

Article

Reductive Catalytic Fractionation of Flax Shive over Ru/C Catalysts

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Abstract: Flax shive is the main waste (up to 70 wt %) in the production of flax fiber. It represents the lignified parts of the flax stem mainly in the form of small straws. Complex processing of such wastes is a significant problem due to the heterogeneity of the chemical structure of lignin. This article presents the results of reductive catalytic fractionation (RCF) of flax shive in ethanol and isopropanol at elevated temperatures (225–250 °C) in the presence of a bifunctional catalyst (Ru/C) and molecular hydrogen. This provides solvolytic depolymerization of lignin and hemicelluloses presented in flax shive. Catalytic hydrogenation effectively stabilizes the formed lignin intermediates and prevents repolymerization reactions producing the lignin fraction with a high degree of depolymerization. RCF of flax shive produces solid products with a high cellulose content and liquid products consisting mainly of monophenolic compounds. Furthermore, the effect of different characteristics (the ruthenium content, particle size, and support acidity) of the bifunctional catalysts containing ruthenium nanoparticles supported on mesoporous, graphite-like carbon material Sibunit[®]-4 on the yield and composition of the products of hydrogenation of flax shive in sub- and super-critical ethanol has been studied. Bifunctional catalysts Ru/C used in the RCF of flax shive increase its conversion from 44 to 56 wt % and the yield of monophenols from 1.1 to 10.2 wt % (based on the weight of lignin in the sample). Using the best Ru/C catalyst containing 3% of Ru on oxidized at 400 °C carbon support, the high degree of delignification (up to 79.0%), cellulose yield (up to 67.2 wt %), and monophenols yield (up to 9.5 wt %) have been obtained.

Keywords: flax shive; reductive catalytic fractionation; Ru/C catalysts; valorization; biomass



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1. Introduction

The depletion of fossil resources and CO₂ emissions, negatively affecting the environment, require new methods for use of renewable plant raw materials, including agricultural waste, to ensure environmental safety and social and economic sustainability [1].

Flax shive is the nonfibrous fraction of flax straw. It has a highly lignified structure and represents an agricultural waste widespread in Europe and North America. The flax shive composition includes lignin (~25%), cellulose (50%), and hemicelluloses (20%) [2,3]. Lignin is one of the three main (20–30 wt %) polymeric components of plant biomass. It is formed by biochemical oxidation of the coniferyl, sinapic, and p-coumaric alcohols and consists mainly of the corresponding phenylpropane units [4]. The lignin of herbaceous plants contains all three structural units. herbaceous biomass has the potential of becoming the largest renewable source of bioproducts and biofuels. Lignin is conventionally extracted

by sulfate and sulfite pulping of the lignocellulosic raw materials. Such lignins are more condensed than native ones and contain sulfur, which is a catalytic poison and a dangerous pollutant. An intensively studied method for obtaining relatively pure and more reactive lignin is organosolv pulping. However, even such a sustainable method results in partial condensation of lignin with the simultaneous cleavage of the β -aryl ether bonds [5].

Recently, new methods for efficient conversion of lignins and lignocellulosic biomass to fuel components and chemical products have been developed [6–9]. Reductive catalytic fractionation (RCF) of plant biomass is one of these methods, which includes catalytic depolymerization of lignin and isolation of cellulose [10,11]. The lignin obtained in this way contains macromolecular components with high oxygen content [12,13]. Their selective depolymerization and deoxygenation uses the catalysts based on noble metals (e.g., Au, Pd, Pt, and Ru) and less expensive but also less active transitional metals (e.g., Fe, Cu, and Ni) [14,15]. Ru is most efficient catalyst for the aqueous-phase hydrogenation of biosourced compounds [16]. On the other hand Ru is least expensive noble metal [17].

A presence of acid catalysts in the reaction mixture accelerate RCF process and results in lignin monomers yields increase due to acidolysis of ether bonds between phenylpropane units [18,19]. Our group previously studied supported ruthenium catalysts based on oxidized graphite-like carbon Sibunit[®]-4 (containing acid surface species [20,21]) for lignin and wood conversion, and subsequently set out to identify lower cost, easily available, and highly efficient catalysts to enhance the efficiency of the lignin conversion process [22–24].

This study investigates the biorefining of flax shive using the reductive catalytic fractionation (RCF) process over bifunctional catalysts bearing nanodispersed ruthenium, supported on carbon material Sibunit[®]-4 (S4) containing acidic surface functional groups. herein, various fractions of Ru/C catalysts based on S4 oxidized at different temperature were prepared and characterized. Lastly, catalysts were evaluated in reductive depolymerization of lignin. The effect of the main catalysts characteristics (acidity and Ru content) and the process conditions (temperature, solvent) on the flax shive biomass conversion, yields of gaseous, liquid, and solid products, and composition of the liquid products and their molecular weight distribution was studied.

2. Results and Discussion

2.1. Catalysts Preparation and Characterization

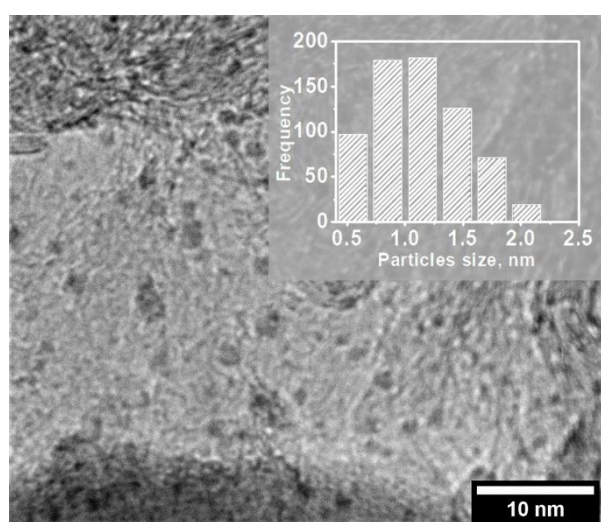
In early works [22–24], the reductive catalytic fractionation of woody biomass with powder Ru/C catalysts based on graphite-like mesoporous carbon Sibunit[®]-4 (S4) was considered. In this work, a number of catalyst characteristics were varied, including temperature of the support oxidation, the ruthenium content and the fractional composition of the catalyst (granular or powder).

