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Microwave-Assisted One-Step Conversion of Wood Wastes into Levulinic Acid

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Abstract: This study aimed to evaluate the use of softwood and hardwood waste for the production of levulinic acid by one-stage conversion using microwave radiation combined with acid catalysis. The analysis demonstrated that the type and concentration of the acid used, the concentration of biomass in the reaction mixture and pressure value had the greatest impact on the yield of levulinic acid. The highest efficiency of carbohydrate conversion to levulinic acid, regardless of the type of raw material, was achieved using a pressure of 225 PSI and sulfuric acid as a catalyst. Maximum yield from biomass, ca. 16.5% for cherry wood chips and ca. 25% for pine chips, was obtained using sulfuric acid at a concentration of 1% *v/v* and 2% *v/v*, respectively, for the following process parameters: Exposure time 20 min, biomass concentration 3.3%, and the pressure of 225 PSI. The ratio of actual yield to theoretical yield was high: 64.7% ± 4.5% for pine chips and 43.4% ± 1.0% for cherry wood chips. High efficiency of the presented method of biomass conversion to levulinic acid indicates the possibility of its use for waste management in the wood processing industry. High concentration of levulinic acid in the post-reaction mixture allows for cost-effective extraction and purification of the compound.

Keywords: levulinic acid production; microwave-assisted; wood waste; one-step conversion

1. Introduction

Currently, one of the main directions of waste lignocellulosic biomass management is its thermochemical conversion to biofuels like hydrogen, biogas, syngas obtained in pyrolysis, gasification, carbonization, hydrothermal liquefaction and bioconversion to ethanol [1–7]. The use of waste biomass from the agro-food industry in the production of cellulosic ethanol is a prospective solution that provides the possibility of industrial application on a large scale. Currently, the use of non-wood waste biomass, such as corn stover, rye or rice straw, as a raw material for the production of second-generation bioethanol, does not encounter any major technological problems, provided that appropriate pretreatment and optimization methods are selected and highly active cellulolytic enzymes are applied [8–10]. On the other hand, biotechnological management of softwood and hardwood waste still encounters problems. These wastes contain, respectively, 45%–50% and 40%–55% *w/w* cellulose, 25%–35% and 24%–40% *w/w* hemicellulose and 25%–35% and 18%–25% *w/w* lignin, which are difficult to bio-convert to ethanol [11,12]. An alternative method of utilizing wood waste may be the production of other high added-value compounds, e.g., levulinic acid, which in 2004 was recognized by the United States Department of Energy (DOE) "as one of the top 12 bio-based platform chemicals" [13]. This compound can be used directly as a plasticizer, food additive, dye for textiles, an additive for biofuels and fodders, antifreeze, a compound with antibacterial activity, in the production of polymeric resins, and as a substrate for the synthesis of valerian esters (e.g., methyl, ethyl and propyl valerate) added to conventional fuels, or as a precursor of substances used by the pharmaceutical, biofuel, cosmetic and chemical industries [14–16].

Levulinic acid (LA, 4-oxopentanoic acid) is an organic compound containing both a keto group and a carboxylic group, classified as a keto acid. Its synthesis is done by dehydration of C6 sugars in an acidic medium at an elevated temperature, mostly with the use of H_2SO_4 and HCl [17]. Synthesis of LA from cellulose starts with acid hydrolysis of the polysaccharide to simple sugars. The next step is the isomerization of glucose to fructose and then dehydration of fructose to 5-hydroxymethylfurfural (HMF). During the dehydration of fructose, formic acid and humines are also formed. The last step in the thermochemical synthesis of levulinic acid is the rehydration of HMF to the final product (Figure 1) [18].

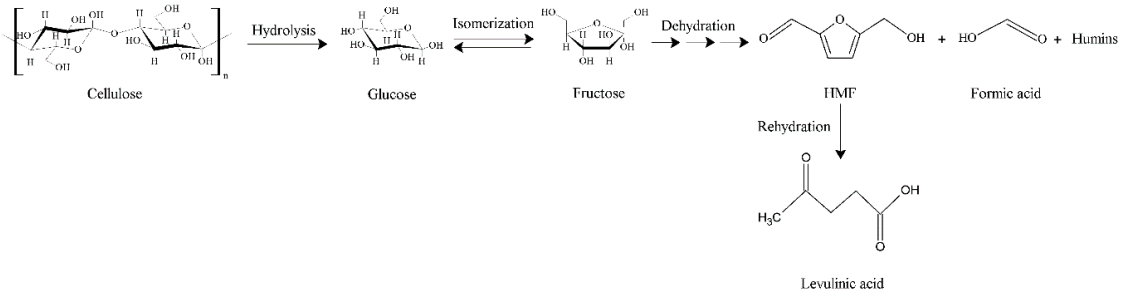

Figure 1. The mechanism of cellulose hydrolysis to levulinic acid (LA).

Acid hydrolysis can be carried out under homogeneous conditions, i.e., using concentrated mineral acid such as H_2SO_4 or HCl, or using heterogeneous acid catalysts, i.e., diluted acid with an additional metal catalyst (e.g., platinum, ruthenium and nickel) [19]. The advantages of homogeneous acid catalysis are high efficiency and low price of reagents, whereas the disadvantages include the need to use devices with increased resistance to corrosion and the need to recover mineral acids in order to increase the profitability of the process. The main benefit of using heterogeneous acid catalysis is less of an environmental impact due to the reduction of reagents used in the process, but the final yield is significantly lower compared to homogeneous acid catalysis [18]. The efficiency of levulinic acid production technology is determined not only by the type of catalysis but also by the composition of lignocellulosic biomass, mainly the presence of lignins, xylan and inorganic salts [20,21]. The profitability of levulinic acid production depends also on the efficiency of the conversion of substrates to the final product and on the concentration of LA in the solution, which directly affects the costs of the extraction and purification process. The stoichiometry of the reaction indicates that one mole of hexose (180 g/mol) produces one mole of LA (116 g/mol), so the maximum achievable LA yield is 64.4%. It is usually assumed that 50%–60% of the theoretical yield is a quite high degree of biomass conversion. For this reason, further work on improving the production process of levulinic acid should be done to achieve a higher efficiency of this process [22]. One of the proposed improvements in the production of levulinic acid is the conversion process carried out in a two-stage system. The first stage involves pretreatment and acid or enzymatic hydrolysis of lignocellulosic biomass, which ensures a high concentration of hexoses necessary for the production of levulinic acid. The pretreatment and acid hydrolysis process is usually carried out at an elevated temperature and pressure. In the second stage, also most frequently carried out at a higher temperature and pressure, hexoses are dehydrated to form levulinic acid [23].

