.42
	SR OMO	77.06[b] 65.92	3.59	1.77	0.44	72.09	98.08

Reaction conditions: dissolution: 80% sulfuric acid, 25 °C, 1 hour; inversion: dilution by 15 times, boiling, 3 hours. [a] SR OMO – solid residue after oxidation with molecular oxygen [b] yield wt.% per cellulose.

Hydrolysis of oxidized substrates permits to obtain a glucose yield of about 66–71 wt.% per the substrate or 73–83 wt.% per the cellulose contained in the solid residue. At the same time, there is a significant difference between the weight loss during hydrolysis and the total yield of detected products – about 20–25 wt.%. This difference may be due to incomplete hydrolysis of soluble polysaccharides. Indeed, the gel-permeation chromatography technique determined the molecular weight characteristics of the hydrolysis products of oxidized sunflower seed husks (Fig. 2) and identified three main products: glucose (retention time 28.75 minutes), oligomers containing 4 (27 min) and 8 (25.5 min) anhydroglucose units. Cellobiose (28.25 min) and other oligomers are observed as minor impurities only.

Therefore, glucose tetra- and octamers are the most stable, and their hydrolysis to glucose can limit the inversion process. An increase in the duration of hydrolysis, which is necessary for the conversion of these oligomers into glucose, leads to decrease in the yield of glucose due to the dehydration reaction and the formation of 5-HMF. To solve this problem the inversion stage (hydrolysis of dissolved cellulose) under autoclave conditions at the temperature of ~ 120 °C during a short time (10–20 min) is recommended [34].

Figure 2. Gel-permeation chromatogram of hydrolysis products of oxidized sunflower seed husks. Conditions of hydrolysis: dissolution with 80% sulfuric acid, 1 hour, 25°C; dilution, boiling 1.5 or 3 hours
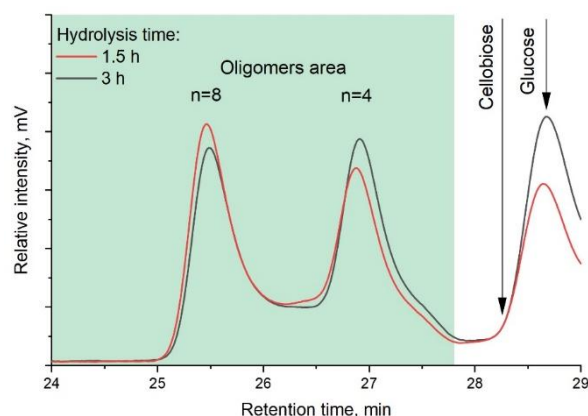
Conclusion

Oxidation of agricultural waste, flax shives (*Linum usitatissimum*), sunflower seed husks (*Helianthus annuus*) and buckwheat husks (*Fagopyrum esculentum*) with molecular oxygen and nitrobenzene were studied. It has been shown that despite the distant phylogenetic relationship of these species (the common taxon is the class of dicotyledonous), their lignins have a very similar reactivity. They contain a close amount of methoxyl groups (10–13 wt % per lignin) and give close yields of aromatic aldehydes, vanillin and syringaldehyde, while oxidizing both with nitrobenzene (17–19%) and oxygen (14–16%). These results suggest that the lignins of most herbaceous plants belonging to dicotyledonous will give yields of aromatic aldehydes close to those obtained in this study. Therefore, a preliminary conclusion about the suitability of herbaceous plants for oxidation to aromatic aldehydes may be made based on the maximum content of lignin in a feedstock. In the framework of the presented study, this is the flax shives. It should keep in mind that many herbaceous plants contain other polyphenols along with lignin, which can overestimate the results of the lignin content analysis and inhibit the lignin oxidation by oxygen.

The obtained results show higher content of methoxyl groups in lignoacids obtained by the oxidation of flax shives compared with Klason lignin. This comparison indicates a greater reactivity of methoxylated phenylpropane units during oxidation in an alkaline medium. Thus, non-methoxylated structural units (H) are more condensed and less prone for solubilyzation compared to guaiacyl (G) and syringyl (S) PPUs.

The yield of cellulose in the process of oxidation of flax shives and sunflower seed husks is higher by ⅓ than for buckwheat husks. The study of the process of acid-catalyzed hydrolysis of cellulosic products obtained by the oxidation processes showed that they are hydrolyzed more easily and efficiently compared to the initial substrates. Most of all, these differences are manifested in the processs of autohydrolysis in a pure water without catalysts, and its level out with increasing the activity of the catalysts.

The stage of inversion of oligomers upon hydrolysis with sulfuric acid is limited by the hydrolysis of the relatively stable glucose tetra- and octamers.

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