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Conversion of Carbohydrates in Lignocellulosic Biomass after Chemical Pretreatment

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Abstract: The aim of the study was to determine the quantitative and qualitative changes taking place in biomass components actively participating in methane fermentation, i.e., in carbohydrates, as a result of chemical pretreatment. Analyses were conducted on agricultural waste (corn stover, also called corn straw, and corncobs) as materials most commonly used in methane fermentation, as well as poplar wood, a material relatively rarely used in biogas production. Pretreatment with the aim of increasing efficiency of methane fermentation was carried out with the use of acid and alkaline solutions of different concentrations. The effect of pretreatment on carbohydrates was analyzed based on the quantitative and qualitative changes in this component. Due to the structural heterogeneity of carbohydrates, their varied reactivity and fermentability were determined in terms of holocellulose, cellulose, and pentosans. The chemical structure of cellulose was also analyzed. It is shown in this study that chemical pretreatment causes transformations of carbohydrate components, which differ quantitatively and qualitatively in the compared raw materials. It was found that the alkaline treatment caused smaller changes in the percentage shares of the carbohydrate biomass components as compared to the acid treatment. Moreover, it was observed that the compared materials differ in terms of quantitative changes in their chemical composition depending on the composition of the raw material prior to pretreatment. In the case of corn waste subjected to the action of 1 and 3% NaOH, the share of pentosans in the biomass increased. It was established that this is a change with a positive effect on fermentation efficiency. The action of acids and alkalis on the biomass led to similar structural changes in cellulose, which are adverse for the fermentation process.

Keywords: biogas production; carbohydrate yield; cellulose; holocellulose; pentosans

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1. Introduction

Carbon-neutral fuels from lignocellulosic biomass can play a significant role in mitigating challenges associated with climate change and meeting the planet's energy and material demands [1–3]. However, the cell wall content of compounds resistant to the action of bacteria hinders the energy use of biomass, particularly in fermentation processes taking place under anaerobic conditions [4,5]. Chemical changes of cellulose and lignin during methane fermentation based on miscanthus and sorghum were described by Waliszewska et al. [6] and Waliszewska et al. [7], respectively. Knowledge regarding the methods as well as the advantages and disadvantages of the pretreatment of biomass in preparation for fermentation is also extensive [8]. However, the literature presents very limited information concerning the analysis of chemical changes taking place during pretreatment, which are significant when predicting fermentation efficiency.

Cellulose, a major biomass cell wall component, is a polysaccharide composed of linear chains ranging from several hundred to several thousand repeating D-glucose units bound together covalently by (1–4) β glycosidic linkages. The crystalline structure is formed by transverse hydrogen bonds found between the chains [9]. Numerous ether and ester linkages, as well as covalent bonds, such as glycosidic or C-C bonds found between lignin and the lignin–carbohydrate complex (LCC), hinder the enzymatic hydrolysis of biomass components and their fermentation [6]. For this reason, a commonly recommended solution is to apply pretreatment prior to biomass fermentation [10–13]. Many pretreatment processes have been developed to overcome biomass recalcitrance and to promote the effective enzymatic conversion of carbohydrate polymers into monomeric sugars [5,13–16]. The authors of the abovementioned studies described pretreatment efficiency; however, limited information was presented regarding the chemical changes of carbohydrates actively involved in methane fermentation.

Lignocellulosic wood materials can be used as substrates to produce biogas because they are abundant, cheap, and renewable. An example of such a material may be poplar, which is selected to produce energy as the most promising species owing to its rapid growth even in poor quality soils [15]. In general, poplar has a high cellulose content (42–49%), low amounts of ash and extractives, and moderate lignin (21–29%) and hemicellulose (16–23%) levels [15,17]. These properties make it a desirable feedstock for the production of biogas and other biomass-based materials [15,18]. However, it is a wood material characterized by high contents of rigid lignin and crystalline cellulose. For this reason, pretreatment, which promotes the release of carbohydrates, should be considered.

Biomass fermentation is hindered by the crystallinity of cellulose, its degree of polymerization, the surface availability, and the presence of lignin [19]. The literature shows that a beneficial effect is subjecting the raw material prior to conversion to pre-treatment [19], which changes the physical and chemical structure of the lignocellulosic biomass [20]. In the methane fermentation process, the most desirable product of the decomposition of lignocellulosic structures is glucose [21]. There are many types of pretreatment of lignocellulosic raw materials, including mechanical treatment, physicochemical processes, or biological treatment.

Pretreatment is also carried out with chemicals such as bases, acids, organic solvents, and ionic liquids. Alkaline treatment causes the biomass to swell, resulting in a reduction in the degree of polymerization and the crystallinity of the cellulose. It breaks the structure of the lignin and the bond between the lignin and carbohydrates in the biomass, making them more available [22–24]. Concentrated acids provide rapid polysaccharide conversion, with little degradation of sugars [25,26]. However, they have to be recovered for powerful treatment to be economically viable [27]. Diluted acids with a concentration below 4% under elevated temperature conditions hydrolyze hemicelluloses to monomers [23,28,29]. The disadvantage of the action of diluted acids under elevated temperature conditions may be the formation of fermentation inhibitors [24].

Within this study, changes in carbohydrates caused by acid and alkaline pretreatment were investigated in the context of improving the attractiveness of biomass as a substrate in the production of biofuels. As mentioned above, the literature concerning the chemical pretreatment of lignocellulose biomass is extensive. In this study, knowledge regarding changes in carbohydrates triggered by this process has been supplemented. The investigated carbohydrates included both those that are less abundant, but actively participate in fermentation, i.e., low-polymer hemicelluloses, and high-polymer cellulose dominant in the cell wall structure and only partly fermentable. In this study, we investigated which of them disintegrate during pretreatment and are removed from the biomass in the form of simple sugars, thus not participating in the fermentation process. It was also studied whether, owing to pretreatment, cellulose loses its crystalline structure and the bond energy decreases, thus making it more predisposed to fermentation, or whether it loses the amorphous fraction, and, as a result, its fermentability may be reduced.

2. Materials and Methods

2.1. Materials

The analyses were conducted on corn waste from the feed production process in the form of corncobs and corn stover. *Populus* L. harvested from short rotation was used as the wood material.

