

Hydrolytic Conversion of Sawdust as a Step of Complex Wood Waste Processing

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Biomass can be considered as a potential resource for the production of renewable fuels. Lignocellulose biomass is a widely available, renewable, biodegradable, and biocompatible resource that can potentially reduce the dependence of modern society on fossil resources. It is a potential feedstock for the production of heat, electricity, fuel, chemicals, and other bioderived products. Considerable attention of researchers is directed to the conversion of biomass into bioenergy through chemical, biochemical, or thermochemical processes. Hydrolysis is considered to be one of the important steps to convert biomass into valuable chemicals. During hydrolysis, liquid rich in sugars with a certain amount of dissolved lignin, usually called hydrolysate, is formed. In this paper, the influence of the catalyst type, temperature, catalyst concentration, and solvent type on the conversion and composition of hydrolysate was studied. The highest yield of hydrolysis products (hexoses and pentoses) reached up to 80 wt. % at a temperature of 220 °C in water medium in the presence of 1.5 wt. % of sulfuric acid.

1. Introduction

Harvesting is one of the main human activities related to the use of natural resources. However, harvesting has a number of negative consequences associated with waste generation. Logging waste is wood residues that are formed during the process of felling trees, processing wood, and removing branches and bark. These wastes can occupy significant areas and negatively affect the environment (Gryazkin et al., 2017). Current trends require the involvement of all possible resources in the production cycle. Therefore, the recycling of harvesting waste is an urgent area of research (Medvedev et al., 2020).

One of the promising methods of processing logging waste is hydrolysis, which allows valuable chemicals and energy to be obtained from wood residues (Pandey, 2022). Hydrolysis of wood is the process of decomposition of cellulose and hemicellulose – the main wood components – with water in the presence of the catalysts. As a result of hydrolysis, sugars, which can then be used to produce ethanol, biogas, or other products, are formed (Dussan et al., 2014).

One of the main advantages of wood hydrolysis is that it allows valuable products to be produced from logging waste that would otherwise be discarded or burned. In addition, hydrolysis can be more environmentally friendly than other methods of wood processing, as it does not require the use of large amounts of chemicals and does not generate harmful emissions (Marcolongo et al., 2021). In general, the hydrolysis of logging waste is a promising area that can help reduce the negative impact of logging on the environment and ensure the production of valuable products from waste.

Chemicals such as acids, alkalis, organic solvents, and ionic liquids are widely used to hydrolyze lignocellulose biomass. During hydrolysis, liquid rich in sugars with a certain amount of dissolved lignin, usually called hydrolysate, is formed (Liu, 2015). The hydrolysate is rich in pentose and is considered unsuitable for the production of bioethanol due to the need to use genetically modified microorganisms (Kaparaju et al., 2009). Also, an unfavorable factor is the high sensitivity of fermenting microorganisms to inhibitors, such as furfural and hydroxymethylfurfural, present in the hydrolysate (Torry-Smith et al., 2003).

During acid hydrolysis, the type of acid, concentration of reagents, temperature, solid-liquid ratio, and reaction time significantly affect the degradation of lignin. The disadvantage of acid hydrolysis is that it is ineffective at removing lignin. It also produces inhibitors such as formic acid, acetic acid, and furfural, which do not contribute to subsequent processing (Rodrigues Gurgel da Silva et al., 2019). Alkaline hydrolysis is the most commonly used method of removing lignin and hemicellulose from lignocellulose materials (Agbor et al., 2011). In addition, although alkaline treatment can significantly improve the enzymatic characteristics of lignocellulose biomass. Hydrolysis in organic solvents removes lignin and hemicellulose. After the separation of solid and liquid, a solid fraction rich in high-purity dextran remains (Choi et al., 2019). Ionic liquids as a "green" solvent have the advantages of low vapor pressure, high-temperature resistance, chemical stability, non-flammability, and chemical controllability (Abushammala and Mao, 2020).

The use of enzymes is one of the newest strategies in the decomposition strategy of lignocellulose biomass (Tocco et al., 2021). Studies on enzymes decomposing lignin are focused on enzyme systems containing lignin peroxidase, manganese-dependent peroxidase, and laccase (Dong et al., 2014). In addition, some enzymes are indirectly involved in the degradation of lignin, such as aryl alcohol oxidase, glyoxal oxidase, and glucose oxidase (Janusz et al., 2017). Under the catalytic action of these enzymes, lignin undergoes a number of chemical changes: side chain oxidation, aliphatic side chain, aromatic ring break, demethoxylation, decarboxylation and chain break, and finally, the lignin macromolecule is cleaved into monomers (Bugg et al., 2011).