Irrespective of the type of catalysis and the conditions for the conversion of biomass to levulinic acid, the compound is produced at elevated temperature and pressure. Therefore, one of the possibilities of improving the efficiency and cost-effectiveness of LA production process is using a method of heating biomass with high energy efficiency that guarantees a rapid increase in temperature in the reaction medium. Microwave radiation is a method of heating biomass in an aqueous solution with a reduced energy demand that provides a quick direct increase in the temperature of the reaction medium, without the need for classical heat exchange processes [24–26]. Compared to a conventional heat exchange method, microwave radiation is characterized by: (I) A better energy balance, (II) elimination

of heat losses resulting from heating the tank in which the biomass is located, (III) a faster achievement of the desired temperature, (IV) shorter reaction time with higher efficiency, (V) uniform temperature distribution in the entire biomass volume when the radiators are properly selected and (VI) better control of reaction temperature due to the possibility of immediate cessation of heating. Due to these features, microwave radiation can be an alternative to the conventional method of biomass heating, especially in technologies that use thermochemical conversion of biomass. It is worth emphasizing that the interaction of microwaves with lignocellulose is not limited to the increase in temperature of the reaction medium. The movement of dipoles in the oscillating electromagnetic field breaks the hydrogen bonds in the cellulose, which results in increased efficiency of enzymatic hydrolysis [24]. Therefore, microwaves are often recommended for thermochemical decomposition of lignocellulosic biomass [27], extraction of lignin from biomass [28,29] and degradation of lignocellulosic biomass used as raw material for the production of biomethane and bioethanol [30–34]. The efficiency of cellulose hydrolysis and final glucose concentration are highly dependent on the precise selection of process parameters optimized for a given raw material [35,36]. As a result of the high pressure and temperature of the microwave pretreatment and the lack of proper mixing of biomass, zones with a much higher temperature (so-called hot spots) may be created. Under such conditions, a high degree of cellulose hydrolysis is observed, which is accompanied by partial delignification of biomass and the formation of high concentrations of sugar dehydration products. Thus, this method of heating is particularly useful in the production of levulinic acid [28,37,38].

The production of levulinic acid using microwave radiation is relatively poorly recognized and described. Few previously published reports refer primarily to the use of microwaves for the conversion of model substances such as xylan and cellulose or non-wood lignocellulose biomass to furan compounds [18,25,38]. In this work, an attempt has been made to develop an original method of managing wood waste in the production of levulinic acid with the use of microwaves. For this purpose, we evaluated the suitability of microwave radiation in various process conditions using different mineral acids for the production of levulinic acid from two types of waste wood chips: Softwood (pine chips) and hardwood (sweet cherry wood chips). Studies on the influence of process parameters of microwave treatment on the efficiency of LA production process included: The use of nitric, phosphoric and sulfuric acids in two concentrations, at different pressure values during microwave treatment, and exposure time from 10 to 30 min, with a different biomass concentration in solution.

2. Results and Discussion

2.1. LA Production from Pine Chips at Different Pressure Values

In the first stage of the study, experiments were conducted to determine the influence of pressure during microwave processing on efficiency of LA production from pine wood cellulose, using various process parameters (reaction time, biomass and sulfuric acid concentration). Pressure values of 54, 114 and 225 PSI and three levels of reaction time and biomass concentration, as well as two sulfuric acid concentration values (1% and 2% *v*/*v*) were used. This made it possible to evaluate the impact of the analyzed process parameters on LA production efficiency in 54 experimental variants (Figures 2 and 3).

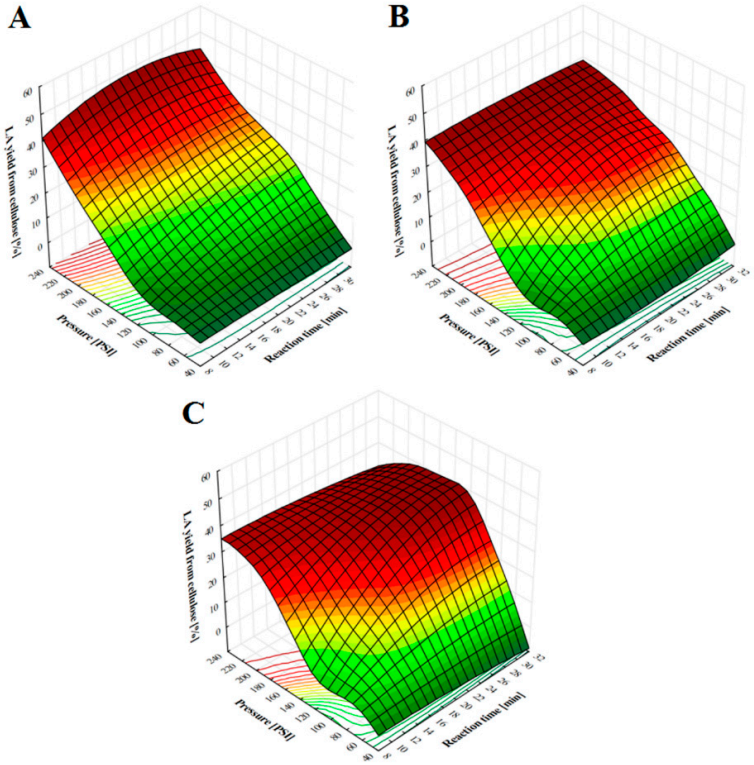

Figure 2. Response surface plot showing the effect of the interaction between pressure and reaction time of microwave-assisted conversion of pine chips on yield of production of levulinic acid from cellulose using sulfuric acid at a concentration of 1% and biomass content of 3.3% (**A**), 5% (**B**) and 10% (**C**).