The biomass subjected to chemical treatment was conditioned under laboratory conditions until 7–9% relative moisture content was achieved. Then, it was ground in a grain mill to a 2.0 mm fraction. The prepared material was subjected to chemical treatment with acid and alkaline solutions at different concentrations. Samples of 50 g raw material were weighed to flasks of 1000 cm^3 and supplemented with 500 cm^3 sulfuric acid solution at a concentration of 3 and 7% and sodium hydroxide solution at a concentration of 1 and 3%.Then, they were heated on heating plates at a temperature of 100 °C for 3 h. The prepared material was filtered and rinsed with water until pH = 7. The material, after hydrolysis and rinsing, was conditioned until approx. 10% relative moisture content was achieved, and then ground in a grain mill to the analytical fraction of 0.4–1.0 mm. The a material was used in the quantitative and qualitative analyses.

2.2. Methods

2.2.1. Quantity Identification

The content of holocellulose was tested by the chlorine method according to Browning [30]. The Seifert method, with a mixture of acetylacetone, 1,4-dioxane, and hydrochloric acid, was used to determine the cellulose content [30]. Pentosans were determined according to the procedure presented in the standard: TAPPI T 223 cm-01 [31].

Simple sugars, i.e., glucose and arabinose, were analyzed by liquid chromatography according to ASTM (2015). The determinations were performed using the Elit LaChrom system (VWR-Hitachi: Avantor, VWR International, LLC, Radnor, PA, USA) consisting of an autosampler (model L-2200), pump (model L-2130), and a refractive index detector (model L-2490). The analyses were carried out isocratically. A Rezex ROA 300 × 7.8 mm column (Phenomenex) was used. The mobile phase was 0.005 M sulfuric acid. The flow rate was 0.6 mL/min, and the temperature was 40 °C. Standards were used to identify the peaks obtained on the chromatograms. The concentration of the sample was determined from the peak area. This was carried out by integrating a computer (EzChrom Elite software) running in an external standard mode. The determination of the sugar content was repeated three times for each batch of the sample (from each level), and the means and standard deviations were calculated.

2.2.2. Quality Identification

Fourier Transform Infrared Spectroscopy (FTIR)

An Alfa FTIR spectrometer manufactured by Bruker Optics GmbH was used to obtain the infrared spectra. A total of 2 mg of the cellulose powder samples was dispersed in the KBr matrix in an amount of 200 mg and then compressed. The sample was taken with 32 scans ranging from 4000 to 400 cm^{-1} using a resolution of 4 cm^{-1}. The mean value was determined from three different measurements of each cellulose sample.

The energy of hydrogen bonds (E_H) for several OH stretching bands was calculated using Equation (1) [32,33]:

$$E_H = \frac{1}{k}\frac{v_0 - v}{v_0} \tag{1}$$

where ν_0 is the standard frequency corresponding to free OH groups (3650 cm^{-1}); ν is the frequency of bonded OH groups; and k is a constant ($1/k = 2.625 \times 10^2$ kJ).

The LOI and A1430/A898 values were calculated according to [34].

X-ray Diffraction

The crystallinity of cellulose was analyzed based on averages of wide-angle X-ray scattering (WAXS) using Cu Ka radiation at 30 kV and 25 mA anode excitation. The X-ray diffraction pattern was recorded for angles in the range of 2Θ = 5°–30° and steps of 0.04°/3 s. Deconvolution of the peaks was performed by the method proposed by Hindeleh and Johnson [35], improved and programmed by Rabiej [36]. After separation of the X-ray diffraction lines, the crystallinity index (C_rI) of the lignocellulosic materials after chemical treatment was calculated by comparing the areas under the crystalline peaks and the amorphous curve.

$$C_rI = \left(\frac{P_K}{P_A + P_K}\right)\cdot 100\% \tag{2}$$

where:

P_A—area of the amorphous fraction,
P_K—total area of maxima originating from the crystalline fraction,
C_rI—the degree of crystallinity of the repetition [%].

2.2.3. Statistical Analysis

Statistical analysis was performed using Dell™ Statistica™ 13.1 software. The obtained results of the percentage of carbohydrate components were subjected to an analysis of variance (ANOVA), and significant differences were determined between the mean values of the control sample and the sample treated with the Tukey HSD test for $\alpha = 0.05$.

3. Results

3.1. Quantity Identification of Holocellulose, Cellulose, and Pentosans

The percentage shares of the carbohydrate components contained in the lignocellulose material before and after the chemical treatment are presented in Table 1. In the control poplar sample, the share of holocellulose was 74.8%, while for corn waste it was 59.6% and 66.4% for corncobs and corn straw, respectively. Kačík et al. [37], in their analyses of the chemical composition in different poplar varieties, recorded a higher holocellulose share compared to the levels presented in this study, i.e., ranging from 80.8 to 84.8%. In turn, Adebayo et al. [38] reported a share of holocellulose at 63.2–69.2%. As a result of the pretreatment using sulfuric acid, the percentage share of holocellulose decreased in the case of poplar wood, while it increased in corn waste. The obtained differences were statistically significant. A similar trend for the changes was recorded in the case of pretreatment using sodium hydroxide, showing a reduction in the case of wood and an increase for corn waste, with the increase being even greater than for acid treatment. The greatest amounts of holocellulose, amounting to 96.8%, were recorded for corncobs subjected to preliminary hydrolysis with 3% NaOH. The observed increase in the share of holocellulose in corn waste is probably connected to the losses of the other components of this biomass, e.g., low-molecular-weight extractives or lignin. Another cause for the increased share of holocellulose in corn waste may be connected to the formation of the so-called pseudolignin, which is a product containing both carbohydrates and lignin and which is assayed as holocellulose, or rather hololignin, formed as a result of chemical changes in the biomass [39,40].

