



Article Catalytic Transformation of Biomass-Derived Hemicellulose Sugars by the One-Pot Method into Oxalic, Lactic, and Levulinic Acids Using a Homogeneous H₂SO₄ Catalyst

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Abstract: This article presents the conditions for the conversion of hemicellulose with different contents of C6 and C5 carbohydrates and uronic acids based on the OrganoCat process, and the abbreviations M1, M2, and M3 are used. Homogenous catalysis with sulfuric acid (VI) in the concentration range of 0.1-1 M was used in the study to determine its activity on the ability to transform a hemicellulose mixture. The process was carried out using the one-pot technique in the temperature range of 100-250 °C for 1-5 h. Based on the use of the chromatographic technique (HPLC-RID) together with a comparison with standard substances, the resulting chemical compounds were determined and identified from the post-reaction mixtures. The degree of covalence of the raw material, the selectivity of the obtained chemical compounds, and the yield of lactic acid were also determined. Based on the M1 mixture at the temperature of 100 °C with 0.1 M sulfuric acid (VI) as a catalyst. The formation of oxalic acid was also observed, which is present in all post-reaction mixtures, regardless of the composition of the raw material, temperature, and time. Its efficiency was determined at an average level of 90%.

Keywords: oxalic acid; levulinic acid; oxalic acid; hemicellulose; H₂SO₄; biomass conversion

1. Introduction

Lignocellulosic biomass consists of a cell wall (see Figure 1), which is composed of cellulose 40–55% d.m., hemicellulose 24–40% d.m., lignin 18–25% d.m., and a minority of other extracts and inorganic compounds—the so-called ash [1]. The proportions of the basic polymers in lignocellulosic materials vary, reflecting genetic and environmental influences.

Lignocellulosic biomass shows great potential for the production of liquid biofuels, given its large-scale availability, low cost, and low greenhouse gas emissions. It is also the starting material for obtaining many valuable chemical feedstocks, especially acids such as levulinic acid, oxalic acid, lactic acid, and formic acid.

Lignocellulosic biomass sources are inedible raw materials [2,3]. The idea behind the production of chemical raw materials based on waste lignocellulosic biomass is to turn industrially useless waste into useful raw materials.

The technologies being developed are designed to use multiple primary and secondary sources of biomass. The primary sources are energy crops, e.g., miscanthus, bamboo, switch millet, Pennsylvania hogweed, and energy willow. Residues from production processes comprise the secondary sources, which include waste from agriculture, e.g., crop residues (straw middlings), from forestry (sawdust, shavings, offcuts, bark waste, and leaves), and from the processing of plant products (pomace, pulp, rice husks, nuts, soybean and sunflower shells, and corn cobs). Tertiary sources are organic waste from municipal facilities, biodegradable waste from landscaping, dried manure, and waste paper.



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Figure 1. Scheme of mixtures of biomass-derived hemicellulose carbohydrates obtained from OrganoCat technology.

Hemicelluloses are branched heteropolymers that have a lower molecular weight than cellulose [4–6]. They are composed of pentoses (e.g., xylose and arabinose), hexoses (e.g., mannose, galactose, glucose, and rhamnose), and uronic acids (e.g., glucuronic acid).

The presence of branched side chains and their amorphous nature make these polymers more susceptible to hydrolysis than cellulose. Hemicelluloses are grouped into xylans, xyloglucans, mannans, and glucomannans. There are also other types of hemicelluloses, such as arabinogalactan, galactoglucomannan, arabinoglucuronoxylan, and glucuronoxylan.

While the efficient fractionation and subsequent valorisation of the components is desirable, the ability to efficiently recycle the water, solvents, and catalysts used in pretreatment is also critical to the economic viability. To circumvent these issues, the OrganoCat technology developed by Weidener et al. [7] uses an organic acid as a catalyst to mildly hydrolyse amorphous, non-cellulosic sugar polymers at 125–160 °C, minimising monosaccharide degradation such as dehydration and subsequent oligomerisation.

The relationship between the plant wall composition of ten different lignocellulosic materials and its role in acid pretreatment was investigated using the OrganoCat process as a prototypical approach for full valorisation, determining aspects such as enzymatic degradation of the pulp after pretreatment, hydrolysis of hemicellulose, and lignin yield and quality. In the work on the OrganoCat process [8], a comprehensive characterisation of the composition and structure of polysaccharides and lignin was carried out to provide information on their structural characteristics, and the composition of the relevant fractions of the lignocellulosic stream was determined. The work on the OrganoCat process did not consider the possibility of using the polysaccharide mixture in the catalytic extraction of valuable chemical compounds such as carboxylic acids, e.g., oxalic acid, lactic acid, or levulinic acid.

Oxalic acid is mainly manufactured by the oxidation of carbohydrates (e.g., glucose) using nitric acid or air in the presence of vanadium pentoxide [9,10]. Oxalic acid has reducing properties and forms compounds called chelates, so it is widely used in the food industry—it prevents the browning of vegetables and fruits, which delays their ageing process.