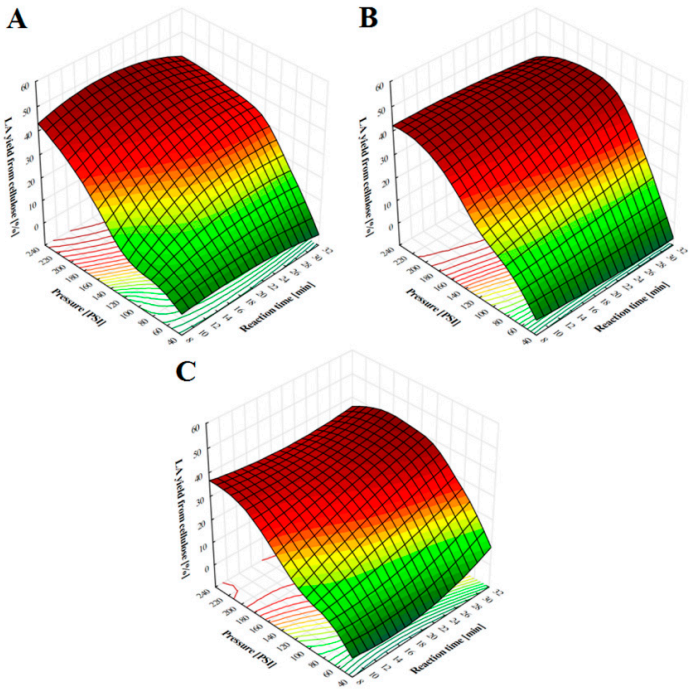

Figure 3. Response surface plot showing the effect of the interaction between pressure and reaction time of microwave-assisted conversion of pine chips on yield of production of levulinic acid from cellulose using sulfuric acid at a concentration of 2% with biomass content of 3.3% (**A**), 5% (**B**) and 10% (**C**).

During the microwave treatment of wood biomass catalyzed by sulfuric acid, cellulose and hemicellulose are first hydrolyzed to pentoses and hexoses, which are the key compounds in the synthesis of levulinic acid. In the next stage, hexoses are dehydrated to 5-HMF in inorganic acids environment that are protons source (Brønsted acid catalysts), and then 5-HMF is rehydrated to LA [39].

It was observed that the increase in pressure during the microwave treatment resulted in an increased LA yield from pine wood cellulose, regardless of the concentration of sulfuric acid used (1% or 2% *v*/*v*). The highest LA yields were obtained in processes using 1% *v*/*v* H_2SO_4 in the reaction medium at a pressure of 225 PSI, irrespective of other variables. Under these conditions, applying a biomass concentration of 3.3% and an exposure time of 20 min resulted in the highest LA yield of about 44% (Figure 2A). A biomass concentration of 3.3% at the same pressure (225 PSI) and 1% *v*/*v* H_2SO_4, resulted in a LA yield from pine wood cellulose of around 37%, regardless of the duration of the microwave treatment (Figure 2A). Under the same conditions but with a higher biomass concentration, a decrease in average LA yield from pine wood cellulose was observed, by up to 4% for 5% biomass concentration, and about 9% for 10% biomass concentration (Figure 2B,C). The duration of the microwave treatment with 1% *v*/*v* sulfuric acid had little effect on LA production efficiency from pine wood cellulose. With increasing reaction time, there was no observed significant increase in LA yield from cellulose. The main factors affecting the efficiency of the process were high pressure of about 225 PSI and low biomass concentration in a solution of ca. 3.3% (Figure 2).

Similar relationships involving biomass concentration, exposure time and pressure were also observed for 2% *v*/*v* concentration of sulfuric acid in the conversion process of pine chips to levulinic acid (Figure 3).

The application of a higher concentration of sulfuric acid increased the yield of levulinic acid to ca. 50% at 225 PSI, exposure time of 20 min and a 3.3% concentration of biomass (Figure 3A). The biomass concentration also affected the yield. For example, the use of H_2SO_4 at a concentration of 2% *v*/*v* increased the maximum yield by 5% for a biomass concentration of 3.3%, relative to the yield obtained using 1% *v*/*v* H_2SO_4. The yield increased by 10% for 5% biomass concentration (Figure 3A,B). For pine chips, the maximum yield of LA production was observed when the biomass concentration was 10%, regardless of the sulfuric acid concentration (no statistically significant differences; Figures 2C and 3C). It is worth noting that the application of higher concentrations of sulfuric acid (2% *v*/*v*) increased the yield of LA from cellulose at lower pressure (114 PSI) by up to 16% for 3.3% biomass concentration, and ca. 8% for 5% biomass concentration, compared to the yields obtained for 1% *v*/*v* H_2SO_4 (Figure 3A,B). The results of our study indicate the usefulness of microwave radiation in the production of levulinic acid from softwood waste. It should be noted that high yield can be obtained when the pressure is increased to 225 PSI and after optimizing the other process parameters, i.e., the catalyst and biomass concentration. For this reason, the pressure of 225 PSI was used in the implementation of the next stage of the study, where we analyzed the impact of biomass concentration, type and concentration of the catalyst and duration of the process on the efficiency of soft- and hardwood chips conversion to LA.

The positive effect of high pressure and associated temperature of the reaction on the effectiveness of carbohydrate conversion to LA was also observed by other authors. However, they did not use microwave radiation for heating the reaction medium. Fang and Hanna (2002) used sorghum grains for LA production. They observed that elevated reaction temperature and higher catalyst concentration increased the yield of the process [14]. Chang et al., (2007) reported that the yield of the LA production from wheat straw also depended on the process temperature, but above a certain value of this parameter (210 °C) the yield decreased [17]. Similar to the present study, Girisuta et al., (2008), who used the water hyacinth plant biomass for LA production, observed an almost negligible effect of the prolongation of carbohydrate dehydration time (even up to 60 min) on the increase of process efficiency [40]. The positive effect of the increased catalyst concentration (H_2SO_4 solution) on the carbohydrate conversion efficiency was also reported by Cao et al., (2018), who used red seaweed to produce LA under low-temperature microwave processing conditions [41].

2.2. LA Production from Soft- and Hardwood Chips Using Nitric, Phosphoric and Sulfuric Acid under Various Process Conditions

The next stage of our study focused on the use of soft- and hardwood waste, i.e., pine and sweet cherry chips, for the production of levulinic acid using microwave radiation and various catalysts. Optimization of process parameters included the analysis of the type and concentration of various mineral acids (nitric, phosphoric and sulfuric acid) on the LA production process at a constant pressure of 225 PSI, but with different exposure times and biomass concentrations. The efficiency of the process was determined on the basis of the yield from biomass, the yield related to the theoretical one, LA concentration in solution and LA production from 1 g of wood chips biomass.