The reported percentage share of cellulose in the control material was 40.1% for poplar wood and slightly less, i.e., 31.2% and 38.3%, for corn waste. According to Kačík et al. [37], the share of cellulose in poplar varieties ranged from 42.2 to 47.5%. Similar values o 35 and 42% for corn stover and poplar wood, respectively, were also reported by Baral and Shah [41]. Analyses of the chemical composition of corncobs were also conducted by Kanengoni et al. [42], who obtained higher shares of cellulose, within the range of 45–55%. In the described experiment following chemical treatment, in all the tested raw materials a significant increase was found in the share of cellulose, with greater changes observed for corn waste compared to poplar wood. Moreover, in both poplar wood and corn waste, greater changes in the share of cellulose were caused by acid solutions rather than alkaline solutions. Studies on the changes in the share of cellulose in poplar wood following alkaline treatment were conducted by Yuan et al. [43]. The authors observed a similar trend for changes in the share of cellulose: from 41.9% for the control sample to 51.3% for hydrolysis residue. The authors explained the increase in the share of cellulose by greater degradation of hemicellulose during alkaline treatment. Moreover, swelling of the cellulose caused by alkaline solutions contributes to the hydrolysis of ß and gamma cellulose.

Table 1. Percentage shares of carbohydrate compounds in *Populus* L. and corn waste before and after pretreatment.

Carbohydrate	**Pretreatment**	***Populus* L.**		**Corn Waste**			
				Corncobs		**Corn Straw**	
Holocellulose	Control	$74.8^{a} \pm 0.1$	Δ	$59.6^{a} \pm 1.1$	Δ	$66.4^{a} \pm 0.7$	Δ
	1% NaOH	$70.9^{b} \pm 0.26$	−5.3	$89.1^{c} \pm 1.5$	49.6	$89.9^{c} \pm 0.2$	35.5
	3% NaOH	$71.5^{b} \pm 0.2$	−4.4	$96.8^{d} \pm 0.1$	62.4	$94.8^{d} \pm 0.2$	42.8
	3% H_2SO_4	$64.7^{c} \pm 0.3$	−13.6	$79.6^{b} \pm 0.2$	33.5	$75.8^{b} \pm 0.0$	14.2
	7% H_2SO_4	$64.6^{c} \pm 0.3$	−13.6	$79.5^{b} \pm 0.2$	33.3	$75.6^{b} \pm 0.1$	13.8
Cellulose	Control	$40.1^{a} \pm 0.2$	Δ	$31.2^{a} \pm 0.1$	Δ	$38.3^{a} \pm 0.1$	Δ
	1% NaOH	$48.9^{b} \pm 1.2$	22.0	$47.2^{b} \pm 0.4$	51.1	$56.3^{b} \pm 0.1$	47.0
	3% NaOH	$53.2^{c} \pm 0.6$	32.7	$56.5^{c} \pm 0.5$	81.0	$64.7^{c} \pm 0.5$	69.0
	3% H_2SO_4	$52.6^{c} \pm 0.6$	31.1	$64.3^{d} \pm 0.7$	105.9	$64.8^{c} \pm 0.4$	69.1
	7% H_2SO_4	$56.1^{d} \pm 0.4$	39.9	$68.7^{e} \pm 0.5$	120.0	$67.4^{d} \pm 0.0$	75.9
Pentosans	Control	$22.3^{a} \pm 0.5$	Δ	$31.2^{a} \pm 0.6$	Δ	$31.0^{a} \pm 0.9$	Δ
	1% NaOH	$21.8^{a} \pm 0.3$	−2.2	$33.0^{a} \pm 0.6$	5.5	$37.0^{b} \pm 1.7$	19.3
	3% NaOH	$18.4^{b} \pm 0.5$	−17.3	$41.6^{b} \pm 1.5$	35.9	$40.6^{b} \pm 0.1$	30.7
	3% H_2SO_4	$14.4^{c} \pm 0.5$	−35.5	$13.1^{d} \pm 0.6$	−57.9	$12.1^{c} \pm 0.4$	−60.9
	7% H_2SO_4	$10.1^{d} \pm 0.2$	−54.5	$13.7^{c} \pm 0.2$	−56.2	$8.0^{b} \pm 0.3$	−74.3

Identical superscripts (a, b, c, d, e) in a column denote no significant difference ($p < 0.05$) between mean values according to Tukey's HSD test (ANOVA). Δ—the percentage change of the parameter for the sample after pretreatment compared to the parameter for the control sample.

The share of pentosans for the control poplar samples was slightly over 20%, while for corn waste it was higher, at over 30%. The difference in the share of pentosans seems to be crucial for chemical transformations occurring during pretreatment and fermentation. Li et al. [44] reported the share of pentosans within the range of 12 to 26% for poplar wood. Following alkaline treatment, the share of pentosans increased in corn waste, while it decreased in wood. In turn, Gupta and Lee [45] investigated changes in the contents of five carbon sugars as a result of hydrolysis with NaOH solutions. The authors conducted their studies on corn stover and poplar varieties with low and high lignin contents. Their analyses showed that the higher the reaction temperature and NaOH concentration, the smaller the amount of the five carbon sugars for all the investigated variants. The authors explained the changes as owing to the greater reactivity of hemicellulose compared to cellulose due to its amorphous structure, which facilitates the agent's access to reactive sites. This trend was confirmed in the described experiment only for wood. In the case of corn waste, the pentosans underwent opposite changes, which were advantageous from the point of view of fermentation processes. In turn, in the case of sulfuric acid hydrolysis, the content of pentosans decreased in all the samples, while the obtained percentage shares of pentosans differed statistically from those in the control sample. Moreover, the acid at a higher concentration caused greater losses of pentosans. These losses confirm the susceptibility of pentosans to acid hydrolysis and indicate that, after such pretreatment, the chance for their presence in the hydrolysis residue is much lower. This corresponds to the biogas yield of this raw material reported by Stachowiak et al. [46].

3.2. Quantitative Identification of Glucose and Arabinose

Studies on the contents of glucose and arabinose in poplar wood (Figure 1) showed that each treatment variant of this material caused an increase in the content of glucose and a reduction in arabinose content. This corresponds with the results of the analyses for the higher percentage share of cellulose and a lower share of pentosans following pretreatment (Table 1). In the corn material, acid and alkaline treatment also led to increased percentage shares of glucose. However, differences were observed in the case of changes in the share of arabinose. Although the share of arabinose decreased in the case of acid treatment, it increased following alkaline treatment. This is consistent with the increase in the percentage share of pentosans in this treatment variant (Table 1).