Lactic acid (2-hydroxypropanoic acid, LA) is a commonly used chemical compound. Among others, it is an intermediate from which chemical compounds such as propylene glycol, propylene oxide, acrylic acid, and poly(lactic acid) are synthesised. 2-Hydroxypropanoic acid is widely used in various industries: food, pharmaceutical, as well as cosmetic industries [1]. The demand for this valuable raw material is increasing from year to year and, in 2015, its production volume was as high as 3.3×10^5 tonnes. Lactic acid is conventionally produced by fermentation.

Levulinic acid (LE) has been identified as a promising bio-compound derived from biomass. It is a platform molecule that is used as a precursor for pharmaceuticals, plasticisers, and various other additives [1,11–17]. It arises as a result of depolymerisation and dehydration of the cellulose fraction [18]. It can be obtained through hydrolysis/dehydration of aldohexoses such as glucose and fructose, or hexose-containing polymers such as starch and cellulose via an intermediate product such as 5-HMF followed by hydration to carboxylic acids, e.g., levulinic acid or formic acid. The conversion of biomass-based glucose to levulinic acid (LE) makes use of the Na-BEA commercial zeolite catalyst as well as the homogeneous H_2SO_4 catalyst in the one-pot process [19]. The glucose conversion process allowed to obtain the following acids: levulinic acid, lactic acid, pyruvic acid, and formic acid. The highest yield of levulinic acid was achieved when it was processed for 1–5 h at 200–250 °C with 0.1 g and 0.6 g of the Na-BEA catalyst.

In the recent literature [20], authors review increasing attention to supported by ionic liquid catalysts (SILCs) as catalysts for biomass valorisation, because they are a bridge between homogeneous and heterogeneous catalysis. These catalysts can be used as biofuel precursors, 5-hydroxymethyl furfural (HMF), and reducing carbohydrates for production of chemicals and fuels in industries. From the recent literature [21], hydrothermal transformation of microcrystalline cellulose (isolated from birch wood) under the influence of Al_2O_3 - B_2O_3 mixed oxide solid acid catalysts into valuable products such as 5-hydroxymethyl furfural or levulinic acid was studied. They found considerable activity toward the acid conversion of glucose into 5-hydroxymethylfurfural at a low temperature of 180 °C and into levulinic acid at 215 °C.

In the patent literature, one can find descriptions of solutions for obtaining chemical compounds from lignocellulosic material. In one patent description [22], a method of obtaining furfural from lignocellulosic material in the form of rye straw is described, consisting of impregnation of this material with sulfuric acid, followed by its acid hydrolysis and dehydration in an autoclave at an elevated temperature and separation of the supernatant containing furfural from the hydrolysis residue. According to this invention, the straw pre-hydrated with an aqueous solution of sulfuric acid is subjected to acid hydrolysis and dehydration in an autoclave at 121 °C for 60–120 min, then the supernatant containing furfural is separated from the hydrolysis residue by cooling to room temperature and centrifuging this residue. In another patent description [23], a method of obtaining furfural from lignocellulosic material in the form of rye straw is described, consisting of impregnation of this material with sulfuric acid, followed by its acid hydrolysis and dehydration in an autoclave at an elevated temperature and separation of the supernatant containing furfural from the hydrolysis residue. According to this invention, the straw pre-hydrated with an aqueous solution of sulfuric acid is subjected to acid hydrolysis and dehydration in an autoclave at 121 °C for 60–120 min, then the supernatant containing furfural is separated from the hydrolysis residue by cooling to room temperature and centrifuging this residue. A further invention [24] relates to a method for the hydrothermal conversion of cellulose and the use of Lewis acid and acid containing a Dawson structural polyacid catalyst for the hydrothermal conversion of cellulose and the production of lactic acid. The catalyst is a silver-substituted Dawson's structural composite polyacid catalyst $Ag_xH_{6-x}P_2M_{18}O_{62}$ (x = 1-6). The catalyst is used in the hydrothermal conversion of cellulose for the directional conversion of cellulose to lactic acid. The catalyst has high activity, cellulose can be completely converted, the yield of lactic acid is up to 57.8%, and the recycling efficiency is high. The entire process is free of wastewater and waste gases and is environmentally friendly and green.

An important conclusion from the cited publications and patents is that lignocellulose is still a very in-demand raw material, and technological solutions are concerned with the pretreatment of biomass. What is lacking, however, are wide-ranging attempts to

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further utilize the mixture of carbohydrates by chemical means toward, for example, carboxylic acids.

The purpose of the process is to develop a method for obtaining C1–C3 carboxylic acids from a mixture of C6 and C5 carbohydrates derived from waste lignocellulosic biomass—the hemicellulosic fraction using the one-pot method. The transformation process of the hemicellulosic fraction is carried out using homogeneous catalysts, which solves the important problem of managing the waste material, allowing its use as a raw material for the production of carboxylic acids, as well as the recovery of the catalyst from the post-reaction mixture and its reuse, which is important in economic terms.