It was found that the type of catalyst (mineral acid) clearly affected both the amount of LA produced and the yield from pine chips in relation to the theoretical one (Tables 1 and 2, Figure 4). The highest yields from biomass, ca. 23%, and the highest yield compared to the theoretical one, 64.7% ± 4.5%, were obtained for pine chips with the use of 2% sulfuric acid concentration, 3.3% biomass concentration during a 20 min exposure (Figure 4F, Table 2). High LA yield (64.7%) in relation to theoretical yield was also obtained due to the conversion of hemicellulose pentoses to levulinic acid during microwave treatment of wood biomass in a strong inorganic acids environment. Pentoses, mainly xylose, first dehydrate to furfural, which is converted to furfuryl alcohol (via the gas phase hydrogenation step) and then to levulinic acid by hydrolytic ring opening [42]. The high degree of conversion of lignocellulosic biomass to LA is also due to the strong impact of microwaves on the cellulose structure. Electromagnetic radiation in the microwave frequency range causes the degradation of hydrogen bonds in the cellulose molecule, which enhances the acid hydrolysis of this biopolymer and, as a result, promotes the production of levulinic acid [24].

Table 1. Influence of reaction time, biomass content, concentration and type of inorganic acid on microwave-assisted production of levulinic acid from pine chips.

Reaction Time (min)	Biomass Content (%)	Concentration of Levulinic Acid (g/L)						Production of Levulinic Acid (mg/g of DW)					
		1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3	1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3
10	10.0	4.37 ± 0.09	4.49 ± 0.20	0.42 ± 0.10	0.48 ± 0.30	0.15 ± 0.01	0.10 ± 0.03	175.1 ± 3.4	179.5 ± 7.8	16.8 ± 4.0	19.1 ± 11.8	5.9 ± 0.2	4.1 ± 1.4
10	5.0	4.62 ± 0.10	5.34 ± 0.22	0.39 ± 0.11	0.87 ± 0.19	0.07 ± 0.01	0.09 ± 0.02	185.1 ± 3.8	213.5 ± 8.6	15.6 ± 4.4	34.7 ± 7.4	2.8 ± 0.4	3.6 ± 0.8
10	3.3	4.71 ± 0.05	5.28 ± 0.04	0.23 ± 0.02	0.59 ± 0.06	0.04 ± 0.04	0.03 ± 0.03	188.4 ± 2.0	211.1 ± 1.4	9.2 ± 0.8	23.6 ± 2.4	1.6 ± 1.6	1.1 ± 1.0
20	10.0	4.43 ± 0.22	4.34 ± 0.21	1.15 ± 0.53	1.10 ± 0.29	0.22 ± 0.01	0.25 ± 0.01	177.2 ± 8.8	173.5 ± 8.2	46.0 ± 21.2	44.0 ± 11.6	8.7 ± 0.2	10.0 ± 0.4
20	5.0	4.77 ± 0.12	5.41 ± 0.52	0.84 ± 0.19	1.48 ± 0.21	0.13 ± 0.01	0.14 ± 0.02	190.8 ± 4.8	216.5 ± 20.7	33.47 ± 7.4	59.1 ± 8.2	5.1 ± 0.2	5.5 ± 0.6
20	3.3	5.41 ± 0.07	5.79 ± 0.40	0.97 ± 0.34	1.26 ± 0.06	0.11 ± 0.04	0.05 ± 0.02	216.4 ± 2.8	231.5 ± 16.0	38.8 ± 13.6	50.4 ± 2.4	4.4 ± 1.6	1.9 ± 0.6
30	10.0	4.28 ± 0.22	4.67 ± 0.04	1.44 ± 0.43	2.10 ± 0.14	0.22 ± 0.02	0.26 ± 0.01	171.3 ± 8.8	186.7 ± 1.4	57.6 ± 17.2	84.0 ± 5.6	8.7 ± 0.6	10.5 ± 0.2
30	5.0	4.77 ± 0.10	5.27 ± 0.14	1.42 ± 0.33	2.54 ± 0.27	0.19 ± 0.01	0.16 ± 0.05	190.7 ± 3.8	210.8 ± 5.6	56.7 ± 13.0	101.6 ± 10.8	7.6 ± 0.4	6.3 ± 1.8
30	3.3	5.10 ± 0.28	5.18 ± 0.44	0.77 ± 0.22	2.10 ± 0.15	0.09 ± 0.01	0.06 ± 0.02	203.9 ± 11.2	207.1 ± 17.4	30.8 ± 8.8	84.0 ± 6.0	3.5 ± 0.2	2.4 ± 0.8

Table 2. Influence of reaction time, biomass content, concentration and type of inorganic acid on yield of levulinic acid production (based on cellulose content in raw material) from pine chips.

Reaction Time (min)	Biomass Content (%)	Yield of Levulinic Acid Production (% of Theoretical)					
		1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3
10	10.0	48.9 ± 1.0	50.2 ± 2.2	4.7 ± 1.1	5.3 ± 3.3	1.6 ± 0.1	1.2 ± 0.4
10	5.0	51.7 ± 1.1	59.7 ± 2.4	4.4 ± 1.2	9.7 ± 2.1	0.8 ± 0.1	1.0 ± 0.2
10	3.3	52.7 ± 0.6	59.0 ± 0.4	2.6 ± 0.2	6.6 ± 0.7	0.5 ± 0.5	0.3 ± 0.3
20	10.0	49.5 ± 2.5	48.5 ± 2.3	12.9 ± 5.9	12.3 ± 3.2	2.4 ± 0.1	2.8 ± 0.1
20	5.0	53.3 ± 1.3	60.5 ± 5.8	9.4 ± 2.1	16.5 ± 2.3	1.4 ± 0.1	1.5 ± 0.2
20	3.3	60.5 ± 0.8	64.7 ± 4.5	10.9 ± 3.8	14.1 ± 0.7	1.2 ± 0.5	0.5 ± 0.2
30	10.0	47.9 ± 2.5	52.2 ± 0.4	16.1 ± 4.8	23.5 ± 1.6	2.4 ± 0.2	2.9 ± 0.1
30	5.0	53.3 ± 1.1	58.9 ± 1.6	15.8 ± 3.6	28.4 ± 3.0	2.1 ± 0.1	1.8 ± 0.5
30	3.3	57.0 ± 3.1	57.9 ± 4.9	8.6 ± 2.5	23.5 ± 1.7	1.0 ± 0.1	0.7 ± 0.2