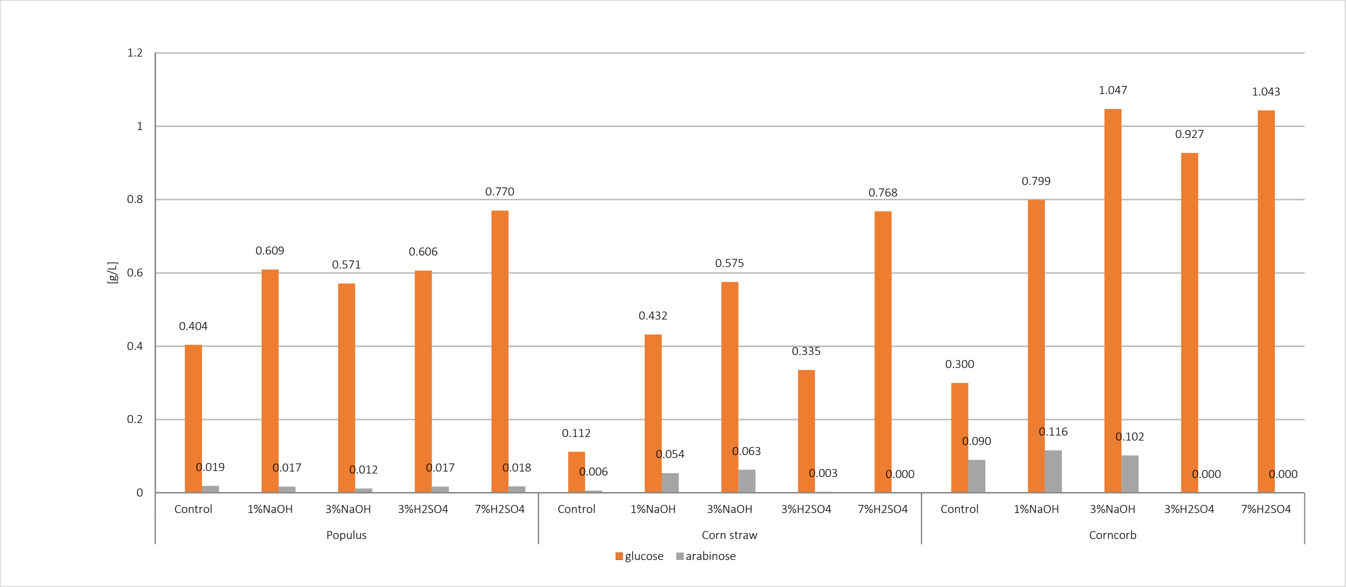

Figure 1. Contents (g/L) of glucose and arabinose in *Populus* L. and corn waste before and after pretreatment.

3.3. Qualitative Identification of Cellulose by Fourier Transform Infrared (FTIR) Spectroscopy and X-ray Diffraction

Figures 2–4 present the spectra of the cellulose isolated from poplar wood and corn waste before and after pretreatment. Their courses are similar, as all of them contain the same bands characteristic for cellulose (3400 cm^{-1}—OH, 2800 cm^{-1} CH, CH_2, while in the case of fingerprints, 1700–1200 cm^{-1}, they contain bands typical of C-O, C-O-C bonds). However, these bands differ in absorbance. This made it possible to determine the E_H and LOI parameters (Table 2).

Preliminary hydrolysis aims at a reduction of intensity of intermolecular interactions and the share of the cellulose crystalline structure [47]. Table 2 presents results of analyses of cellulose structure, i.e., the energy of hydrogen bonds and the lateral order index (E_H and LOI) for tested raw materials before and after pretreatment. In the control samples the energy of hydrogen bonds (E_H) varies in the compared plant species and it is higher for corn waste than for poplar wood. As a result of the treatment with alkali and acid solutions the energy of hydrogen bonds is greater compared to the control samples. An increase in the value of this parameter indicates changes within hydrogen bonds of cellulose towards enhanced intermolecular interactions of cellulose in all tested biomass variants. The lateral order index (LOI) for these variants is also greater after pretreatment. This change results from an increased share of the ordered structure in cellulose and it is highest in the case of corncobs. These results suggest that the structure of cellulose in corn waste is more stable after chemical treatment and thus less susceptible to fermentation. However, it needs to be remembered that these findings refer to cellulose, which is a residue after pretreatment, because of which the content of cellulose increased by as much as 120% (for 7% H_2SO_4) (Table 1).