2. Results and Discussion

A homogeneous process was prepared as follows: 0.1 M, 0.2 M, 0.5 M, and 1 M of aqueous H_2SO_4 (v = 20 mL), followed by 0.45 g of hemicellulose mixture, were added. Four Teflon-filled autoclaves were prepared, into which aqueous solutions of sulfuric acid and the appropriate amount of carbohydrates were transferred. The process was carried out at temperatures in the range of 100–250 °C for 1 and 5 h. The autoclaves were then cooled down and their solutions were neutralised with 10% aqueous NaOH solution. Samples for HPLC-RID analysis were prepared by filtering with a syringe filter with a grain size of 0.45 μ m. The analysis of the potential products formed during the hemicellulose sugar mixture conversion with a 1 h process time is summarised in Tables 1–3 and that with a 5 h process time is summarised in Tables 4–6.

Table 1. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydrates using the homogeneous H_2SO_4 catalyst in the liquid phase, with a 1 h process time for mixture 1.

Mixture 1 Process Time 1 h	Process	Raw Material	Yield to	Yield to	Yield to				Selectivit	y (%)			
Catalyst Concentration	Temp. (°C)	(%)	OA (%)	LE (%)	LA (%)	DHA	PAC	OA	LA	FA	LE	AC	PA
0.1 M H ₂ SO ₄		87.84	14.60	0.00	64.57	0.00	0.00	16.62	73.52	6.31	0.00	3.55	0.00
0.2 M H ₂ SO ₄	100	94.89	51.48	0.00	35.73	0.00	0.44	54.26	37.66	4.54	0.00	3.11	0.00
0.5 M H ₂ SO ₄	100	97.78	71.03	0.00	26.38	0.38	0.00	72.64	26.98	0.00	0.00	0.00	0.00
1 M H ₂ SO ₄		98.88	84.81	0.00	13.85	0.00	0.00	85.77	14.01	0.23	0.00	0.00	0.00
0.1 M H ₂ SO ₄	200	16.84	16.84	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
0.2 M H ₂ SO ₄		52.01	52.01	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
0.5 M H ₂ SO ₄		84.42	84.42	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
1 M H ₂ SO ₄		90.95	90.17	0.00	0.00	0.00	0.00	99.14	0.86	0.00	0.00	0.00	0.00
0.1 M H ₂ SO ₄		31.18	31.18	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00
0.2 M H ₂ SO ₄		88.58	83.73	0.00	0.00	0.00	0.00	94.52	0.00	0.00	0.00	2.86	0.00
0.5 M H ₂ SO ₄	220	100.00	96.65	2.26	0.00	0.00	0.00	96.65	0.00	0.00	2.26	1.09	0.00
1 M H ₂ SO ₄		100.00	82.09	0.88	0.00	0.00	0.00	82.09	0.00	0.13	0.88	0.50	0.00
0.1 M H ₂ SO ₄		36.65	35.73	0.00	0.93	0.00	0.00	97.47	2.53	0.00	0.00	0.00	0.00
0.2 M H ₂ SO ₄		99.12	83.47	2.24	0.00	0.00	0.00	84.21	0.00	1.07	2.26	3.90	8.57
0.5 M H ₂ SO ₄	250	99.38	95.66	2.05	0.00	0.00	0.00	96.25	0.00	0.58	2.07	1.10	0.00
1 M H ₂ SO ₄		100.00	99.06	0.63	0.00	0.00	0.12	99.06	0.00	0.19	0.63	0.00	0.00

DHA—dihydroxyacetone, PAC—pyruvic acid, OA—oxalic acid, LA—lactic acid, FA—formic acid, LE—levulinic acid, AC—acetic acid, PA—propionic acid.