The sulfuric acid used as a catalyst, regardless of its concentration, gave the highest LA yield and the highest concentration of levulinic acid compared to the two other mineral acids. The lowest conversion of carbohydrates to LA was obtained using nitric acid, regardless of its concentration. In this case, the maximum yield from biomass was ca. 1%, the yield related to the theoretical one was about 2.4%, and the concentration of LA was 0.26 ± 0.01 g/L (10.5 ± 0.2 mg/g DW - dry weight; Figure 4A,B, Tables 1 and 2). Phosphoric acid provided a higher efficiency of softwood waste conversion than nitric acid. Higher concentrations of phosphoric acid (2% *v*/*v*) proved to be more effective: The LA yield from pine chips increased by ca. 5% (about 12% in relation to the theoretical yield). The concentration of LA in the solution was also higher (by about 1.1 g/L), and the productivity from biomass increased by ca. 44 mg/g DW, compared to the lower phosphoric acid concentration (Figure 4C,D, Tables 1 and 2). It is worth noting that the relative increase in conversion efficiency with a higher concentration of phosphoric acid (2% *v*/*v*) was more pronounced than that observed when the concentration of sulfuric acid was increased (Figure 4E,F, Tables 1 and 2). When nitric or phosphoric acid was used as a catalyst, the exposure time was the main factor affecting the efficiency of the pine chips conversion to LA. Extending the exposure time to 30 min resulted in an increased yield and concentration of LA in the medium (Figure 4A–D, Tables 1 and 2).

However, when sulfuric acid was used as a catalyst during microwave treatment, the efficiency of the conversion process depended mainly on the biomass concentration rather than on the reaction time. The maximum efficiency was achieved at 3.3% concentration of pine chips and exposure time of 20 min (Figure 4E,F, Tables 1 and 2). Microwave treatment with 2% *v*/*v* sulfuric acid at 225 PSI ensured a high concentration of LA in solution (about 5.79 ± 0.40 g/L), which allowed for an implementation of a cost-effective purification process by distillation under reduced pressure (Table 1) [43].

Among the mineral acids, H_2SO_4 and HCl are considered most suitable for levulinic acid production due to their strong dehydration properties. In our studies, the highest efficiency of LA production was obtained using sulfuric acid. Compared to HCl, the reaction carried out with H_2SO_4 requires lower activation energy necessary for full dehydration of fructose in the process of obtaining LA from biomass (Figure 1.) [44].

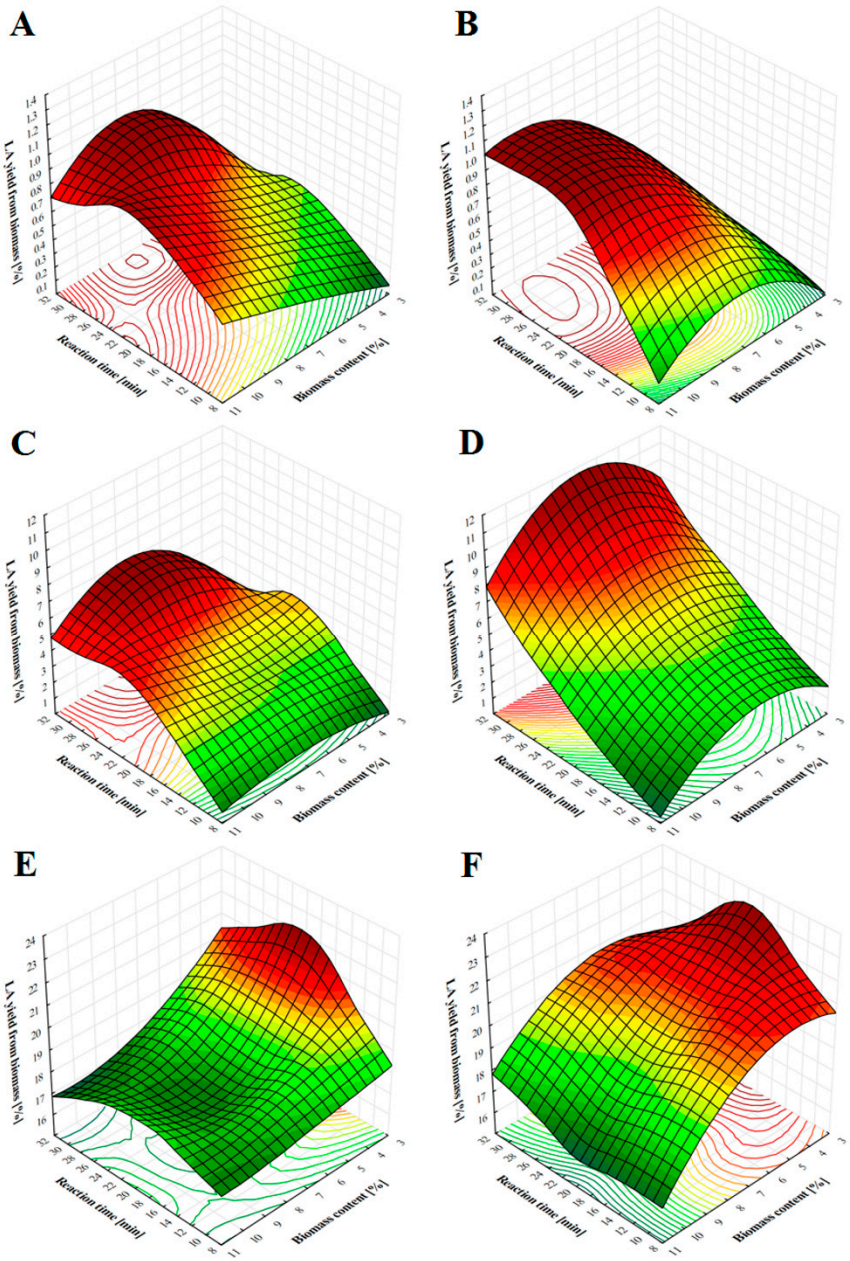

Figure 4. Response surface plot showing the effect of the interaction between biomass content of pine chips and reaction time of microwave-assisted conversion on yield of production of levulinic acid from biomass using nitric acid at a concentration of 1% (**A**) and 2% (**B**), phosphoric acid at a concentration of 1% (**C**) and 2% (**D**) and sulfuric acid at a concentration of 1% (**E**) and 2% (**F**).

In experiments with the conversion of sweet cherry chips (hardwood raw material) to LA, the highest values of efficiency indicators were also observed when sulfuric acid was used as the catalyst (Figure 5E,F, Tables 3 and 4).