Despite the numerous studies, acid-catalyzed hydrolysis remains the main way to produce monosaccharides and lignin from the lignocellulosic biomass. The acid concentration and process conditions strongly affect the effectiveness of the hydrolysis. To improve the economic feasibility, the systematic optimization of biomass hydrolysis is a critical issue. The conversion of the feedstock and the yield of hydrolysis products strongly depend on the catalyst, process temperature, particle size of the feedstock, nature and composition of the feedstock, biomass-catalyst and biomass-water ratio, as well as the composition of the solvent. This work is focused on several parameters such as catalyst type, catalyst concentration, process temperature, and solvent composition. For the first time, the hydrolysis of wood bark as one of the main products in forestry was studied.

2. Materials and Methods

2.1 Waste composition

The wood waste (pine and birch sawdust and bark) was purchased from the harvesting company of Tver region, Russia. The feedstock was dried at 90 ± 5 °C for 12 h and milled until the mesh of 0.25 mm. The wood waste was analyzed in terms of elemental composition, fractional composition, humidity, and ash content. The humidity and ash content were estimated according to the standard procedure. The elemental composition was studied using CHNS-O EMA502 analyzer (VELP Scientifica, Italy). The content of extractives was estimated using the Soxhlet extraction apparatus according to Ostroukhova et al. (2018). Analysis of cellulose, hemicelluloses, and lignin content was carried out according to RU2534067 and EA005492 Patents.

The composition and properties of the wood waste used in this work are presented in Table 1.

Table 1: Composition of wood waste

Parameter	Sawdust		Bark	
	pinewood	birch	pinewood	birch
Humidity, wt. %	7.0	5.2	2.2	2.3
Ash content, wt. %	3.6	1.4	2.7	3.6
Cellulose, wt. %	53.1	39.5	50.3	42.7
Hemicelluloses, wt. %	7.9	17.9	8.3	19.1
Lignin, wt. %	25.4	31.1	28.1	27.2
Extractives, wt. %	6.3	4.9	8.4	5.1
C, wt. %	48.8	50.2	50.4	50.9
H, wt. %	6.1	6.0	5.9	5.8
N, wt. %	0.1	0.6	0.3	0.7
O, wt. %	44.6	42.2	43.4	42.6

Softwood sawdust is characterized by a higher content of extractives, lignin, and cellulose, as well as carbon and nitrogen, compared with hardwood sawdust. Also, for pine sawdust, there is a lower ash content, unlike birch sawdust.

2.2 Hydrolysis procedure

The hydrolytic processing of the studied wood waste was carried out in a stainless-steel batch reactor PARR – 4307 (Parr Instrument, USA) with a Teflon liner to avoid the corrosion of the equipment. In typical experiment, 0.5 g of dry biomass sample milled to the fraction with the particle size below 0.25 mm, and 15 mL of the solvent containing 1.5 wt. % of catalyst were put into the reactor cell. To prevent oxidation of hydrolysis products, the reactor was purged with nitrogen. Since hydrolysis was carried out under an auto pressure (partial pressure of water vapor), the nitrogen pressure was set to 0.1 MPa. The process was carried out for 2 h at operational conditions. The hydrolysis process was performed using water as a solvent and hydrolysis reagent. Also, the water-alcohol mixtures with an alcohol content of 15, 30, 45, 60 wt. % were studied. The hydrolysis process was carried out in the temperature range of 160-220 °C using alkaline and acid-type catalysts. The influence of temperature, catalyst concentration, and solvent composition was studied. The analysis of the products was carried out by HPLC using the Ultimate chromatograph. The conversion of wood waste was determined gravimetrically by the difference in the mass of the feedstock and the dry residue according to Eq(1).

$$X = \frac{m_f - m_r}{m_f} \cdot 100\% \quad (1)$$

where X – feedstock conversion, %; m_f – a mass of the initial feedstock, g; m_r – a mass of the solid residue, g.