Mixture 2 Process Time 1 h	Process	Raw Material	Yield to	Yield to	Yield to				Selectivit	y (%)			
Catalyst Concentration	Temp. (°C)	(%)	OA (%)	LE (%)	LA (%)	DHA	OA	LA	FA	LE	AC	PA	ACt
0.1 M H ₂ SO ₄		77.24	14.41	0.00	57.74	0.00	18.65	74.75	1.97	0.00	1.58	0.00	3.05
0.2 M H ₂ SO ₄	100	86.66	42.67	0.00	36.49	0.00	49.24	42.11	5.46	0.00	3.20	0.00	0.00
0.5 M H ₂ SO ₄	100	92.19	69.48	0.00	21.84	0.00	75.36	23.69	0.57	0.00	0.38	0.00	0.00
1 M H ₂ SO ₄		95.08	77.89	0.00	16.10	0.00	81.93	16.93	0.69	0.00	0.45	0.00	0.00
0.1 M H ₂ SO ₄		30.07	26.42	0.00	1.62	0.00	87.86	5.38	3.68	0.00	3.08	0.00	0.00
0.2 M H ₂ SO ₄	• • • •	70.71	57.54	0.00	8.17	0.00	81.37	11.56	4.10	0.00	2.96	0.00	0.00
0.5 M H ₂ SO ₄	200	83.82	83.82	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
1 M H ₂ SO ₄		84.01	82.24	0.00	1.43	0.00	97.90	1.70	0.41	0.00	0.00	0.00	0.00
0.1 M H ₂ SO ₄		66.32	63.32	0.00	0.81	1.15	95.48	1.22	0.00	0.00	2.15	0.00	0.00
0.2 M H ₂ SO ₄	220	98.17	94.32	0.00	0.36	1.10	96.08	0.37	0.00	0.00	2.46	0.00	0.00
0.5 M H ₂ SO ₄	220	100.00	95.70	2.27	0.00	0.00	95.70	0.00	0.81	2.27	1.22	0.00	0.00
1 M H ₂ SO ₄		100.00	97.63	1.26	0.00	0.00	97.63	0.00	0.37	1.26	0.74	0.00	0.00
0.1 M H ₂ SO ₄		100.00	98.16	1.47	0.00	0.00	98.16	0.00	0.00	1.47	0.36	0.00	0.00
0.2 M H ₂ SO ₄	250	100.00	83.56	8.06	0.00	0.00	83.56	0.00	3.26	8.06	5.13	0.00	0.00
0.5 M H ₂ SO ₄	250	100.00	75.11	2.73	0.00	0.00	75.11	0.00	1.11	2.73	0.00	21.05	0.00
1 M H ₂ SO ₄		99.46	96.59	1.22	0.00	0.00	97.12	0.00	0.68	1.23	0.97	0.00	0.00

Table 2. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydrates using the homogeneous H_2SO_4 catalyst in the liquid phase, with a 1 h process time for mixture 2.

DHA—dihydroxyacetone, OA—oxalic acid, LA—lactic acid, FA—formic acid, LE—levulinic acid, AC—acetic acid, PA—propionic acid, ACt—acetone.

Table 3. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydratesusing the homogeneous H_2SO_4 catalyst in the liquid phase, with a 1 h process time for mixture 3.

Mixture 3 Process Time 1 h	Process	Raw Material	Yield to OA	Yield to LE	Yield to LA				Sele	ctivity (%)				
Catalyst 7 Concentration	Temp. (° C)	Conversion (%)	(%)	(%)	(%)	5- HMF	DHA	OA	LA	FA	LE	AC	PA	ACt
0.1 M H ₂ SO ₄		75.50	27.94	0.00	44.65	0.00	0.00	37.01	59.13	2.59	0.00	1.27	0.00	0.00
$0.2 \text{ M} \text{H}_2 \text{SO}_4$	100	79.73	47.03	0.00	26.74	0.00	0.00	58.99	33.54	4.33	0.00	3.14	0.00	0.00
$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	100 - 200 - 220 - 220 -	88.30	67.85	0.00	20.45	0.00	0.00	76.84	23.16	0.00	0.00	0.00	0.00	0.00
1 M H ₂ SO ₄		93.97	82.10	0.00	10.45	0.00	0.00	87.37	11.13	0.85	0.00	0.43	0.00	0.22
0.1 M H ₂ SO ₄	200 —	27.79	22.72	0.00	1.82	0.00	0.00	81.78	6.54	6.09	0.00	5.58	0.00	0.00
0.2 M H ₂ SO ₄		55.32	44.36	0.00	6.83	0.00	0.00	80.19	12.34	4.01	0.00	3.45	0.00	0.00
$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$		93.11	83.14	0.00	3.24	0.00	0.00	89.30	3.48	4.88	0.00	2.34	0.00	0.00
1 M H ₂ SO ₄		94.36	94.36	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1 M H ₂ SO ₄		82.01	80.89	0.00	0.00	0.00	0.00	98.62	0.00	1.38	0.00	0.00	0.00	0.00
$0.2 \text{ M} \text{H}_2 \text{SO}_4$	220	97.53	86.82	0.00	1.23	4.53	2.68	89.02	1.26	0.00	0.00	2.53	0.00	0.00
$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	220	99.81	98.93	0.00	0.00	0.00	0.00	99.12	0.00	0.53	0.00	0.35	0.00	0.00
1 M H ₂ SO ₄		99.60	98.84	0.00	0.00	0.00	0.00	99.23	0.00	0.30	0.00	0.47	0.00	0.00
0.1 M H ₂ SO ₄		100.00	87.81	2.59	0.00	0.00	0.00	87.81	0.00	4.47	2.59	4.04	1.10	0.00
0.2 M H ₂ SO ₄	250	97.78	85.30	0.00	0.00	0.00	0.00	87.23	0.00	1.92	0.00	3.57	7.28	0.00
0.5 M H ₂ SO ₄	200	98.34	95.83	0.89	0.00	0.00	0.00	97.45	0.00	0.86	0.91	0.79	0.00	0.00
1 M H ₂ SO ₄		100.00	99.24	0.00	0.00	0.00	0.00	99.24	0.00	0.76	0.00	0.00	0.00	0.00

5-HMF—5-hydroxymethylfurfural, DHA—dihydroxyacetone, OA—oxalic acid, LA—lactic acid, FA—formic acid, LE—levulinic acid, AC—acetic acid, PA—propionic acid, ACt—acetone.