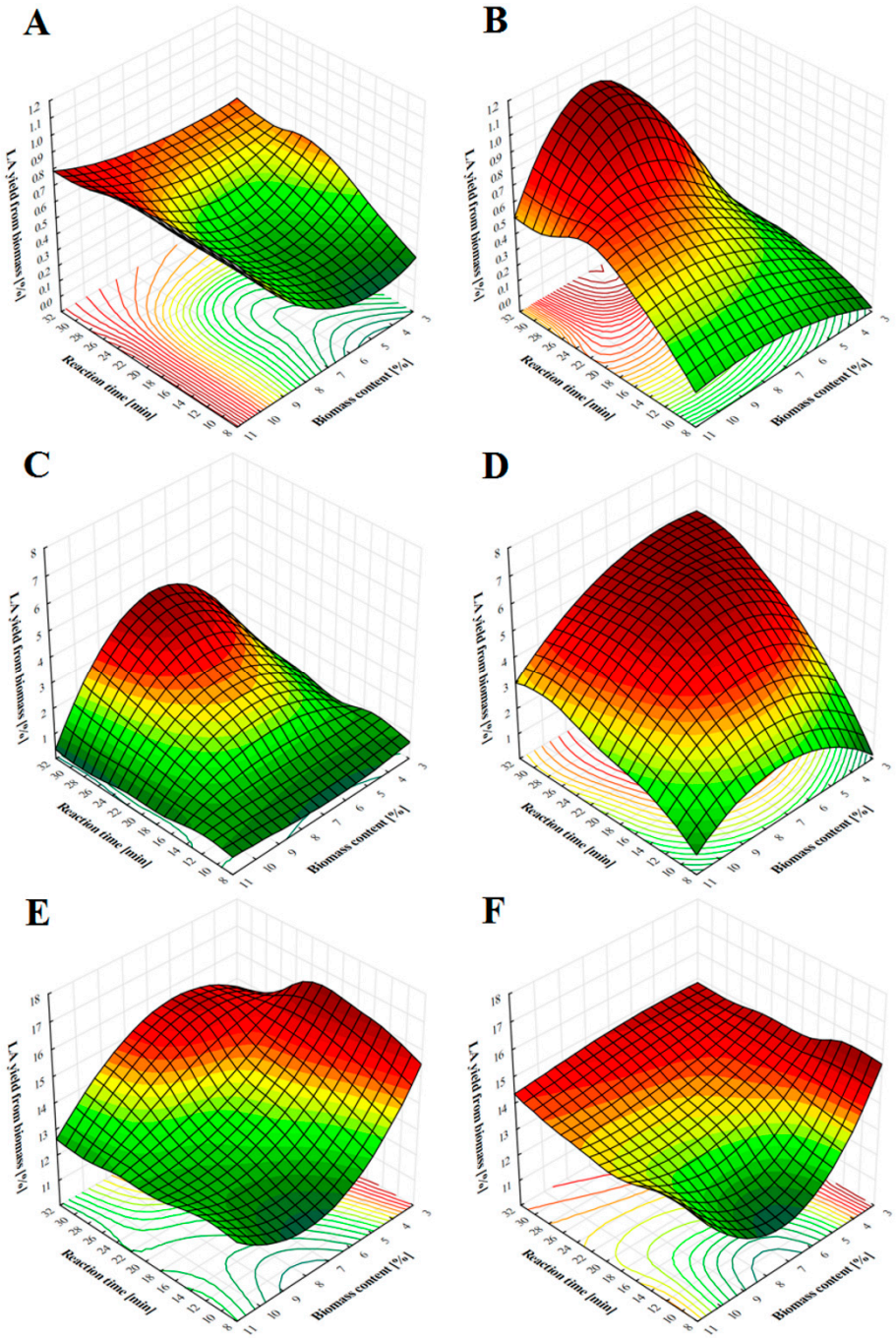

Figure 5. Response surface plot showing the effect of the interaction between biomass content of sweet cherry chips and reaction time of microwave-assisted conversion on the yield of production of levulinic acid using nitric acid at a concentration of 1% (**A**) and 2% (**B**), phosphoric acid at a concentration of 1% (**C**) and 2% (**D**) and sulfuric acid at a concentration of 1% (**E**) and 2% (**F**).

Table 3. Influence of reaction time, biomass content, concentration and type of inorganic acid on microwave-assisted production of levulinic acid from sweet cherry chips.

Reaction Time (min)	Biomass Content (%)	Concentration of Levulinic Acid (g/L)						Production of Levulinic Acid (mg/g of DW)					
		1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3	1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3
10	10.0	3.13 ± 0.15	3.24 ± 0.14	0.19 ± 0.08	0.49 ± 0.19	0.17 ± 0.05	0.06 ± 0.06	125.1 ± 5.8	129.6 ± 5.6	7.6 ± 3.2	19.6 ± 7.6	6.8 ± 2.0	2.4 ± 2.4
10	5.0	3.34 ± 0.25	3.20 ± 0.18	0.15 ± 0.05	0.58 ± 0.24	0.06 ± 0.06	0.03 ± 0.03	133.6 ± 10.0	127.9 ± 7.0	5.9 ± 1.8	23.2 ± 9.6	2.3 ± 2.2	1.1 ± 1.0
10	3.3	3.83 ± 0.30	3.76 ± 0.20	0.20 ± 0.10	0.32 ± 0.04	0.07 ± 0.07	0.00 ± 0.00	153.1 ± 11.8	150.4 ± 8.0	8.0 ± 4.0	12.7 ± 1.4	2.8 ± 2.8	0.0 ± 0.0
20	10.0	3.17 ± 0.22	3.35 ± 0.14	0.34 ± 0.13	0.87 ± 0.30	0.17 ± 0.01	0.16 ± 0.07	126.8 ± 8.8	133.9 ± 5.4	13.6 ± 5.2	34.7 ± 11.8	6.8 ± 0.4	6.4 ± 2.8
20	5.0	3.64 ± 0.11	3.52 ± 0.19	0.55 ± 0.28	1.33 ± 0.55	0.09 ± 0.04	0.09 ± 0.06	145.5 ± 4.2	140.8 ± 7.6	22.0 ± 11.2	53.2 ± 22.0	3.6 ± 1.6	3.5 ± 2.2
20	3.3	4.04 ± 0.10	3.70 ± 0.18	0.27 ± 0.01	1.12 ± 0.31	0.14 ± 0.07	0.04 ± 0.04	161.5 ± 3.8	148.0 ± 7.2	10.8 ± 0.4	44.7 ± 12.2	5.5 ± 2.6	1.5 ± 1.4
30	10.0	3.36 ± 0.03	3.57 ± 0.21	0.46 ± 0.10	0.99 ± 0.01	0.18 ± 0.07	0.19 ± 0.08	134.4 ± 1.2	142.7 ± 8.2	18.3 ± 3.8	39.5 ± 0.25	7.2 ± 2.8	7.6 ± 3.2
30	5.0	3.89 ± 0.23	3.70 ± 0.09	0.92 ± 0.45	1.47 ± 0.29	0.15 ± 0.04	0.17 ± 0.06	155.6 ± 9.2	147.9 ± 3.4	36.8 ± 18.0	58.7 ± 11.4	6.0 ± 1.6	6.7 ± 2.2
30	3.3	3.74 ± 0.16	3.70 ± 0.34	0.47 ± 0.05	1.47 ± 0.38	0.15 ± 0.07	0.00 ± 0.00	149.7 ± 6.2	148.0 ± 13.6	18.7 ± 1.8	58.7 ± 15.0	6.0 ± 2.8	0.0 ± 0.0