Firstly, four carbon supports were prepared based on S4: initial powder S4, this powder oxidized at 400 and 450 °C, granular S4 oxidized at 500 °C. The supports were labeled as: S4, S400, S450, S500 g, respectively (Table 1). Varying the oxidation temperature allows us to obtain different amounts of oxidized centers on the surface of the carbon which can affect not only the acidic properties, but also the distribution of active component. The granular support was used for the estimation of diffusion limits. Secondly, Ru-containing catalysts with 3 wt % of Ru were prepared based on the obtained supports (Tables 1 and 2). Catalysts were labeled 3RSg, 3RS500g, 3RS400, 3RS450, respectively. In order to decrease the amount of the noble metal we also obtained the catalyst with 1 wt % of Ru (1RS450) based on S450 support.

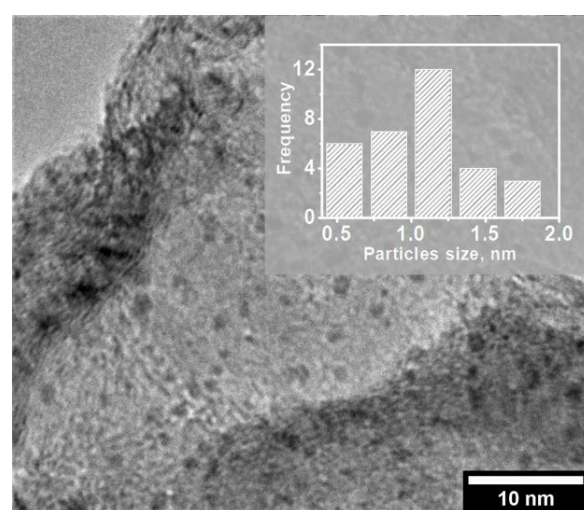
Table 1. Texture and acid characteristics of carbon support and the supported ruthenium catalysts (3 wt % of Ru).

Support	Code	BET Surface Area S_{BET} , m ² /g		Pore Volume V_{pore} , cm ³ /g		Average Pore Size $\langle d_{\text{pore}} \rangle$, nm		pH_{pzc} ¹	
		Support	Catalyst	Support	Catalyst	Support	Catalyst	Support	Catalyst
Sibunit-4	S4	364	273	0.51	0.32	5.66	4.77	7.66	8.05
Sibunit-4 oxidized at 400 °C	S400	332	300	0.42	0.37	5.06	5.01	6.88	7.12
Sibunit-4 oxidized at 450 °C	S450	380	341/368 ²	0.53	0.50/0.52 ²	5.66	5.88/4.80 ²	5.33	6.89/6.06 ²
Sibunit-4 oxidized at 500 °C (grains)	S500g	287	233	0.37	0.28	5.14	4.80	3.34	6.44

¹ pH_{pzc} is the pH of the point of zero charge. ² 1 wt % Ru catalyst.



(a)



(b)

Figure 1. Transmission electron microscopy images of (a) the 3%Ru/Sib-4 and (b) 1%Ru/Sib-4-ox-450 catalysts.**Table 2.** Ru particle sizes and dispersion in the prepared catalysts (results of statistical processing of the TEM data, Figure 1).

Support	Ruthenium Content, wt %	Code	Ru Particle Size, nm ¹				D_{Ru}
			d_{min}	d_{max}	$\langle d_1 \rangle$	$\langle d_5 \rangle$	
Sibunit-4, grains ²	3	3RSg	0.76	3.46	1.42 ± 0.02	1.71	0.77
Sibunit-4 oxidized at 500 °C ² , grains	3	3RS500g	0.69	3.14	1.30 ± 0.01	1.53	0.85
Sibunit-4 oxidized at 400 °C ³	3	3RS400	0.66	3.00	1.19 ± 0.01	1.40	0.94
Sibunit-4 oxidized at 450 °C ³	3	3RS450	0.52	2.37	1.13 ± 0.01	1.39	0.94
Sibunit-4 oxidized at 450 °C ³	1	1RS450	0.52	1.79	1.06 ± 0.03	1.27	1.03

¹ d_{min} and d_{max} —the minimum and maximum particle diameters, $\langle d_1 \rangle = \sum d_i / N$ —the mean linear particle size, $\langle d_5 \rangle = \sum d_i^3 / \sum d_i^2$ —the mean volume-surface particle size, D_{Ru} —the dispersion of Ru ² 1.0–1.6 mm fraction.

³ 56–94 μm fraction.

Texture properties, morphology and acid properties of the supports and catalysts were studied using N₂ adsorption (Table 1), transmission electron microscopy (TEM) (Table 2, Figure 1) and acid titration (Table 2). An increase in the temperature of the oxidative treatment of the carbon support (CS) and the deposition of ruthenium reduced the specific surface area S_{BET} , pore volume V_{pore} , and average pore size d_{pore} , probably due to partial destruction of the graphite-like structure of the Sibunit-4 CS during oxidation and blocking of some support pores with particles of the active component due to its precipitation (Table 1).

An increase in the temperature of the oxidative treatment of the CS also results in a decrease in the pH_{pzc} value, which apparently results from an increase in the concentration of the surface acid species [25]. The deposition of ruthenium is accompanied by a slight increase in the pH_{pzc} values (Table 1) obviously due to deactivation of the acid sites as a result of Ru particle deposition.

The statistical analysis of TEM images was performed to investigate Ru particles distribution in relation to Ru loadings (1 and 3 wt %) and catalyst support acidity (Table 2). All the catalysts based on the oxidized supports have a smaller ruthenium particle size and a narrower pore size distribution as compared with the initial support (Tables 1 and 2, Figure 1). The average ruthenium particle diameter decreases in the series 3RSg > 3RS500g > 3RS400 > 3RS450 > 1RS450 (Table 2). This can be explained by the interaction of negatively charged surface oxidized centers, the number of which increases with temperature of the support oxidative treatment, with ruthenium ions. The distribution of ruthenium particles on granular supports is less uniform.

Ru loading as low as 1 wt % gives a better Ru distribution in comparison to 3 wt % catalysts providing smaller ruthenium particle size (Table 2, Figure 1). Ru dispersion in the 1RS450 catalyst, appeared to be higher than 1 (Table 2). Taking into account the error in the mean particle diameter measurements, a conclusion may be made, that for 1RS450 catalyst all ruthenium atoms are located on the surface and fully available for the reaction.