Mixture 1 Process Time 5 h	Process	Raw Material	Yield to OA	Yield to LE	Yield to LA			Selectiv	ity (%)		
Catalyst Concentration	Temp. (°C)	p. (°C) Conversion (%) (%) (%)		FRU	OA	LA	FA	LE	AC		
0.1 M H ₂ SO ₄	180	99.78	94.29	4.54	0.14	0.00	94.50	0.14	0.81	4.55	0.00
0.2 M H ₂ SO ₄		99.37	89.74	6.28	0.00	0.00	90.30	0.00	0.94	6.32	2.43
0.5 M H ₂ SO ₄		99.62	96.45	2.40	0.00	0.00	96.82	0.00	0.31	2.41	0.46
1 M H ₂ SO ₄		100.00	97.72	1.74	0.00	0.00	97.72	0.00	0.00	1.74	0.54
0.1 M H ₂ SO ₄	200	100.00	77.35	13.04	2.68	0.00	77.35	2.68	6.04	13.04	0.89
0.2 M H ₂ SO ₄		100.00	88.11	5.70	1.75	0.00	88.11	1.75	3.80	5.70	0.65
0.5 M H ₂ SO ₄		99.04	94.98	2.32	0.85	0.00	95.90	0.86	0.90	2.34	0.00
1 M H ₂ SO ₄		99.45	97.94	1.05	0.20	0.00	98.49	0.20	0.09	1.06	0.17
0.1 M H ₂ SO ₄		98.94	82.90	8.26	2.20	1.28	83.79	2.22	2.79	8.35	1.56
0.2 M H ₂ SO ₄		100.00	92.98	4.70	1.50	0.00	92.98	1.50	0.82	4.70	0.00
0.5 M H ₂ SO ₄	220	100.00	96.01	2.59	0.46	0.35	96.01	0.46	0.30	2.59	0.28
1 M H ₂ SO ₄		99.36	98.03	1.14	0.20	0.00	98.66	0.20	0.00	1.15	0.00
0.1 M H ₂ SO ₄		100.00	85.89	9.29	1.55	0.00	85.89	1.55	1.61	9.29	1.65
0.2 M H ₂ SO ₄		100.00	89.90	5.96	2.25	0.00	89.90	2.25	0.00	5.96	1.90
0.5 M H ₂ SO ₄	250	100.00	95.76	3.07	0.41	0.00	95.76	0.41	0.00	3.07	0.77
1 M H ₂ SO ₄		100.00	98.98	0.90	0.12	0.00	98.98	0.12	0.00	0.90	0.00

Table 4. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydrates using the homogeneous H_2SO_4 catalyst in the liquid phase, with a 5 h process time for mixture 1.

FRU-fructose, OA-oxalic acid, LA-lactic acid, FA-formic acid, LE-levulinic acid, AC-acetic acid.

Table 5. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydrates using the homogeneous H_2SO_4 catalyst in the liquid phase, with a 5 h process time for mixture 2.

Mixture 2 Process Time 5 h	Process	Raw Material	Yield to	Yield to LE	Yield to LA			Sele	ectivity (%)			
Catalyst Concentration	- iemp. (C)	(%)	UA (%)	(78)	(/0)	FRU	PAC	OA	LA	FA	LE	AC
0.1 M H ₂ SO ₄		100.00	82.04	11.57	0.00	0.00	0.63	82.04	0.00	2.21	11.57	3.55
0.2 M H ₂ SO ₄	-	99.13	90.21	4.86	0.00	0.00	0.00	91.00	0.00	1.07	4.90	3.03
0.5 M H ₂ SO ₄	- 180	98.92	94.87	1.96	0.00	0.00	0.31	95.90	0.00	0.52	1.98	1.28
1 M H ₂ SO ₄		99.78	99.26	0.28	0.00	0.00	0.07	99.48	0.00	0.23	0.28	0.00
0.1 M H ₂ SO ₄		100.00	81.52	9.12	3.01	0.00	0.00	81.52	3.01	5.57	9.12	0.79
0.2 M H ₂ SO ₄	200	100.00	89.02	4.32	1.73	0.00	0.00	89.02	1.73	3.86	4.32	1.07
0.5 M H ₂ SO ₄	- 200	99.50	96.21	2.07	0.54	0.00	0.00	96.69	0.54	0.50	2.08	0.19
$1 \text{ M H}_2\text{SO}_4$		100.00	98.54	1.05	0.29	0.00	0.00	98.54	0.29	0.12	1.05	0.00
$0.1 \text{ M} \text{ H}_2 \text{SO}_4$		98.28	80.67	7.41	3.43	1.81	0.00	82.08	3.49	3.60	7.54	1.48
$0.2 \text{ M} \text{ H}_2 \text{SO}_4$	220	100.00	92.98	4.70	1.50	0.00	0.00	92.98	1.50	0.00	4.70	0.82
$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	220	100.00	97.48	1.83	0.57	0.00	0.00	97.48	0.57	0.00	1.83	0.12
$1 \text{ M H}_2\text{SO}_4$		99.36	97.79	1.03	0.44	0.00	0.00	98.41	0.45	0.00	1.04	0.10
$0.1 \text{ M H}_2\text{SO}_4$		99.29	83.11	8.21	1.89	2.73	0.00	83.71	1.90	1.96	8.27	1.44
$0.2 \text{ M H}_2\text{SO}_4$	250	99.91	31.37	29.29	0.26	0.32	0.00	31.40	0.26	0.00	29.32	38.71
0.5 M H ₂ SO ₄	250	100.00	97.80	1.33	0.25	0.00	0.00	97.80	0.25	0.18	1.33	0.44
1 M H ₂ SO ₄		100.00	98.96	0.69	0.17	0.00	0.00	98.96	0.17	0.00	0.69	0.19
		TDU			1 0 4 1'	· 1 T A	1	· 1 TA	<u> </u>	· 1 I T	1 1.	· · 1