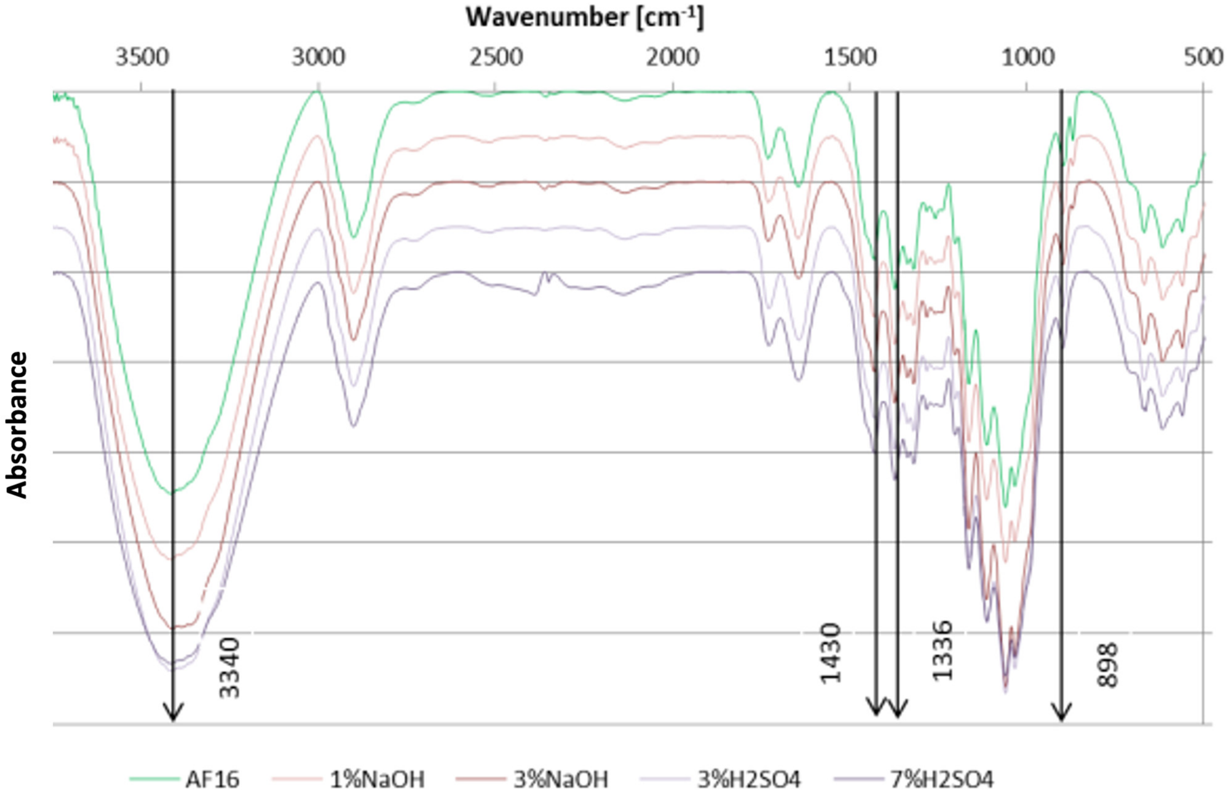

Figure 2. FTIR spectrum of poplar cellulose before and after pretreatment.

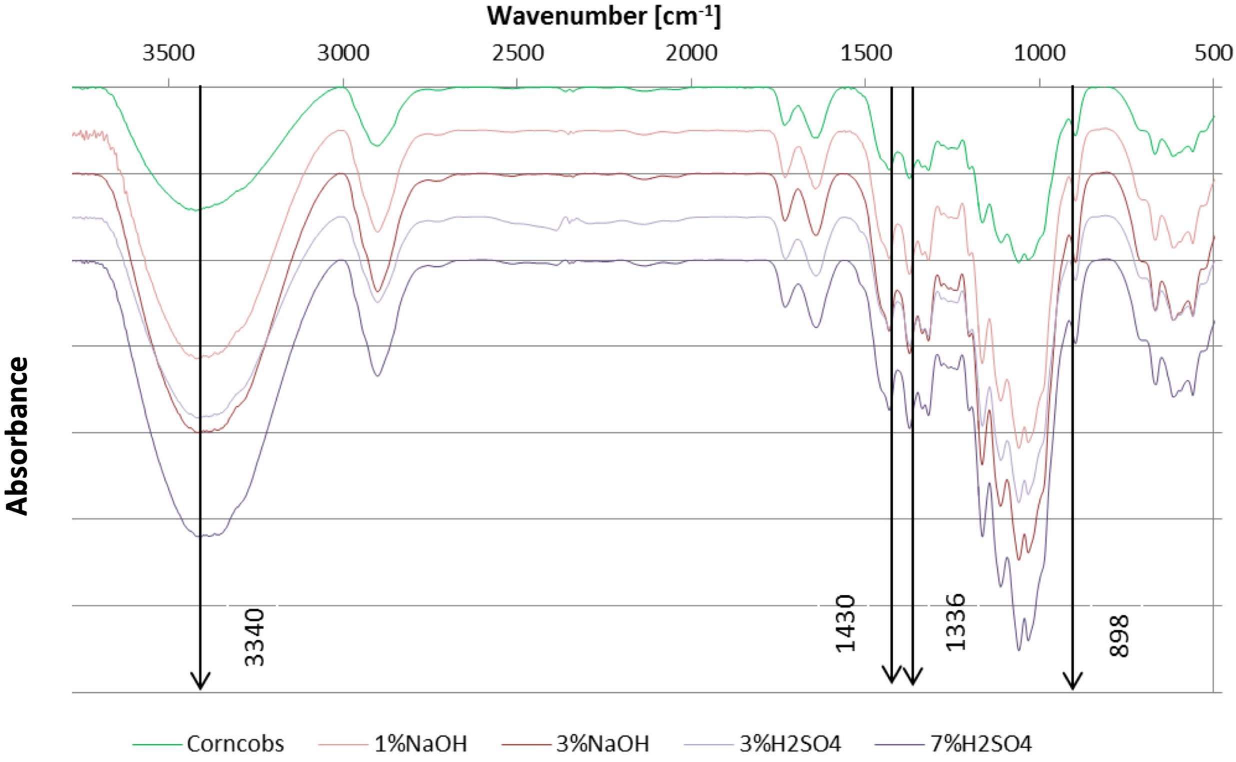

Figure 3. FTIR spectrum of corncob cellulose before and after pretreatment.