The X-ray photoelectron spectroscopy (XPS) was used for a quantitative and qualitative analysis of the obtained catalysts (Table 3, Figure 2). The XPS shows that for all the samples, the most intense peaks are observed in the range of 284–285 eV, which is typical of graphite. In the range of 285–287 eV, there are peaks attributed to carbonyl, hydroxyl, and ether groups, as well as fragments of carboxyl groups. The Ru 3d_{5/2} peak observed near 281 eV is typical for oxidized ruthenium RuO₂. Metallic ruthenium is characterized by a peak near 280 eV; however, this shift toward higher binding energies can also be explained by the relaxation shift observed for very fine metallic particles [26,27].

Table 3. Surface elemental composition of the catalyst determined by XPS.

Catalyst.	C		O		Ru	
	at %	wt %	at %	wt %	at %	wt %
3RS450	91.9	84.9	7.5	9.2	0.6	4.7
1RS450	92.0	85.0	7.6	9.4	0.4	3.1

2.2. Catalytic hydrogenation of Flax Shive in Ethanol

The choice of the process temperature, duration and hydrogen pressure is based on the analysis of literature [11,19,24,28]. The results of experiments on hydrogenation of flax shive in ethanol without and with the different Ru/C catalysts are given in Table 4.

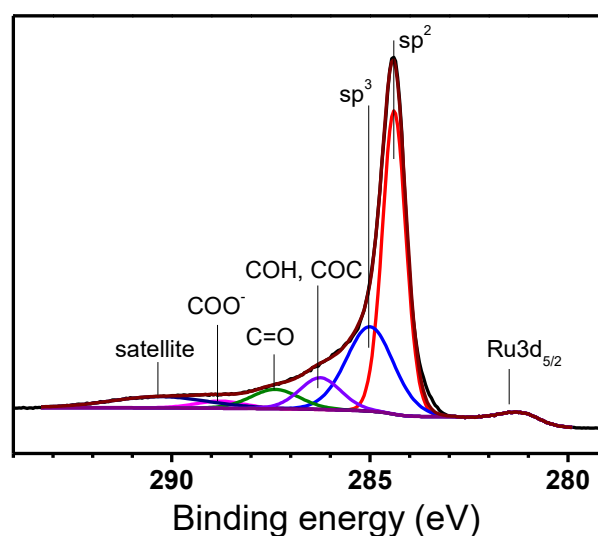


Figure 2. C 1s spectrum of the 3RS450.

Table 4. Results of noncatalytic and catalytic hydrogenation of flax shive in subcritical ethanol at 225 °C.

No.	Catalyst	Conversion ¹ , wt %	Liquid Yield	Solid Yield	Gas Yield	Monophenols ² , wt %
1	no	44.1	38.5	41.0	5.6	1.52
2	3RS450	55.3	42.5	33.0	1.6	5.65
3	1RS450	52.2	44.5	41.0	7.7	4.30
4	3RS500g	46.7	41.0	40.0	5.7	3.54
5	3RS400	50.5	41.5	45.6	9.0	4.78
6	3RSg	56.3	39.8	39.0	16.5	4.44
7	S450	39.0	34.5	41.0	4.5	2.24
8	3RS450 ³	43.5	21.4	56.5	16.8	3.47
9	3RS450 ⁴	87.6	31.6	12.4	37.8	5.27

¹ Conversion to the liquid and gaseous products; ² per flax shive sample mass; ³ isopropanol as a solvent; ⁴ the process temperature 250 °C.

During hydrogenation of flax shive in subcritical ethanol, the catalysts significantly intensify the biomass conversion (from 44 to 56 wt %) and increase the yield of liquids (from 38 to 44 wt %) and gases (from 5.6 to 16 wt %). While using the catalysts, the yield of monophenols grows significantly (from 1.5 to 3.5–5.6 wt %) (Table 4). These characteristics are improved due to the depolymerization of native lignin in the presence of the catalysts, which accelerates the cleavage of the C–O and C–C bonds [29].

The maximum yield of monophenols (5.6 wt % per shive and 10.2 wt % per lignin), which are the most valuable products, is obtained using the catalyst oxidized at 450 °C and containing 3 wt % of Ru. The reductive catalytic fractionation of flax shive with the use of the carbon support (Sib-4) yields 2.24 wt % of monophenols. When using the granular catalysts (runs 4 and 6), the monophenol yield does not exceed 4.4 wt %. It should be noted that the use of the granular 3% Ru/C catalyst on CS oxidized at 500 °C enhances the gas yield up to 16.5 wt %.

Thus, the highest efficiency of the catalytic process is attained by the 3RS450 characterized by the maximum specific surface area and porosity (Table 1) and the minimum ruthenium particle size (Table 2).

The catalysts change the CO₂ yield of the process insignificantly, but fundamentally increase the CO and CH₄ yields, from trace amounts to 2–7 wt % per shive weight (Table 5). The catalysts on the support oxidized at 450 °C is most active in the shive conversion (Table 5) and gives the highest CO and CH₄ yields. The growth of the CO yield is caused

by the intensification of decarbonylation of the Gibbert ketones [30–33] formed on the catalyst metal sites. Methane is formed mainly at hydrocracking of the aliphatic structural fragments of lignin [34,35]. Increase the CO and CO₂ yields in the presence of catalyst indicates the catalytic deoxygenation of the lignin structural fragments.

Table 5. Yield and composition of the gaseous products of hydrogenolysis of flax shive.

No.	Catalyst	CO wt %	CO ₂ wt %	CH ₄ mass %
1	no	-	5.6	-
2	3RS450	3.6	6.8	2.2
3	1RS450	1.8	5.9	traces
4	3RS500g	traces	5.7	traces
5	3RS400	1.4	6.6	1.0
6	3RSg	7.4	6.5	2.6
7	Sib-4 (450)	traces	4.5	traces
8	3RS450 ¹	4.9	7.6	7.6
9	3RS450 ²	18.3	13.2	6.3

¹ Isopropanol as a solvent. ² the process temperature 250 °C.

Table 6 shows the data on the composition of the solid residue of the flax shive hydrogenation process. The highest (79.5 wt %) cellulose and the lowest (15.5 wt %) lignin content in the solid product were obtained with the most active 3RS450 catalyst. The comparison of the data given in Tables 3–5 shows that 3RS450 catalyst both destroys the ether bonds of the lignin structure and partially prevents destruction of the cellulose polymer chain.