FRU—fructose, PAC—pyruvic acid, OA—oxalic acid, LA—lactic acid, FA—formic acid, LE—levulinic acid, AC—acetic acid.

Mixture 3 Process Time 5 h	Process - Temp. (°C)	Raw Material	Yield to	Yield to LE	Yield to LA			Sele	ctivity (%)			
Catalyst Concentration	- Temp. (C)	(%)	UA (%)	(%)	(70)	FRU	PAC	OA	LA	FA	LE	AC
0.1 M H ₂ SO ₄	-	99.80	94.78	0.00	0.00	0.00	0.95	94.97	0.00	1.30	0.00	2.78
0.2 M H ₂ SO ₄		98.21	94.36	1.23	0.00	0.00	0.00	96.09	0.00	0.94	1.25	1.73
0.5 M H ₂ SO ₄	- 180	99.25	96.85	0.70	0.94	0.00	0.00	97.59	0.95	0.55	0.71	0.20
$1 \text{ M H}_2\text{SO}_4$		99.74	98.99	0.38	0.00	0.00	0.00	99.25	0.00	0.22	0.38	0.14
0.1 M H ₂ SO ₄	-	99.10	90.38	2.51	3.46	0.00	0.00	91.20	3.49	2.77	2.54	0.00
0.2 M H ₂ SO ₄		100.00	94.08	1.96	1.70	0.00	0.00	94.08	1.70	1.87	1.96	0.40
0.5 M H ₂ SO ₄	- 200	100.00	97.85	1.07	0.61	0.00	0.00	97.85	0.61	0.47	1.07	0.00
1 M H ₂ SO ₄		100.00	99.03	0.53	0.35	0.00	0.00	99.03	0.35	0.09	0.53	0.00
0.1 M H ₂ SO ₄		100.00	90.08	2.49	4.13	0.00	0.00	90.08	4.13	2.51	2.49	0.79
0.2 M H ₂ SO ₄		99.02	93.35	1.40	2.96	1.32	0.00	94.27	2.99	0.00	1.42	0.00
0.5 M H ₂ SO ₄	- 220	100.00	97.28	1.11	0.68	0.00	0.00	97.28	0.68	0.94	1.11	0.00
1 M H ₂ SO ₄		99.21	97.42	0.37	0.77	0.54	0.00	98.19	0.77	0.00	0.37	0.12
0.1 M H ₂ SO ₄		98.09	84.27	3.30	2.02	5.87	0.00	85.91	2.06	1.78	3.37	1.01
0.2 M H ₂ SO ₄	-	99.91	95.36	1.61	0.70	1.03	0.00	95.44	0.70	0.55	1.61	0.67
0.5 M H ₂ SO ₄	- 250	100.00	98.32	0.66	0.36	0.00	0.00	98.32	0.36	0.13	0.66	0.53
$1 \text{ M H}_2\text{SO}_4$	-	100.00	99.17	0.45	0.20	0.00	0.00	99.17	0.20	0.00	0.45	0.19

Table 6. The results of HPLC analysis for the catalytic conversion of hemicellulose carbohydrates using the homogeneous H_2SO_4 catalyst in the liquid phase, with a 5 h process time for mixture 3.

FRU—fructose, PAC—pyruvic acid, OA—oxalic acid, LA—lactic acid, FA—formic acid, LE—levulinic acid, AC—acetic acid.