3. Results and Discussion

In this work, acid and base catalysts were used for the hydrolysis of the wood waste. The feedstock was dried in the air and milled to a mesh of 0.25 mm. The influence of the catalyst nature was studied using aqueous solutions of NaOH, KOH, HCl, H₂SO₄, HNO₃, CH₃COOH, and HCOOH with a concentration of 1.5 wt. %. The hydrolysis temperature was chosen to be 200 °C. The hydrolysis was carried out for 2 h.

When the alkali was used as a catalyst, the feedstock conversion was lower than that obtained in the acid presence (See Table 2, Lines 1 and 2). It is known that the catalysis by alkalis is limited by the oxidative processes that take place during the polysaccharide hydrolysis (Lv et al., 2024). In the hydrolysis of sawdust in the presence of alkalis, about 50 and 30 wt. % of hemicelluloses were converted for pine and birch sawdust. The cellulose conversion was found to be about 20 wt. % in both cases. Similar results were obtained during the hydrolysis of pine and birch bark; however, the conversion of polysaccharides for pine bark was slightly higher (See Table 3, Lines 1 and 2). The conversion for birch bark was slightly lower than that for the birch sawdust. The partial oxidation of the hydrolysis products resulting in the production of hydroxylic acids was observed for all feedstock studied when the alkali was used as a catalyst. Slight depolymerization of lignin was noticed in this case as the phenolic compounds were observed in the hydrolysate.

Table 2: Catalyst influence on the hydrolysis of the sawdust

Line	Catalyst	Conversion, wt. %		Hexose yield, wt. %		Pentose yield, wt. %	
		Pine sawdust	Birch sawdust	Pine sawdust	Birch sawdust	Pine sawdust	Birch sawdust
1	NaOH	16.4	19.2	9.6	8.7	4.2	8.5
2	KOH	15.7	18.7	9.8	8.9	3.8	7.7
3	HCl	32.5	46.4	25.2	25.8	7.3	13.1
4	H ₂ SO ₄	36.3	50.8	28.5	27.7	7.8	17.7
5	HNO ₃	39.5	53.6	27.6	26.1	6.2	15.4
6	CH ₃ COOH	36.1	50.5	28.4	27.4	7.7	17.6
7	HCOOH	38.4	52.9	29.4	27.1	7.1	14.5
8	H ₃ [PMO ₁₂ O ₄₀]	40.2	54.2	32.4	30.8	7.8	17.1
9	H ₇ [PW ₁₂ O ₄₂]	40.8	54.6	33.0	31.4	7.8	17.5
10	SiO ₂	10.6	13.6	8.4	8.9	2.2	4.7
11	Al ₂ O ₃	10.8	14.1	8.5	9.1	2.3	5.0
12	H-ZSM-5	14.3	17.5	10.4	10.3	3.9	7.2

The hydrolysis of the wood waste in the presence of mineral acids and acetic acid showed similar values of the conversion and monosaccharides yield (See Table 2, Table 3, Lines 3-7). The 2-5 wt. % higher conversion of the feedstock was observed when nitric and formic acids were used as catalysts. Meanwhile, nitric acid led to a partial oxidation of the monosaccharides with the formation of ca. 5 wt. % of hydroxylic acids. In the presence of formic acid, partial hydrogenolysis (less than 0.5 wt. %) was observed as the catalyst used has hydrogen-donor properties.

Table 3: Catalyst influence on the hydrolysis of the bark

Line	Catalyst	Conversion, wt. %		Hexose yield, wt. %		Pentose yield, wt. %	
		Pine bark	Birch bark	Pine bark	Birch bark	Pine bark	Birch bark
1	NaOH	19.9	17.1	11.2	7.4	4.7	7.4
2	KOH	18.8	16.8	10.1	7.2	4.2	6.1
3	HCl	34.1	40.1	27.4	24.4	7.4	13.7
4	H ₂ SO ₄	38.3	47.4	30.5	26.6	8.1	18.9
5	HNO ₃	41.4	50.1	28.1	25.7	8.2	10.4
6	CH ₃ COOH	38.0	46.9	30.2	26.2	7.5	14.3
7	HCOOH	40.2	48.2	29.8	25.5	7.4	10.2
8	H ₃ [PMo ₁₂ O ₄₀]	43.8	52.8	34.4	28.6	7.6	14.8
9	H ₇ [PW ₁₂ O ₄₂]	44.4	53.1	34.8	29.3	7.7	14.8
10	SiO ₂	13.5	11.2	10.4	7.5	3.1	2.4
11	Al ₂ O ₃	14.3	13.0	10.9	8.1	3.5	2.9
12	H-ZSM-5	15.2	15.4	11.3	8.7	4.1	3.2