Table 6. Composition of the solid product, degree of delignification, and cellulose yield in noncatalytic and catalytic hydrogenation of flax shive in subcritical ethanol at 225 °C.

No.	Catalysts	Composition of Solid Products			Degree of Delignification, %	Cellulose Yield, wt %
		Hemicelluloses	Lignin	Cellulose		
1	no	4.2	27.3	68.5	63.3	55.4
2	3RS450	5.8	15.5	79.5	83.2	51.8
3	1RS450	10.4	16.3	73.3	78.1	59.3
4	3RS500g	3.0	19.2	77.8	74.8	61.3
5	3RS400	11.4	14.0	74.6	79.0	67.2
6	3RSg	5.7	25.1	69.2	66.6	55.3
7	Sib-4 (450)	3.1	27.6	69.3	64.9	52.9
8	3RS450 ¹	7.8	24.7	67.5	54.9	74.1
9	3RS450 ²	2.1	9.2	88.7	93.1	39.7

¹ Isopropanol as a solvent. ² The process temperature 250 °C.

It should be noted that addition of oxidized Sibunit without ruthenium reduces the hemicellulose yield, whereas ruthenium reached catalysts increase it (Table 6). The decomposition of hemicelluloses into soluble products can be caused by the acidic properties of the carbon support, and deposition of ruthenium onto Sibunit reduces its acidity (Table 1).

It should be emphasized that the use of the 3RS400 catalyst leads to the formation of a solid product with the highest (67.2 wt %) cellulose yield at high degree of delignification (79.0%). Increasing the process temperature up to 250 °C leads to a higher degree of delignification (up to 93%) and stronger depolymerization of cellulose, the yield of which drops to 40 wt %.

Despite the obviously higher hydrogen donating activity of isopropanol as compared to ethanol, the use of this secondary alcohol as a solvent reduces the hydrogenation efficiency: The degree of delignification decreases to 55% from 83% for ethanol and the cellulose yield increases to 74% from 52% in ethanol. This can be caused by several factors, for example, the isopropanol amount used in the experiment (0.8 mol) is less than the

ethanol amount (1.05 mol). This leads to the weaker extraction of lignin from the flax shive and, therefore, retards its depolymerization.

Thus, the maximum degree of delignification (up to 83%) is obtained with the 3RS450 catalyst used in the reductive catalytic fractionation of flax shive in the subcritical ethanol medium. However, the use of the 3RS400 catalyst ensures the higher (up to 67 wt %) cellulose yield at the comparable degree of delignification (79 wt %).

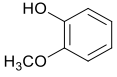
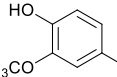
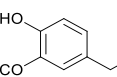
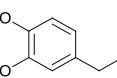
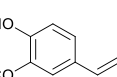
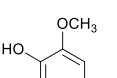
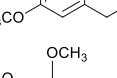
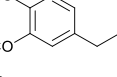
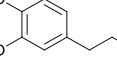
2.3. Characteristics of the Liquid Products of Reductive Catalytic Fractionation of Flax Shive

GC-MS analysis of the liquid product composition of the flax shive hydrogenation showed that the products of lignin conversion are mainly guaiacyl derivatives and, to a lesser extent, syringyl derivatives, since flax shive have a high content of guaiacyl-type fragments [36]. The main products are guaiacylpropanol (1), guaiacylpropene (2), and guaiacylpropane (3) (Tables 7–9).

Table 7. Yield (relative to the areas of all peaks, %) and composition of monomeric methoxyphenols included in the liquid products of noncatalytic and catalytic hydrogenation of flax shive in subcritical ethanol at 225 °C.

Substance	Structure	Catalyst						
		Non	3RS450	1RS450	3RS500g	3RS400	3RSg	Sib-4 450
Guaiacol		3.5	1.4	1.0	3.1	0.8	2.4	2.7
Guaiacylmethane		0.3	0.0	0.4	1.2	0.4	0.9	0.6
Guaiacylethane		5.1	5.4	3.2	7.1	4.8	7.3	5.1
Syringol		-	-	-	-	-	2.4	-
Guaiacylpropane		1.9	30.4	20.3	22.1	19.7	17.7	3.3
Guaiacylpropene		14.7	4.8	16.9	2.6	7.5	4.2	19.9
Syringylethane		0.9	1.5	0.9	1.6	1.2	1.4	1.1
Syringylpropane		0.8	7.74	6.4	5.2	5.5	4.3	1.3
Guaiacylpropanol		2.0	6.9	10.0	2.6	21.5	7.5	1.6
Syringylpropene		2.3	0.2	1.9	0.2	0.7	0.2	3.1
Total monophenol yield per sum of the chromatographed products, %		31.5	61.8	62.1	49.1	64.1	47.9	38.7

Table 8. Yield and composition of monomeric methoxyphenols (wt % per lignin) in the liquid products of noncatalytic and catalytic hydrogenation of flax shive in subcritical ethanol at 225 °C.

Substance	Structure	Sample						
		Non	3RS450	1RS450	3RS500g	3RS400	3RSg	Sib-4 450
Guaiacol		0.36	0.55	0.30	0.77	0.24	0.49	0.40
Guaiacylmethane		0.01	0.01	0.07	0.21	0.10	0.12	0.06
Guaiacylethane		0.21	0.88	0.36	0.73	0.64	0.17	0.31
Guaiacylpropane		0.08	4.95	2.42	2.29	2.64	1.50	0.20
Guaiacylpropene		0.19	1.17	3.2	0.4	1.56	0.52	1.95
Syringylethane		0.04	0.24	0.11	0.16	0.16	0.30	0.18
Syringylpropane		0.03	1.26	0.76	0.54	1.12	0.36	0.08
Guaiacylpropanol		0.08	1.09	1.19	0.27	2.87	0.64	0.10
Syringylpropene		0.14	0.06	0.34	0.02	0.15	0.03	0.24
Total monomer yield, wt %		1.14	10.21	8.75	5.39	9.48	4.67	3.52
Total yield of minor methoxyphenol impurities *, wt %		0.52	2.00	1.61	0.80	1.85	0.96	1.37

* Registered but not included in the table.