Catalytic tests in the homogenous process were performed using different aqueous solutions of sulfuric (VI) acid (H_2SO_4 with a concentration of 0.1, 0.2, 0.5, and 1 M). Based on the collected results in Tables 1 and 2, the conversion of hemicellulosic carbohydrates was maintained at levels between 16 and 100%. During the process, C1–C3 carboxylic acids were formed, such as oxalic acid, lactic acid, levulinic acid, acetic acid, and formic acid (Figure 2), with oxalic acid being formed in the greatest amount and, under specific conditions, with significant amounts of lactic acid and levulinic acid also being formed.



oxalic acid

lactic Acid

levulinic acid

acetic acid

formic acid

Figure 2. Scheme of products from HPLC analysis for the catalytic conversion of hemicellulose *carbohydrates* mixtures using the homogeneous H₂SO₄ catalyst in the liquid phase.

Figure 3 shows a matrix with optimal process parameters for the production of oxalic, lactic, and levulinic acids as a function of temperature, H_2SO_4 catalyst concentration, and process time. Analyzing the effect of process parameters on raw material conversion (see Tables 1–6), it can be concluded that an increase in both temperature and sulfuric acid concentration have a favorable effect on the conversion of all types of hemicellulose mixtures used. The most observed compounds under all conditions are oxalic, lactic, levulinic, and acetic acids, as well as, in some cases, formic acid. Other products observed in the mixture, such as 5-hydroxymethylfurfural, dihydroxyacetone, propionic acid, acetone, fructose, and pyruvic acid, are observed in post-reaction mixtures in insignificant amounts



(selectivity highly below 5%). The most essential products, also taking into account market interests, are lactic, oxalic, and levulinic acids.

Yield for all products below 30%

Process time: 1h or 5h

Figure 3. Matrix analysis of optimal process parameters for the production of oxalic, lactic, and levulinic acids as a function of temperature, H₂SO₄ catalyst concentration, and process time.

The high yield of lactic acid (Figure 4) was only observed with a low H₂SO₄ catalyst concentration (0.1 M) and at a temperature of 100 $^{\circ}$ C with a decreasing order: M1 (64%) > M2 (58%) > M3 (45%) after the 1 h process. Compared with the literature data, this is a very promising result, where the maximal obtained yield of lactic acid was around 58% [24], especially because, in our case, we used a mixture of carbohydrates instead of glucose only. However, the increase in the process time results in a significant reduction in lactic acid in favour of other diverse products; e.g., oxalic, levulinic, formic, and acetic acids.



Figure 4. Lactic acid yield as a function of catalyst concentration, temperature, and mixtures of hemicellulosic raw material—1 h process.

Additionally, it can be concluded that an increase in the concentration of galacturic and glucuronic acids in the substrate mixture results in a decrease in the efficiency of lactic acid production. The most favorable mixture for LA production will be a hemicellulosic mixture with the least amount of pretreatment.

A hemicellulose mixture is not very significant for oxalic acid production performance at higher concentrations of sulfuric acid (0.5 or 1.0 M) and temperature above 200 °C (Figure 5). OA yields at temperatures of 250 °C even reach around 99% (M1), 97% (M2), 99% (M3).



Figure 5. Oxalic acid yield as a function of catalyst concentration, temperature, and mixtures of hemicellulosic raw material—1 h process.

Long process times and high temperatures (above 200 °C) were needed to obtain levulinic acid (Figure 6), which is quite an interesting result because LE has four carbon atoms in the chain compared with other acids, such as lactic acid, which was formed at a lower temperature. The most favourable concentration was 0.2 M H₂SO₄ and a process time of 5 h. The highest amount of levulinic acid was obtained for the M1 mixture (yield 29%) at a temperature of 250 °C and a concentration of 0.2 M H₂SO₄. Our result is not competitive with processes for obtaining LE from fructose or glucose using heterogeneous catalysts, where yields reached 75% [25]. However, our result is still interesting because we used a hemicellulosic mixture of carbohydrates. Unfortunately, under the same process conditions, acetic acid is also formed with a yield of 37.8%, which means these process conditions are not satisfactory for LE production. Therefore, it can be concluded that a heterogeneous catalyst such as zeolite should be used for levulinic acid to manage the more selective cabohydrates to levulinic acid transformation.



Figure 6. Levulinic acid yield as a function of catalyst concentration, temperature, and mixtures of hemicellulosic raw material—5 h process.

In addition, based on the collected results from the catalytic processes carried out using sulfuric acid (VI) using the one-pot method, the results can be determined using reaction paths. Regardless of the process conditions, i.e., temperature and time, compounds such as fructose, dihydroxyacetone, and 5-HMF, as well as a mixture of carboxylic acids such as oxalic, lactic, levulinic, pyruvic, propionic, formic, and acetic acids, are present in the post-reaction mixture. The transformation of hemicellulose to C6 and C5 carbohydrates takes place as a result of dehydration. The carbohydrates C6 and C5 undergo a retroaldol reaction to DHA, and 5-HMF is formed by dehydration. In the presence of fructose, there was an isomerization reaction between glucose and this compound. Subsequently, depending on the intermediate product, specific carboxylic acids can be obtained. In the case of 5-HMF, it is hydrated and, with the opening of the ring, formic acid and levulinic acid are formed. In turn, DHA during its oxidation leads to the formation of oxalic acid, which is the leading compound in this publication. This proves the ability of the catalyst to carry out the oxidation process. In the next stage, the catalyst further leads to the conversion of DHA to pyruvic aldehyde, due to the presence of proton ions and, further, pyruvic aldehyde during hydration is transformed into lactic acid and oxidized to pyruvic acid. Thanks to the presence of an active catalyst, further transformations of lactic acid can still occur, which produce propionic acid (during LA reduction) and acetic acid (during a two-stage decarboxylation reaction and subsequent oxidation).