Table 4. Influence of reaction time, biomass content, concentration and type of inorganic acid on the yield of levulinic acid production (based on cellulose content in raw material) from sweet cherry chips.

Reaction Time (min)	Biomass Content (%)	Yield of Levulinic Acid Production (% of Theoretical)					
		1% H_2SO_4	2% H_2SO_4	1% H_3PO_4	2% H_3PO_4	1% HNO_3	2% HNO_3
10	10.0	33.6 ± 1.6	34.8 ± 1.5	2.0 ± 0.9	5.3 ± 2.0	1.8 ± 0.5	0.7 ± 0.6
10	5.0	35.9 ± 2.7	34.4 ± 1.9	1.58 ± 0.5	6.2 ± 2.6	0.6 ± 0.6	0.3 ± 0.3
10	3.3	41.1 ± 3.2	40.4 ± 2.2	2.2 ± 1.1	3.4 ± 0.4	0.8 ± 0.8	0.0 ± 0.0
20	10.0	34.1 ± 2.4	36.0 ± 1.5	3.7 ± 1.4	9.3 ± 3.2	1.8 ± 0.1	1.7 ± 0.8
20	5.0	39.1 ± 1.1	37.8 ± 2.0	5.9 ± 3.0	14.3 ± 5.9	1.0 ± 0.4	0.9 ± 0.6
20	3.3	43.4 ± 1.0	39.8 ± 1.9	2.9 ± 0.1	12.0 ± 3.3	1.5 ± 0.7	0.4 ± 0.4
30	10.0	36.1 ± 0.3	38.3 ± 2.2	4.9 ± 1.0	10.6 ± 0.1	1.9 ± 0.8	2.0 ± 0.9
30	5.0	41.8 ± 2.5	39.7 ± 0.9	9.9 ± 4.8	15.8 ± 3.1	1.6 ± 0.4	1.8 ± 0.6
30	3.3	40.2 ± 1.7	39.8 ± 3.7	5.0 ± 0.5	15.8 ± 4.0	1.6 ± 0.8	0.0 ± 0.0

The highest yield from biomass, above 16%, was obtained when converting a medium containing 3.3% biomass and 1% *v*/*v* H_2SO_4 during 20 min. For 2% *v*/*v* H_2SO_4, 3% biomass concentration and 10 min exposure time, the yield exceeded 15% (Figure 5E,F). Despite the fact that the content of cellulose in cherry shavings was higher by ca. 2%, the efficiency of the conversion of sweet cherry chips to LA in the presence of phosphoric and sulfuric acid as catalysts was lower than that obtained for pine chips (Table 1, Figure 5).

As in experiments with pine chips, the LA yield from the cherry wood biomass using nitric acid was low (regardless of the catalyst concentration, the maximum yield was about 1.1%; Figure 5A,B). The maximum LA concentration obtained from this raw material with nitric acid catalysis was 0.17 ± 0.01 g/L, and the LA production was 6.8 ± 0.4 mg/g DW (Table 3). The use of phosphoric acid was slightly more efficient, as the maximum biomass yield was 6% (acid concentration 2% v/v, exposure time 30 min, biomass concentration 3.3%; Figure 5D). Adequate to low yield, LA concentrations were also low (1.47 ± 0.29 g/L and 58.7 ± 11.4 mg/g DW) and the yield in relation to the theoretical one was only 15.8 ± 3.1% (Tables 3 and 4). When cherry chips were used as a raw material for the production of LA with sulfuric acid as the catalyst, similar tendency to that of softwood was observed.

The concentration of biomass had the greatest impact on the amount of levulinic acid produced and the efficiency of the production process. The lowest concentration tested (3.3%) was conducive for the efficient conversion of carbohydrates to LA even at the shortest exposure time (Tables 3 and 4, Figure 5E,F). If the catalyst was phosphoric acid, the exposure time and the concentration of the catalyst and biomass in the solution had the greatest impact on the efficiency of the conversion process (Tables 3 and 4, Figure 5C,D).

In the current literature on LA production from wood waste, there is no available data on the efficiency of the microwave-assisted treatment in combination with the use of mineral acids as catalysts. The usefulness of microwave radiation in the production of furan compounds and levulinic acid from lignocellulosic biomass was confirmed by Zhang and Zhao (2010) and Ren et al., (2013), but these authors used ionic liquids as a catalyst [45,46]. Zhang and Zhao (2010) achieved a HMF yield of 52% using pine wood as the raw material and $CrCl_3 \times 6H_2O$ catalysis [45]. Ren et al. (2013) in their model study on the production of levulinic acid from microcrystalline cellulose using $[C_3SO_3Hmim]HSO_4$ as a catalyst reported a yield of 44.5% [46]. Maiti et al. (2018) used acid catalysis with HCl and microwave radiation in the production of levulinic acid from agro-industrial wastes. They reported, as in the present study, a high efficiency of conversion of carbohydrates to levulinic acid with the use of microwave radiation [47]. The analysis of the available literature data as well as the results of the present study clearly indicate that the use of waste raw materials not tested so far must be combined with a careful optimization of process parameters. Liang et al. (2018) used sulfuric acid for the production of levulinic acid from corncobs. They showed a small effect of prolonging the reaction time on the increase in LA concentration. In turn, the efficiency of LA production depended on the cellulose content in the reaction medium, which was also confirmed by the present study [48].