In addition, other aromatic compounds with the carbonyl and ester groups were identified. Their total yield ranged from 0.5 to 2 wt %, depending on the process conditions. Along with the methoxyphenol derivatives, the liquid products contained compounds formed from biomass polysaccharides: furfural derivatives (furfuryl alcohol and difurfuryl ether), methyl esters of the oxy- and hydroxy acids, ethyl levulinate, alcohols, and ketones (1-hydroxy-2-propanone and 3-hydroxy-2-butanone) with yields of 0.6–2.3 wt %. The liquid products contained also ethyl esters of fatty acids (palmitic, stearic, and linoleic). Most of them were obtained without catalysts or using only the support as a catalyst, while in the case of using the ruthenium-containing catalysts, these compounds were found in trace amounts or not found at all.

The use of the ruthenium catalysts in the hydrogenolysis process enhanced the total yield of methoxyphenols in the liquid products by a factor of 1.6–2.3 (Tables 7 and 8). The maximum total yield (9.48 and 10.21 wt %) of methoxyphenols was observed for the 3RS400 and 3RS450 catalysts. When the granular catalysts are used, the monomer yields are twice as low. This is probably due to the slow diffusion of reagents to the inner surface of a catalyst grain in the liquid-phase processes.

Comparing the results of Figure 3 and Tables 2 and 3 shows that the total yield of monomeric methoxyphenols increases with increasing the ruthenium dispersion and

availability: 1RS450 catalyst possess highest dispersion and almost the same surface ruthenium concentration compared to 3RS450.

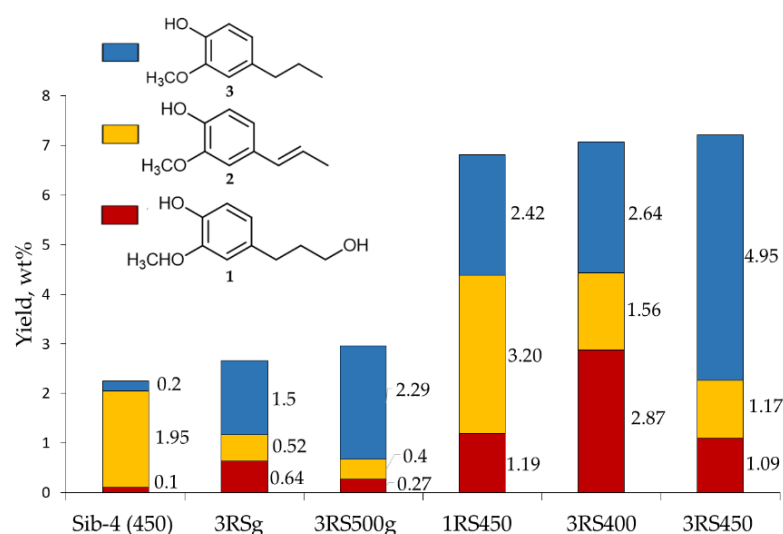


Figure 3. Yields of the methoxyphenols (1), (2), (3) for different catalysts used.

A significant increase (by a factor of more than 20) is noted in the guaiacylpropane (3) yield while growing the total monomeric methoxyphenols yield by a factor of 3 due to the increase of the catalysts activity (Figure 3). This is probably due to the high stability of the guaiacylpropane (3), the final product of hydrogenation, as compared to guaiacylpropene (2) and guaiacylpropanol (1).

The catalysts differ not only in the ruthenium particle size, but also in acidity of the support. Liu et al. showed [37] that, in the process occurring with the Ni@ZIF-8 catalyst at 260 °C for 8 h, monolignols are hydrogenated first along the C=C bond with the formation of substituted propanols, acid-catalyzed dehydration of the latter, and hydrogenation of the resulting propenes to phenylpropanes (Figure 4). The presence of Lewis acid sites, e.g., Zn and Fe, on the catalyst surface is shown to shift the selectivity of product formation from guaiacylpropanol to guaiacylpropane [31,38]. The results presented in Figure 3 allow us comparing the two catalysts, 3RS400 and 3RS450, with different oxidation temperatures and, correspondingly, different acidities. The maximum yield of compound (1) (2.9 wt %) is obtained on the less acidic 3RS400 catalyst, and the maximum yield of compound (3) (4.9 wt %) is done on the more acidic 3RS450 catalyst. This is probably due to the acid-catalyzed dehydration of guaiacylpropanol to guaiacylpropene; hence, the similar regularities of these transformations are observed on the Bronsted (Figure 3) and Lewis [35,36] sites.

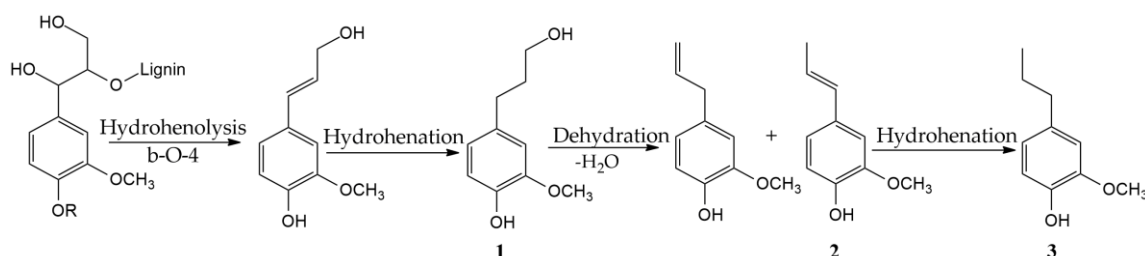


Figure 4. Scheme of the propylguaiacol formation through the cleavage of the β-O-4-bonds and subsequent hydrogenation and dehydration of coniferyl alcohol.

In addition, the use of a ruthenium-containing catalyst leads to the formation of mainly propyl-substituted phenolic compounds, while with the use of the Pd/C catalyst, propanol-substituted compounds are the major ones [28,39,40].

The data reported in [37,41] showed that compound (3) can be formed as a result of the catalytic hydrogenation of the C=C bond of compound (2) formed due to the dehydration of compound (1), which is the result of hydrogenation of coniferyl alcohol (Figure 4). Indeed, the most yields of guaiacylpropene (2) were observed for Sibunit-4 and 1RS450 catalyst (1.9–3.2 wt %), the acid systems with minimum hydrogenating activity.

The liquid products of fractionation of herbaceous plants contain some specific compounds, including ferulic and p-coumaric acid esters [28,40,42]. In the products of flax shive hydrogenation these compounds were not found, and this is apparently due to their almost complete lack or decarboxylation to guaiacylethane, with its maximum content of 0.73 wt % in the presence of the 3RS500g catalyst.