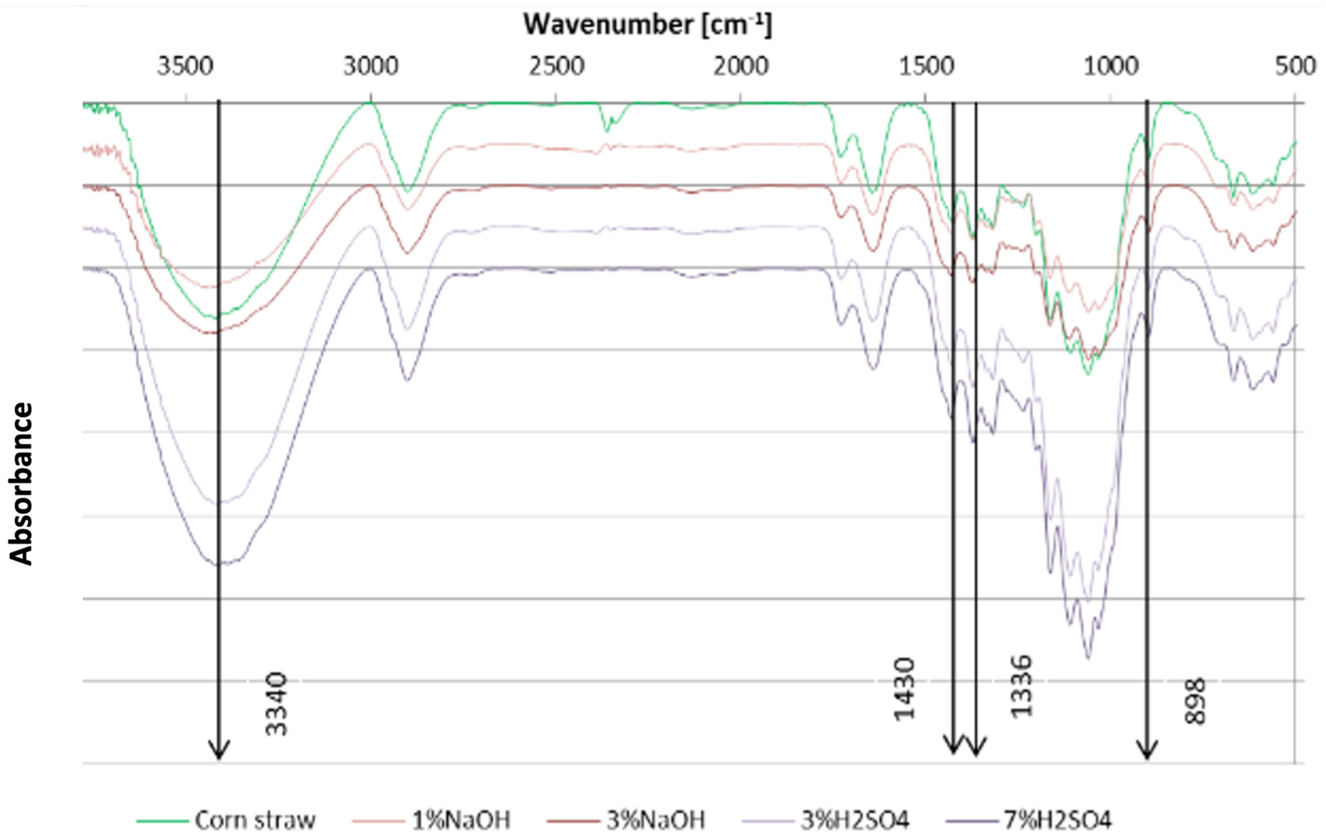

Figure 4. FTIR spectrum of corn straw cellulose before and after pretreatment.

Table 2. Parameters of cellulose structure in the tested raw materials after pretreatment.

Parameter	**Pretreatment**	***Populus* L.**		**Corn Waste**			
				Corncobs		**Corn Straw**	
E_H	Control	16.643	Δ	17.356	Δ	17.459	Δ
	1% NaOH	16.643	0	17.458	0.59	17.644	1.06
	3% NaOH	16.745	0.61	17.458	0.59	17.644	1.06
	3% H_2SO_4	16.745	0.61	17.560	1.17	18.459	5.73
	7% H_2SO_4	16.745	0.61	17.560	1.17	18.459	5.73
LOI	Control	2.267	Δ	1.701	Δ	1.522	Δ
	1% NaOH	2.339	3.19	1.812	6.52	1.575	3.48
	3% NaOH	2.288	0.96	1.871	9.99	1.585	4.14
	3% H_2SO_4	2.390	5.44	1.778	4.52	1.569	3.09
	7% H_2SO_4	2.373	4.70	1.801	5.86	1.559	2.43
C_rI	Control	62	Δ	51	Δ	55	Δ
	1% NaOH	63	1.61	58	13.73	56	1.82
	3% NaOH	69	11.29	58	13.73	59	7.27
	3% H_2SO_4	65	4.84	58	13.73	55	0.00
	7% H_2SO_4	65	4.84	62	21.57	54	−1.82

E_H—energy of the hydrogen bonds, LOI—lateral order index, C_rI—crystallinity index, Δ—the percentage change of the parameter for the sample after pretreatment compared to the parameter for the control sample.

The next step to determine the influence of the applied chemical treatment on the supermolecular structure involved diffractometric tests. The diffraction pattern showed three peaks at 2Θ = 15°, 17° and 22.7° assigned to respective crystallographic planes of cellulose. These peaks came from the lattice planes (1–10), (110) and (200), respectively, which was exactly described in the diffraction patterns (Figures 5–7). However, there are some differences in the intensity value of peaks, especially in the case of plane (200) confirming the influence of chemical pretreatment in lignocellulosic materials. The noted differences in the intensity of the peaks reflect changes in crystallinity of the tested systems. The crystallinity index was calculated by dividing the diffractogram area due to crystalline cellulose by the total area of the original diffractogram after subtraction of the background signal. The crystallinity index (C_rI) of lignocellulosic materials is presented in Table 2.

Calculations of the degree of crystallinity showed a significant effect of the type of raw material used as well as alkalization conditions. In the case of poplar cellulose, a slight increase in the degree of crystallinity was observed as a result of the performed chemical treatment. However, it needs to be stressed here that the application of a 3% NaOH solution was responsible for the greatest increase in C_rI (by approx. 10%) compared to the control. In the case of the corn stover system, no changes were recorded in the degree of crystallinity as a result of chemical modification except for the material treated with a 3% NaOH solution. The greatest structural changes were observed for the corncob system, which was characterized by the highest increase in the degree of crystallinity as a result of the reaction with sodium hydroxide. For this lignocellulose material, crystallinity increased by over 15%, which precisely reflects the greatest change in LOI. Moreover, this indicates that pretreatment in the case of corncobs does not facilitate the fermentation of cellulose, but rather hinders it, since increasing the molecular ordering of cellulose is a result of strong intermolecular interactions. Similar results, i.e., an increase in the share of the crystalline structure of cellulose after hydrolysis, were reported by Zheng et al. [48] and Yuan et al. [49]. However, some findings indicate a reduction in the degree of crystallinity of cellulose following pretreatment [50].