Besides the mineral acids, the catalytic action of heteropolyacids on the hydrolysis of wood waste was studied (See Table 2, Table 3, Lines 8, 9). Phosphor-molybdic and phosphor-tungstic heteropolyacids were found to be able to increase the conversion of the feedstock by ca. 4-5 wt. % in comparison with sulfuric acid due to the higher acid strength. An increase in the conversion was noted to be due to the higher cellulose depolymerization, while the conversion of hemicelluloses was the same as that observed for sulfuric acid. Despite the higher feedstock conversion, the use of heteropolyacids is inappropriate because of the higher price of the catalyst. Heterogeneous materials showing the presence of strong Brønsted and Lewis acid sites were also used in the hydrolysis of wood waste (See Table 2, Table 3, Lines 10-12). In the heterogeneous process, the conversion of the feedstock was found to be 3-4 times lower than that for the homogeneous catalysts.

As sulfuric acid remains to be the most effective catalyst for the hydrolysis of wood waste, it was used for further studies to choose the optimal hydrolysis conditions. The influence of temperature, acid concentration, and solvent was investigated. The temperature effect was studied using 1.5 wt. % aqueous solution of sulfuric acid in a temperature range of 160-220 °C. The hydrolysis duration was chosen to be 2 h. An increase in temperature led to an increase in the conversion for all feedstock studied (Figure 1). The difference in the conversion was proposed to be caused by the difference in the polysaccharide content in the wood waste. Based on the data presented in Table 4, the conversion of hemicelluloses reached up to 99 wt. % and the conversion of cellulose was found to be ca. 95 wt. % at 220 °C.

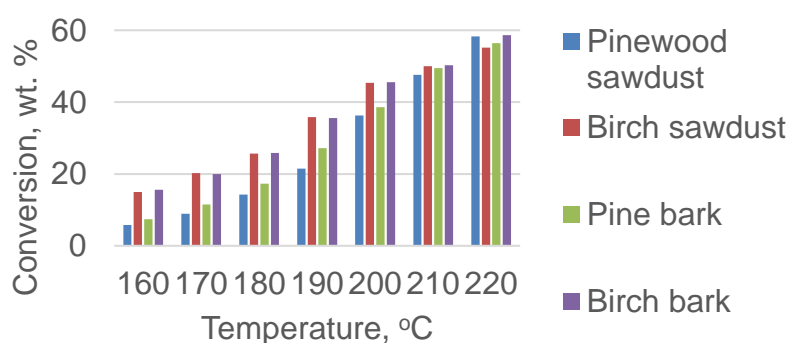


Figure 1: Temperature influence on the conversion of wood waste in acid hydrolysis

The study of the influence of the acid concentration on the conversion of wood waste was carried out in an aqueous medium at 220 °C for 2 h. The sulfuric acid concentration was varied from 0.5 to 5.0 wt. %. An increase in the concentration of the sulfuric acid up to 5 wt. % led to an increase in the conversion of the feedstock (Figure 2). A significant increase in the yield of monosaccharides was observed when the acid concentration was raised to 1.5 wt. %. The further increase in the concentration of acid catalyst led to the partial carbonization of the feedstock and was proposed to be inappropriate (see Table 5).

Table 4: Temperature influence on the yield of monosaccharides in the hydrolysis of sawdust and bark

Temperature, °C	Hexose yield, wt. %				Pentose yield, wt. %			
	Pine sawdust	Birch sawdust	Pine bark	Birch bark	Pine sawdust	Birch sawdust	Pine bark	Birch bark
160	1.6	1.2	2.4	1.2	4.2	13.8	5.0	14.4
170	2.8	4.6	5.1	3.9	6.1	15.6	6.4	16.1
180	6.5	8.1	9.2	7.5	7.8	17.6	8.1	18.3
190	13.7	18.1	19.1	16.7	7.8	17.7	8.1	18.9
200	28.5	27.7	30.5	26.6	7.8	17.7	8.1	18.9
210	39.8	32.3	41.4	31.4	7.8	17.7	8.1	18.9
220	50.5	37.5	48.3	39.7	7.8	17.7	8.1	18.9