Table 9. Data on the molecular weight distribution of the liquid products of reductive catalytic fractionation of flax shive in subcritical ethanol at 225 °C.

No.	Catalyst	M _n (Da)	M _w (Da)	PD
1	no	530	1240	2.34
2	3RS450	430	830	1.95
3	1RS450	450	930	2.07
4	3RS500g	450	1050	2.32
5	3RS400	420	770	1.81
6	3RSg	460	1110	2.39
7	Sib-4 (450)	490	1070	2.20
Ethanol lignin of flax shive *		890	2100	2.35

* Obtained using the technique proposed in [43].

2.4. Molecular Weight Distribution of the Liquid Products

The studied ruthenium catalysts significantly affect the molecular weight distribution of the liquid products of flax shive hydrogenation in ethanol (Figure 5, Table 9). In the absence of a catalyst, the liquids are mainly the products of incomplete depolymerization with the fractions of dimers and small amounts of monomeric compounds. The Ru/C catalysts significantly change the molecular weight distribution profile and, consequently, the qualitative composition of the liquid products. In particular, the region of oligomers with a molecular weight above 1 kDa lacks in the presence of a catalyst; a significant signal intensity shift toward lower molecular weights is observed, which suggests a large amount of monomer fraction in the liquid products. A slight change in the region of dimeric products of catalytic hydrogenation confirms stabilization of the obtained liquids and absence of repolymerization reactions. The maximum depth of lignin depolymerization was obtained with 3RS450 and 3RS400 catalysts.

2.5. Influence of Solvent

Hydrogenation of flax shive in isopropyl alcohol in the presence of the 3RS450 catalyst results in the lower yields of monomeric methoxyphenols as compared to the sub- and supercritical ethanol used (Table 10). These results responds to the data [44]: The use of isopropanol also resulted in a lower monomer yields in comparison with such solvents as ethanol, methanol, and ethylene glycol.

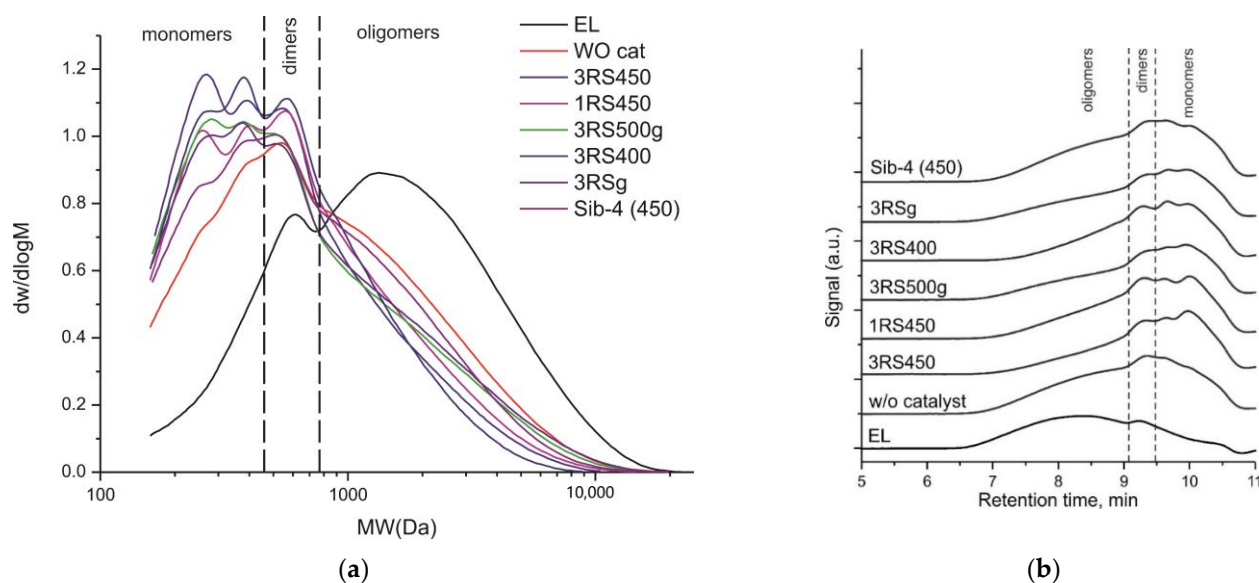
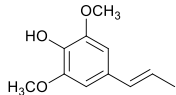


Figure 5. Molecular weight distribution curves (a) and gel permeation chromatograms (b) of the liquid products of reductive catalytic fractionation of flax shive in subcritical ethanol at 225 °C.

Table 10. Effect of solvent on the yield (wt % per lignin) and composition of monomeric methoxyphenols included in the liquid products of hydrogenation of flax shive in the presence of the 3RS450 catalyst.

Substance	Structure	Solvent		
		Subcritical Ethanol (225 °C)	Subcritical Isopropanol (225 °C)	Supercritical Ethanol (250 °C)
Guaiacol	<chem>Oc1ccccc1OC</chem>	0.55	0.19	0.83
Guaiacylmethane	<chem>Oc1ccc(C)cc1OC</chem>	0.01	0.23	0.27
Guaiacylethane	<chem>Oc1ccc(CC)cc1OC</chem>	0.88	1.93	1.28
Syringol-	<chem>COc1cc(O)ccc1OC</chem>	-	-	0.31
Guaiacylpropane	<chem>Oc1ccc(CCC)cc1OC</chem>	4.95	2.49	4.51
Guaiacylpropene	<chem>Oc1ccc(C=C)cc1OC</chem>	1.17	0.27	-
Syringylethane	<chem>COc1cc(O)c(C)cc1OC</chem>	0.24	0.48	0.27
Syringylpropane	<chem>COc1cc(O)c(CCC)cc1OC</chem>	1.26	0.62	1.06
Guaiacylpropanol	<chem>Oc1ccc(CCCO)cc1OC</chem>	1.09	-	0.85

Table 10. Cont.

Substance	Structure	Solvent		
		Subcritical Ethanol (225 °C)	Subcritical Isopropanol (225 °C)	Supercritical Ethanol (250 °C)
Syringylpropene		0.06	-	0.34
Total yield of alkyphenols. wt %		10.21	6.27	9.72
Total yield of minor methoxyphenol impurities *. wt %		2.00	0.33	0.01

* Not given in Table 9.