3. Materials and Methods

The catalytic tests were conducted by the one-pot method using a 0.125 M aqueous hemicellulose mixture solution. Hemicellulose sugar mixture conversion in homogeneous conditions was performed in the temperature range 100–250 °C for 1 h and 5 h using H₂SO₄ (0.1, 0.2, 0.5, and 1 M solutions). Three hemicellulose sugar mixtures were investigated, which contained different ratios of xylose, mannose, galactose, glucose, rhamnose, galacturonic acid, and glucuronic acid (see Figure 7).



Figure 7. Scheme of mixtures of biomass-derived hemicellulose carbohydrates used in the one-pot method.

The mass ratios of the sugar components of the mixtures based on hemicellulose treatment using OrganoCat technology (extracted from the literature [7,8]) with respect to the component with the smallest mass in mg:

Mixture 1 (M1)—lignocellulosic biomass derived from the first leaching step from the OrganoCat process containing a hemicellulosic fraction with the following composition: 27.8 xylose, 2.1 mannose, 2.9 galactose, 3.8 glucose, 1.2 rhamnose, 1.0 galacturonic acid.

Mixture 2 (M2)—lignocellulosic biomass from stage 5 leaching from the OrganoCat process containing a hemicellulosic fraction with the following composition: 68.5 xylose, 1.1 mannose, 3.4 galactose, 9.0 glucose, 1.0 rhamnose, 17.0 galacturonic acid.

Mixture 3 (M3)—lignocellulosic biomass from stage 8 leaching from the OrganoCat process containing a hemicellulosic fraction with the following composition: 50.2 xylose, 1.0 galactose, 2.0 glucose, 1.1 glucuronic acid, 35.6 galacturonic acid.

In the investigated homogeneous process, the autoclave with the products was cooled after the specified process time and the solution was neutralised with 10% aqueous sodium hydroxide solution to pH = 7. The prepared samples were analysed by a HPLC-RID system (HPLC-RID, Shimadzu, Tokyo, Japan) using isocratic elution, Rezex Organic acid ROA H+ 300×7.8 mm, column temperature 40 °C, eluent 0.005 N H₂SO₄.

The analysis of the obtained products during glucose conversion was performed using the HPLC technique. The retention times of the obtained products were compared using the chromatographic method with the retention times of the pure standard components.

4. Conclusions

The results presented herein included a variable mixture of hemicellulosic carbohydrates and a process carried out while varying both the process temperature and concentration of the homogeneous catalyst used. This allowed us to obtain a comprehensive and complete knowledge of the influence of the process conditions on the composition of the final products. The homogeneous process of oxalic acid, lactic acid, and levulinic acid production from three biomass-derived hemicelullosic sugar mixtures was studied using sulfuric acid with different concentrations (0.1–1 M). Process time was also a variable. A process time in the range of 1–5 h was used. The carbohydrate components of the mixtures were based on hemicellulose treatment using OrganoCat technology [7,8]. All three mixtures contained carbohydrates such as xylose, mannose, galactose, glucose, and rhamnose, as well as galacturonic and glucuronic acids. The essence of the one-pot method used in this study is the ability to program the production of oxalic acid, lactic acid, or levulinic acid by controlling the process parameters, such as the temperature and homogeneous catalyst concentration as well as process time. The high yield of lactic acid was only observed with a low H_2SO_4 catalyst concentration, low temperature, and short process time (1 h). The maximal LA yield (64%) was obtained for 100 °C, 0.1 M of sulfuric acid concentration, and 1 h process time for the M1 sugar mixture. Compared with the literature data, this is a very promising result, especially because we considered a mixture of carbohydrates. At higher concentrations of sulfuric acid, oxalic acid is mainly formed with a yield above 99%. Long process times (5 h) and high temperatures were needed to obtain levulinic acid, but only with a maximal yield of 29%, which is not acceptable at the industrial level, thus a heterogeneous catalyst such as zeolite should be further tested.

The one-pot method, used in our research, allows the process to be carried out in a single apparatus without the need to expand it and makes it possible to reduce the duration of the process. Another important advantage of the method is that the developed conditions for conducting the process by the one-pot method can, potentially, be applied to the conversion of biomass including the hemicellulose fraction to carboxylic acids, regardless of the source of the biomass as waste.

The presented results are interesting from a practical point of view because of the lower energy consumption and can be easily used with more environmental friendly catalysts than sulfuric acid as well. A combination of homogeneous and heterogeneous catalysts is an interesting avenue for future research.

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