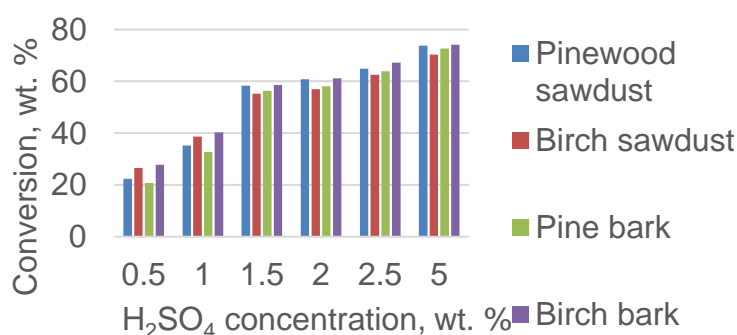


Figure 2: Sulfuric acid concentration influence on the conversion of wood waste in acid hydrolysis

Table 5: Sulfuric acid concentration influence on the yield of monosaccharides in the hydrolysis of sawdust and bark

H ₂ SO ₄ concentration, wt. %	Hexose yield, wt. %				Pentose yield, wt. %			
	Pine sawdust	Birch sawdust	Pine bark	Birch bark	Pine sawdust	Birch sawdust	Pine bark	Birch bark
0.5	15.6	11.3	13.8	11.7	6.7	15.3	7.0	16.1
1.0	27.4	21.0	24.6	21.4	7.8	17.7	8.1	18.9
1.5	50.5	37.5	48.3	39.7	7.8	17.7	8.1	18.9
2.0	52.9	39.1	49.8	42.1	7.9	17.9	8.3	19.1
2.5	51.6	38.5	48.4	39.5	7.6	17.4	7.9	18.3
5.0	40.3	29.9	37.1	30.4	5.2	11.4	4.9	12.3

The further conversion of the hydrolysis products can be carried out by the fermentation, hydrogenation/hydrogenolysis or oxidation of hydrolysate, and liquefaction of the solid residue. In the chemical conversion of hydrolysis products, the solvent plays an important role. Thus, the effect of solvent composition on the hydrolysis was studied. In the experiments, a water-propanol-2 mixture with alcohol concentrations of 15, 30, 45, and 60 wt. % was used. The hydrolysis was carried out at 220 °C using 1.5 wt. % concentration of sulfuric acid. When the water-alcohol mixture was used, a partial hydrolysis of cellulose and hemicelluloses was observed. The conversion of cellulose and hemicelluloses was varied from 90 to 46 wt. % and from 93 to 54 wt. % with an increase in propanol-2 concentration. The delignification process was found to be prevalent. It is known that the treatment of lignocellulose with organic solvents is one of the methods to produce organosoluble lignin. Thus, the effect of alcohol concentration was estimated based on the lignin yield. An increase in the concentration of propanol-2 in the solvent mixture. An increase in the alcohol concentration from 15 to 45 wt. % led to an increase in the lignin yield from 7-9 to 30-34 wt. % (from the total lignin content) for birch waste, and from 5-6 to 27-29 wt. % for pine waste. A significant increase in the lignin yield (up to 52-56 and 49-53 wt. % for birch and pine waste) was observed when the propanol-2 concentration raised to 60 wt. %.

4. Conclusions

Logging waste is a cheap feedstock to obtain valuable chemicals and fuels. Among different methods, hydrolysis is one of the prospective to obtain monosaccharides and lignin. Hydrolysis can also be used for the preliminary

treatment of the feedstock before the liquefaction or pyrolysis. In this work, the effect of the catalyst nature, process conditions, and solvent composition on the hydrolysis of harvesting waste (sawdust and bark) was carried out. Diluted sulfuric acid was found to be the most effective catalyst for the hydrolysis of the feedstock studied as it provides both high conversion and monosaccharide yield. Temperature of 220 °C, acid concentration of 1.5 wt. % were found to be the optimal hydrolysis conditions allowing 99 wt. % and 95 wt. % of hemicelluloses and cellulose to be converted into monosaccharides. The use of the water-alcohol solvent mixture was shown to provide partial (ca. 50 wt. %) hydrolysis of the polysaccharides and lignin extraction (up to 55 wt. %) from the lignocellulosic biomass.

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