The yields and composition of the major monomers during hydrogenation of flax shive in supercritical ethanol (250 °C, 9.7 wt %) are close to the results obtained in subcritical ethanol (225 °C, 10.2 wt %), except for the higher 4-guaiacylthane yield and almost complete lack of guaiacylpropene (2). A higher total yield (27 wt %) of monomeric compounds was obtained in RCF of miscanthus in methanol with the 5% Ru/C catalyst at 250 °C [28]. These differences can be caused by the nature of the hydrogenating substrates (flax and miscanthus), solvent, and also by the higher ruthenium content in the catalyst [28].

Based on the results obtained, several conclusions may be made. First, temperature is the most powerful parameter that determines conversion of flax shive and gas yield. Second, the catalysts acidity increases the carbohydrates conversion. Third, the best yields of monophenols and guaiacylpropane are obtained on the most active catalysts, 3RS450 and 3RS400, possessing highest ruthenium activity and acidity.

3. Materials and Methods

3.1. Catalysts Preparation

To prepare the Ru/C catalysts mesoporous graphite-like carbon material Sibunit[®]-4 (CNCT Boreskov Institute of Catalysis SB RAS, Omsk, Russia) was used [21]. Before catalysts preparation the carbon was cleaned with hot deionized water, air-dried and grinded to the fraction of 56–94 µm. The fractional composition of the initial Sibunit[®]-4 was varied from 1.0 to 1.6 mm.

Oxidized carbon samples were prepared using granular or powder Sibunit[®]-4 carbon support by oxidation with oxygen of a mixture containing 20 vol % of O₂ in N₂ in the presence of water vapor (saturation at 90 °C, vapor pressure 70.1 kPa, flow 200 mL/min) at a specified temperature (400, 450, or 500 °C) for 2 h [21].

The ruthenium catalysts based on the initial and oxidized Sibunit[®]-4 samples (1% and 3% Ru/C) were prepared by incipient wetness impregnation using an aqueous solution of Ru(NO)(NO₃)₃ followed by sample drying at room temperature for 2–3 h and at 60 °C for 12 h. The active component was reduced in a hydrogen stream (30 mL/min) at 300 °C for 2 h (temperature ramp: 1 °C/min). After cooling down to room temperature under hydrogen, the catalyst was passivated using a gas mixture of 1% of O₂ in N₂ flow 30 mL/min [25].

The texture characteristics of the samples were determined from the N₂ adsorption isotherms at 77 K with a automatic analyzer of specific surface area and porosity instrument (Micromeritics ASAP-2020 Plus, USA, 2018).

High-resolution electron microscopy images and the size distribution of ruthenium particles were studied using a transmission electron microscope HT7700 (Hitachi, Tokyo, Japan, 2014) at an accelerating voltage of 110 kV and a resolution of 2 Å. Particle size distribution histograms were obtained by statistical (500–800 particles) analysis of the TEM images. The mean linear (<d_l>) and the mean surface-volume (<d_s>) particle diameters were calculated using the formulas:

$$\langle d_l \rangle = \sum d_i / N, \langle d_s \rangle = \sum d_i^3 / \sum d_i^2 \quad (1)$$

where d_i is the diameter of a deposited particle and N is the total number of particles.

The ruthenium dispersion D_{Ru} in the catalysts was calculated using the formula:

$$D_{Ru} = 6 \times \frac{M_{Ru}}{\alpha_{Ru} \times \rho \times N_0 \times \langle d_s \rangle} \quad (2)$$

where $M_{Ru} = 0.101$ kg/mol is the ruthenium molar weight, $\rho = 12,410$ kg/m³ is the metallic ruthenium density, $\alpha_{Ru} = 6.13 \times 10^{-20}$ is the average effective area of the metal atom on the surface (m²), N_0 is the Avogadro number, and d_s is the weight-average diameter of ruthenium particles [25].

The acidity of the catalysts was estimated by the point of zero charge (pzc) by the Sorenson–de Bruyn method [45].

A Spectrometer (SPECS, Germany, 2007) with a PHOIBOS MCD9 energy analyzer, excited by monochromatic Al K α radiation at an electron collection angle of 90°) was used to obtain photoelectron spectra. The element contents were determined from the survey spectra. At the CasaXPS (Casa Software Ltd., Teignmouth, UK) software processing, the Shirley nonlinear background was subtracted and a Gaussian/Lorentzian peak shape was used.

3.2. Flax Shive Samples Preparation

Flax shive (growing region—Tver region, Russia) was provided by Tver State Technical University. An air dried flax shive was ground in a VR-2 disintegrator (Russia, 2010), after which dry fractionation was carried out on sieves. For this work, we used a flax shive fraction size 0.5–2 mm.

The flax shive components (% of the absolutely dry substrate weight) were cellulose (50.6), lignin (30.4), hemicelluloses (17.1), and ash (1.9). Flax shive was dried at 80 °C to moisture content lower than 1 wt %.

3.3. Hydrogenation of Flax Shive

Flax shive were hydrogenated in a 300 mL autoclave (ChemRe SYStem R-201, Gyeonggi-do, Korea, 2017). The reactor was loaded with 60 mL (1.05 mol) of ethanol or 60 mL (0.80 mol) of isopropanol, 3.0 g of the support, and 0.3 g of the catalyst. The autoclave was sealed and purged with argon to remove air. Then, hydrogen was supplied to an initial pressure of 4 MPa on a manometer. The reaction occurred at a temperature of 225 °C for 3 h under constant stirring at a rate of 1000 rpm. The working pressure in the reactor ranged from 9.1 to 11.5 MPa, depending on the process conditions.

After each run, the reactor was cooled down to room temperature. The gaseous products were collected in a gasometer and their volume was measured and analyzed by gas chromatography (GC). Then, the reaction products were quantitatively collected from the autoclave by washing with ethanol. The mixture of the liquid and solid products was separated by filtration. The solid residue was washed with ethanol until the decolorization of the filtrate.

Ethanol was removed from the product solution using a rotary evaporator and the residue was brought to constant weight in vacuum (1 mmHg) at room temperature. The liquid yield (Y_1) was calculated by the formula (wt %):

$$Y_1 = \frac{m_l}{m_{fs}} \times 100\% \quad (3)$$

where: m_l is the mass of liquid products (g), m_{fs} is the mass of the flax shives (g).