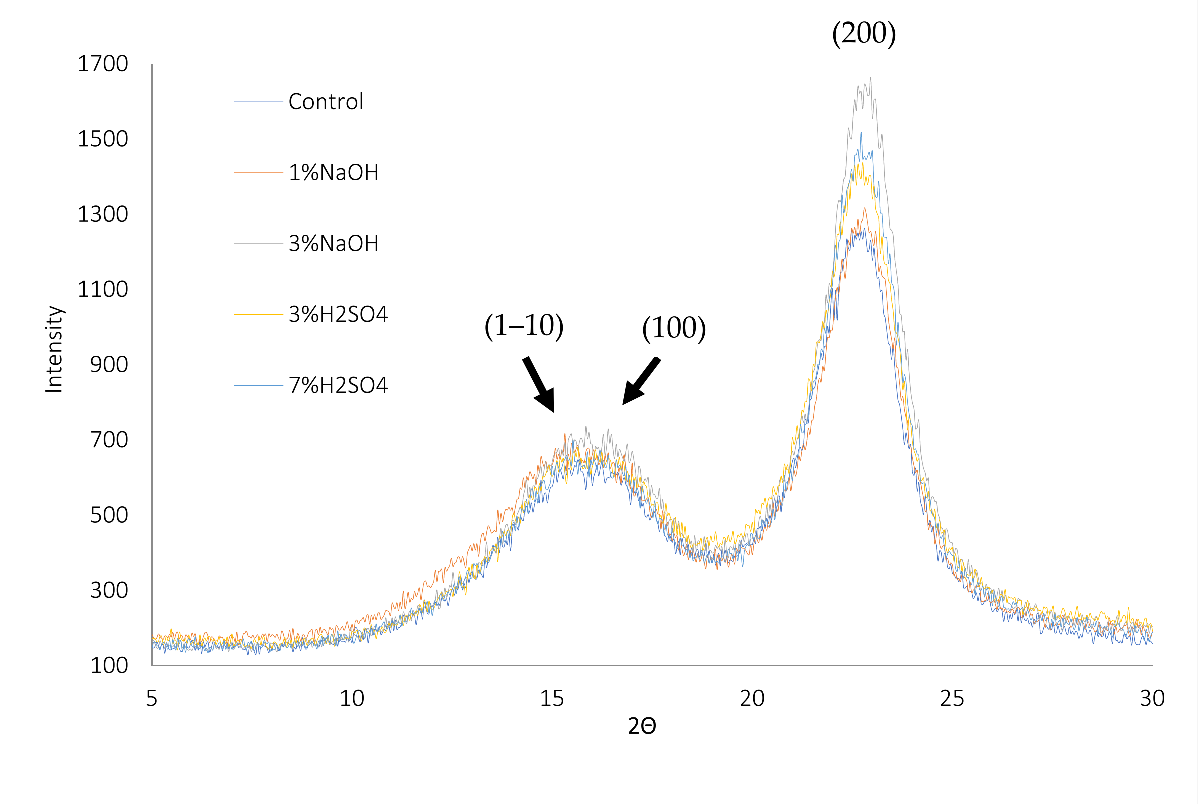

Figure 5. X-ray diffraction pattern of poplar cellulose before and after pretreatment.

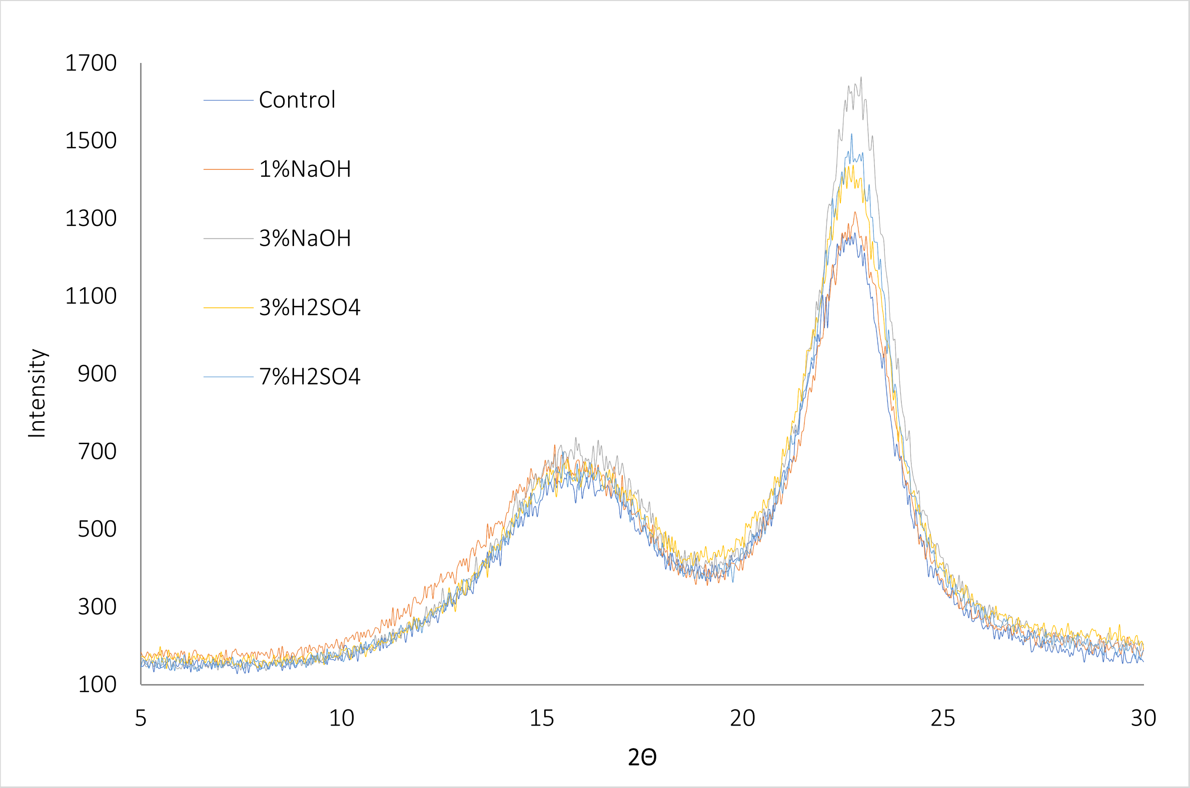

Figure 6. X-ray diffraction pattern of corncob cellulose before and after pretreatment.