The concept of levulinic acid production using the one-stage microwave conversion method, which was the subject of this paper, is an alternative to the method of LA production in a two-stage system with biomass pretreatment as the first stage [23]. The two-stage method ensures a high degree of bioconversion of waste, e.g., from *Quercus mongolica*, however, compared to the one-stage method with the use of microwaves, it is more energy-consuming due to the need for pretreatment at an elevated temperature. Similarly to this work, Jeong et al. (2017) reported that the use of a higher concentration of sulfuric acid (2% *v*/*v*) in the two-step method improved the efficiency of carbohydrate conversion to LA, despite the differences in technology between one- and two-step processes [23].

3. Materials and Methods

3.1. Raw Material

In the present study, pine chips as softwood biomass and sweet cherry chips as hardwood biomass were used, and ground with a beater mill into sizes below 2 mm; their characteristics are presented in Table 1. Both types of wood waste had a similar dry matter content, ca. 93.5%. Softwood raw material was characterized by a lower content of cellulose and hemicellulose compared to cherry chips, ca. 2% and 7%, respectively. In addition, pine shavings contained about 6% more lignin compared to hardwood biomass (Table 5). Other authors confirm higher cellulose content (above 50%) in hardwood biomass and higher lignin content, exceeding 25%, in softwood biomass [15].

Table 5. Characteristics of wood waste used in this research.

Wood Waste	Dry weight Content (%)	Cellulose Content (% DW)	Hemicellulose Content (% DW)	Lignin Content (% DW)
Pine chips	93.07a ± 0.12	49.93a ± 0.87	14.33a ± 2.49	26.68a ± 0.27
Sweet cherry chips	93.97a ± 0.09	52.07a ± 0.76	21.10b ± 0.62	12.44b ± 0.23

The mean values given in columns with different letter index are significantly different ($\alpha < 0.05$).

3.2. Chemical Reagents

All chemical reagents used for the production of levulinic acid, i.e., nitric, phosphoric and sulfuric acid, were analysis-pur (a.p.) and were supplied by Carl Roth GmbH + Co. KG (Karlsruhe). For the chromatographic analysis, sulfuric acid (99.999% *v*/*v*) and levulinic acid with high performance liquid chromatography (HPLC) purity were used. The reagents and standards used in the HPLC analysis were provided by Sigma-Aldrich.

3.3. Production of Levulinic Acid Using Microwave Radiation

Levulinic acid was produced using the Microwave Digestion System Mars 5 (CEM Corporation), which enabled the process to be carried out under controlled pressure conditions. For the conversion process, 1.07 g (1 g DW) of wood chips was placed in a Teflon container HP-500 plus. Then, 10, 20 or 30 mL of a chosen acid solution (H_2SO_4, HCl and HNO_3) at a given concentration (1% and 2%) was added, which corresponded to a biomass concentration of 10.0%, 5.0% and 3.3%, respectively. Levulinic acid was produced by using a microwave generator with the following operating conditions of 1200 W, pressures 54, 114 and 225 PSI, for 10, 20 or 30 min. After the reaction, the solutions were cooled down to ca. 20 °C, neutralized to pH 5.0 with 30% *w*/*v* NaOH and the volume was adjusted to 40 mL with deionized water. A sample was taken for HPLC analysis to determine the concentration of levulinic acid.

3.4. Analytical Methods

3.4.1. Analysis of Wood Waste Composition

Cellulose, hemicellulose and lignin content were determined using two-stage acid hydrolysis according to the NREL protocol [49]. The dry weight (DW) of the raw material was determined using a weighting dryer (Radwag WPS-30S) at 130 °C and 20 s sampling time.

3.4.2. HPLC Analysis

Concentration of levulinic acid was determined by HPLC. All samples analyzed by HPLC were diluted five times with 5 mM H_2SO_4 (mobile phase used for chromatographic analysis) and then filtered through a membrane filter (PES) with an aperture of 0.45 µm. Chromatographic separation was performed with the Agilent Technologies® model 1260 apparatus equipped with a refractometric detector (RID). In the analysis, a Hi-Plex H chromatography column (Agilent Technologies®, Santa Clara, CA, USA) with a guard column was used under isocratic conditions. The mobile phase was 5 mM H_2SO_4 with a flow rate of 0.6 mL/min and temperature of 60 °C. The concentration of levulinic acid was determined using the external standard method (ESTD). The separation of the analyzed compounds was carried out in accordance with the instructions of the column manufacturer [50].

3.5. Computational Methods

LA yield from pine chips cellulose was calculated as follows:

$$\text{LA yield from cellulose } (\%) = \frac{C_{LA}}{C_{Cel}} \times 100\%, \quad (1)$$

where C_{LA} is the levulinic acid concentration in the solution (g/L) and C_{Cel} is the cellulose concentration (g/L).

LA yield from wood chips was calculated according to the following formula:

$$\text{LA yield from biomass } (\%) = \frac{C_{LA}}{C_B} \times 100\%, \quad (2)$$

where C_{LA} is the levulinic acid concentration in the solution (g/L) and C_B is the biomass concentration (g/L).

The ratio of LA yield to the theoretical yield was defined as:

$$\text{Yield of levulinic acid production (\% of theoretical)} = \frac{A_{LA} \times 100\%}{A_{\max LA}}, \quad (3)$$

where A_{LA} is the amount of levulinic acid obtained (mg/g DW of wood waste), $A_{\max LA}$ is the maximum amount of levulinic acid obtainable (mg/g DW of wood waste) assuming that the maximum conversion of hexose to levulinic acid is 64.4% and the amount of hexoses from 1 g of cellulose is 1.111 g [15,51].

3.6. Statistics

All laboratory analyses were performed in triplicate. Statistical analysis was carried out using the Statistica software ver. 12 (analysis of variance, determination of SD). An analysis of variance (ANOVA) test and HSD (honest significant difference) Tukey's test were applied at a significance level of $\alpha < 0.05$.

4. Conclusions

The presented concept of a one-stage conversion of pine chips (softwood) and sweet cherry chips (hardwood) to levulinic acid using microwave radiation combined with sulfuric acid catalysis may be an effective way to utilize wood industry waste by transforming it into a product of high added-value. This method provides a high degree of conversion of carbohydrates contained in softwood and hardwood biomass to LA. The highest yield of LA from pine chips (about 50%) was obtained at a pressure of 225 PSI, biomass concentration of 3.3%, using 2% *v/v* H_2SO_4 during an exposure time of 20 min.

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