The solid residue yield Y_2 was calculated as (wt %):

$$Y_2 = \frac{m_{sr} - m_{cat}}{m_{fs}} \times 100\% \quad (4)$$

where: m_{sr} is the mass of the solid residue after extraction (g), m_{cat} is the mass of the catalyst (g).

The total gas yield (Y_3) (wt %) was calculated using the formula:

$$Y_3 = \frac{m_g}{m_{fs}} \times 100\% \quad (5)$$

where: m_g is the mass of the gaseous products (g).

The conversion of flax shive X_{fs} (wt %) was calculated by the formula:

$$X_{fs} = \frac{m_{fs} - m_{sr}}{m_{fs}} \times 100\% \quad (6)$$

The degree of delignification (X_l) was calculated using the formula (wt %):

$$X_l = \frac{m_{lfs} - m_{lsr}}{m_{lfs}} \times 100\% \quad (7)$$

where: m_{lfs} and m_{lsr} — mass of lignin in flax shives and in the solid residue (g).

The cellulose yield (X_c) (wt %) was calculated using the formula:

$$X_c = \frac{m_{csr}}{m_{cfs}} \times 100\% \quad (8)$$

where: m_{cfs} and m_{csr} are the mass of cellulose in flax shives and in the solid residue.

3.4. Analytical Methods

The composition of the gaseous products of flax hydrogenation in ethanol was analyzed by GC on a chromatograph (Crystal 2000 M, Chromatec JSC SDO, Russia, 2015) with a thermal conductivity detector. Helium was used as a carrier gas (15 mL/min); the detector temperature was 170 °C. For the CO and CH₄ analysis, a column packed with NaX zeolite (3 m × 2 mm) in the isothermal mode at 60 °C was used. The analysis of CO₂ and hydrocarbon gases was made on a column with Porapak Q for 1 min at 60 °C; after that, the temperature was increased to 180 °C at a rate of 10 °C/min.

The residual lignin content in the solid product was determined by hydrolysis with 72% sulfuric acid [46]. The hemicellulose content was determined as content of pentosanes in the obtained hydrolysates by GC. The content and composition of monosaccharides in the hydrolysates were determined by GC with pre column derivatization on a VARIAN-450 GC gas chromatograph (Varian Inc., Palo Alto, CA, USA) with a flame ionization detector and a VF-624ms capillary column with a length of 30 m and an inner diameter of 0.32 mm. The chromatography conditions were helium as a carrier gas, an injector temperature of 250 °C, an initial column temperature of 50 °C (5 min), a rate of 10 °C/min of the temperature growth to 180 °C, and exposure at 180 °C for 37 min. Before the analysis, the hydrolysate was derivatized according to the procedure described in [47] to produce trimethylsilyl derivatives. Sorbitol was used as an internal standard. The peaks were identified using the retention times of tautomeric forms of monosaccharides. Cellulose in the solid products was analyzed using the alcohol-nitric acid (Kürschner-Hoffer) method [48–50].

GC-MS analysis of liquid products was carried out using an Agilent 7890A chromatograph equipped with an Agilent 7000A Triple Quad mass selective detector (Agilent, Santa Clara, CA, USA, 2008) (with an hP-5MS capillary column (30 m × 0.25 mm inner diameter)), by recording the total ion current. The chromatographic separation of products soluble in ethanol was carried out by increasing temperature from 40 to 250 °C at a rate of 3 °C/min. The NIST MS library and literature data were used to identify chromatographic peaks. To quantify the yield of monomer compounds, the standard substances, such as guaiacol, syringol, 2-methoxy-4-methylphenol, isoeugenol, 4-ethylguaiacol, 4-allyl-2,6-

dimethoxyphenol (Sigma–Aldrich, St. Louis, Missouri, USA), ethyl palmitate (Tokyo Chem. Ind., Tokyo, Japan) were used. Phenanthrene was used as an internal standard.

Molecular-weight distribution of the liquid samples were determined by gel permeation chromatography (GPC) on Agilent 1260 Infinity II Multi-Detector GPC/SEC System (Agilent, Santa Clara, CA, USA, 2018). The separation was made by a PLgel Mixed-E column with tetrahydrofuran stabilized with 250 ppm 2,6-di-tert-butyl-4-methylphenol as an eluent. The columns were calibrated with polystyrene calibration kit (Agilent, Santa Clara, CA, USA). The eluent flow was set at 1 mL/min and the volume of the injection loop was 100 µL. All samples were dissolved in eluent with concentration 1 mg/mL and left to dissolve completely overnight. After dissolution all samples were filtered through a 0.22-µm Agilent PTFE membrane filter.

4. Conclusions

Flax shive is a low-value waste residue of the flax fiber production. In this paper, a reductive catalytic fractionation (RCF) of flax shive was studied. The bifunctional ruthenium catalysts based on oxidized Sibunit demonstrated the high efficiency in the reductive fractionation of flax shive at 225 °C for 3 h. In the experiments without a catalyst under these process conditions, the conversion was found to be no more than 44.1 wt % and the content of phenolic monomers in the liquid fractionation products was 1.1 wt %. The use of the Ru/C catalysts result in a significant increase in the monophenol yield (up to 10.2 wt % per lignin weight in the sample)) and enhanced the conversion of flax shive to 56 wt %.

The effect of different characteristics (the ruthenium content, particle size, and substrate oxidation temperature) of the bifunctional Ru/C catalysts on the reductive catalytic fractionation of flax shive was examined. The highest degree of delignification (up to 79.0%) and cellulose yield (up to 67.2 wt %) were obtained with the Ru/C catalyst containing 3 wt % of Ru on carbon support oxidized at 400 °C. In addition, the use of this catalyst ensured the high (up to 9.5 wt %) monophenol yield. The main characteristics of the catalysts that determine the high conversion of lignin to guaiacylpropane are the ruthenium dispersion and surface area. Bronsted acid sites plays an important role in the guaiacylpropane formation due to catalyzing the dehydration of guaiacylpropanol to guaiacylpropene.

The granular ruthenium-containing catalysts showed the low monomer yields and degrees of delignification in comparison with the powdered catalysts due to the low diffusion that limits the transfer of reagents to the inner surface of catalyst grains in the liquid phase.

To conclude, the catalytic conversion of flax shive provides a solution to the problem of its waste utilization. The most promising individual compounds obtained as products of the hydrogenation processing of the flax shive lignin can be guaiacylpropane.

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