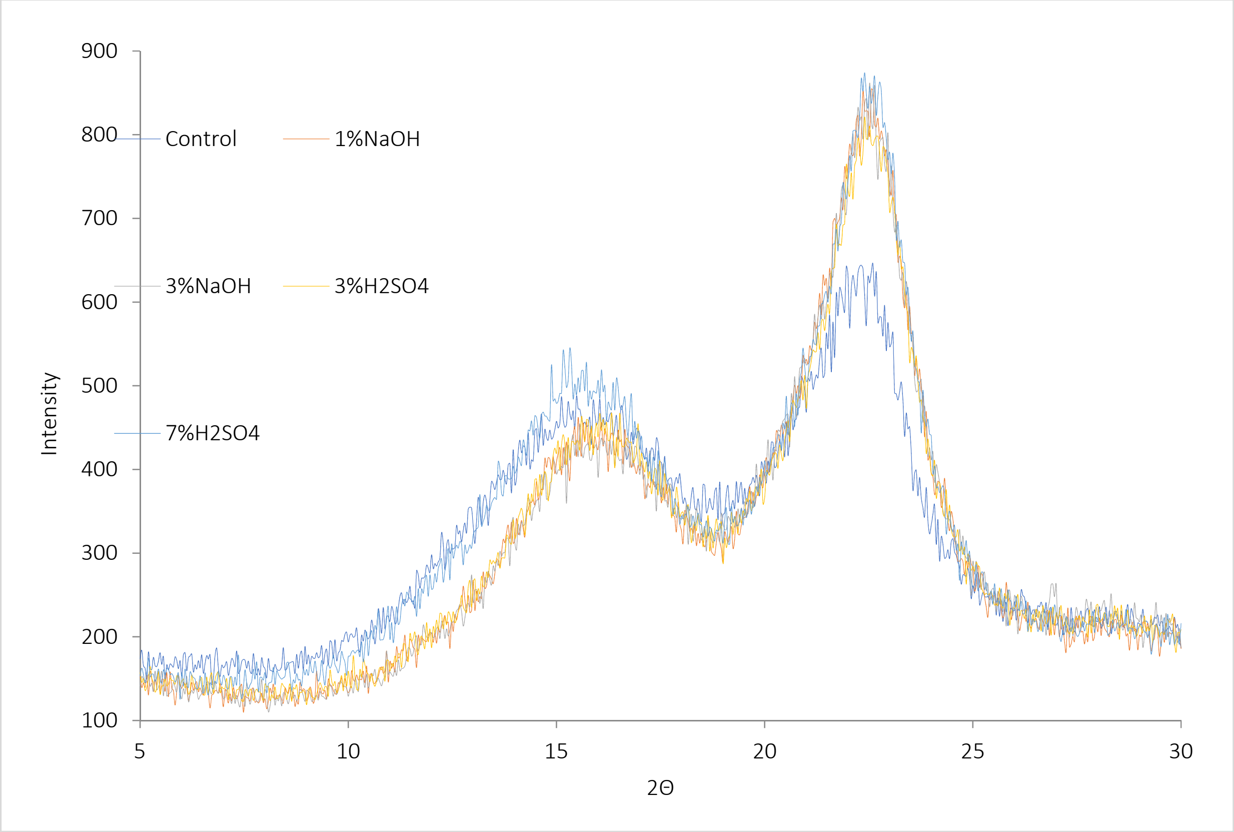

Figure 7. X-ray diffraction pattern of corn straw cellulose before and after pretreatment.

4. Discussion

The results of the analyses concerning the contents of carbohydrate components and cellulose structure suggest that the acid and alkaline pretreatments of poplar wood did not contribute to its increased susceptibility to fermentation. The pretreatments caused an increase in cellulose content, while at the same time its crystallinity and bond energy increased. In corncobs studied by Stachowiak et al. [51], both NaOH and H_2SO_4 increased the percentage of cellulose. The acid treatment produced a greater change than the alkaline treatment. What is more important is that the acid and alkaline pretreatments of poplar resulted in losses of pentosans. Similar results for other biomasses were obtained by other authors [29,51]. This assumption is confirmed by the biogas yields of this material presented by Stachowiak et al. [46]. They indicate that the amounts of biogas and methane after pretreatment of poplar wood are smaller than in the raw material not subjected to the action of acids and alkalis, by over 10% and 70% following alkaline and acid treatment, respectively. The cellulose in corn waste following the acid and alkaline treatment underwent similar changes as in poplar wood. The pentosans in corn waste were also degraded during the acid treatment. Similarly, as in poplar wood, it may be assumed that the content and structure of the carbohydrates did not undergo changes advantageous from the point of view fermentation. This also corresponds to the results concerning biogas yields of the tested corn waste variants, for which Stachowiak et al. [46] reported a reduction in their efficiency by several dozen percent. In contrast, during the alkaline treatment, the amount of pentosans in the hydrolysate increased. This was the only variant of pretreatment that resulted in the conversion of carbohydrates, which is advantageous for biogas production. In this case, the results presented by Stachowiak et al. [46] indicate an increase in the yields of biogas and/or methane. The recorded results confirm the conclusions provided by Dandikas et al. [52] and Stachowiak et al. [46] concerning a significant or even decisive role of pentosans in the fermentation process.

The need to perform the described experiment and write this publication resulted from the common belief that lignocellulosic biomass must be pretreated to increase the efficiency of the fermentation process. Pretreatment has been assumed to be a panacea for the efficiency of the fermentation process. The research carried out as part of the experiment showed that the pretreatment (at least chemical pretreatment) did not improve the efficiency of the fermentation process for the selected biomass materials. Strongly lignified tissues are not appropriate raw materials for fermentation.

5. Conclusions

In this study, we investigated how acid and alkaline pretreatment changes the carbohydrate components of lignocellulose biomass, and it was shown that:

- Components of corn waste are more susceptible to chemical conversion than those of poplar wood;
- Acid pretreatment, in the case of poplar wood and corn waste, caused an increase in the share of cellulose in the hydrolysis residue and its structural stability and also enhanced the degradation of pentosans;
- Alkaline pretreatment, in the case of poplar wood and corn waste, caused an increase in the share of cellulose in the hydrolysis residue and its structural stability; degradation of pentosans was recorded only in poplar wood, while in the hydrolysis residue of corn waste, an increased share of cellulose and pentosans was recorded;
- Only alkaline treatment of corn waste caused changes, which promoted improved efficiency of the fermentation process;
- All the applied pretreatment methods caused changes in the cellulose structure, which were advantageous for the efficiency of biomass fermentation: an increase in the energy of hydrogen bonds, the lateral order index, and the crystallinity index.

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