

Article

Hydrolytic Decomposition of Corncobs to Sugars and Derivatives Using Subcritical Water

Maja Čolnik ¹, Mihael Irgolič ², Amra Perva ¹ and Mojca Škerget ^{1,*}

¹ Laboratory for Separation Processes and Product Design, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia; maja.colnik@um.si (M.Č.); amra.perva@um.si (A.P.)

² Laboratory for Process Systems Engineering and Sustainable Development, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia; mihael.irgolic@um.si

* Correspondence: mojca.skerget@um.si

Abstract: Corncobs are a widespread and renewable by-product of corn cultivation that are typically considered waste or low-value material. Corncobs contain hemicellulose, cellulose, and lignin, which can be converted into valuable products using suitable techniques. Subcritical water is increasingly used as a green medium for the extraction of valuable components from biomass, as it has many advantageous properties (high yield, pure extracts, shorter times) compared to other organic solvents. For this reason, subcritical water was used in this study to extract valuable components from corncobs at different temperatures (150–250 °C) and reaction times (10–60 min). During the decomposition of corncobs, numerous valuable products are formed in the aqueous phase depending on the temperature and reaction time. In addition to sugars and their derivatives, phenolic compounds were also formed, which are of great importance in numerous applications. It was found that at low temperatures (150–170 °C) the hemicellulose in the corncobs begins to decompose and, in particular, the sugars (glucose, xylose, arabinose, and galactose) are initially formed in the aqueous phase. Higher temperatures (200 and 250 °C) are more favorable for the decomposition of corncobs into valuable components. The yield of sugars increases with temperature due to the degradation of the cellulose content of the lignocellulosic biomass. At the same time, several new valuable products (furfural, 5-hydroxymethylfurfural (5-HMF), 1,3-dihydroxyacetone, levulinic acid, and formic acid as well as phenolic components) are formed through the degradation of lignin and the further degradation of sugars. The most important products are certainly the furfurals, which are central platform compounds. The highest furfural content was reached at 200 °C and 60 min and accounted for almost half of all components in the aqueous phase (472.01 ± 5.64 mg/g dry extract). These biomass-derived sugars and derivatives can be used in the production of fuels, pharmaceuticals, biodegradable polymers, and surfactants.

Keywords: corncobs; subcritical water; biomass; valuable compounds; sugars; sugar derivatives



Received: 18 December 2024

Revised: 15 January 2025

Accepted: 16 January 2025

Published: 18 January 2025

Citation: Čolnik, M.; Irgolič, M.; Perva, A.; Škerget, M. Hydrolytic Decomposition of Corncobs to Sugars and Derivatives Using Subcritical Water. *Processes* **2025**, *13*, 267. <https://doi.org/10.3390/pr13010267>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Lignocellulosic biomass from agricultural waste is a renewable, abundant, and cost-effective feedstock with significant potential for sustainable applications. It consists of carbohydrates (cellulose and hemicellulose, which account for almost 75% of the biomass weight) and aromatic polymers (lignin) [1,2]. This abundant biomass can be utilized to produce biofuels, biocomposites, bioplastics, and other value-added products, reducing reliance on petrochemicals [1].

Thermochemical and biochemical processes are used to convert biomass into high-value biofuel and other value-added products [3]. Thermochemical conversion, which includes pyrolysis, torrefaction, gasification, incineration, and hydrothermal conversion, uses heat and chemical processes to produce energy products, while the biochemical conversion of biomass (digestion, fermentation) uses bacteria, microorganisms, or enzymes to produce gaseous and liquid fuels such as biogas and bioethanol [4–6].

The major agricultural wastes like rice straw, wheat straw, corn straw, and sugarcane bagasse are primary sources of lignocellulosic biomass [7,8].

Corncoobs are the material that remains after the kernels have been removed and, together with corn husks, they are the most important by-product of corn and are considered a low-margin by-product. The global production of corn amounted to over 1.15 billion metric tons in 2022/2023 [9]. Corncoobs usually represent about 20–25% of the biomass of a harvested corn crop [10]. This means that global corncob production could be around 230–290 million tons. Corncoobs often cause environmental pollution as they are not effectively disposed of or recycled [11]. On the other hand, corncoobs represent a highly sustainable resource for bio-platform molecules and chemicals that can be used industrially on a large scale [12]. In addition, corncoobs have a high carbohydrate content and high energy density, which makes them one of the most suitable feedstocks for the production of a variety of high-value-added chemicals [12]. Like other lignocellulosic biomass, corncoobs are composed of hemicellulose (42–44%), cellulose (37–38%), and lignin (11–13%) [13,14]. Various studies have shown that corncoobs are a good source of anthocyanins, phenols, and flavonoids [15–17]. On the other hand, they are the most commonly used biomass for the production of furfural on an industrial scale [18]. Corncob residues were also used as a precursor for the production of porous carbon by a simple and direct thermal treatment (one-step steam activation without pre-carbonization). The obtained porous carbon showed superior capacitive performance compared to synthetic polymer-based carbons as electrode material for a supercapacitor [19]. Anukam et al. studied the characterization of corncoobs to determine their gasification potential. Despite the fact that gasification could result in a high ash content, which could contribute to an increase in the concentration of inorganic elements under the conditions of high-temperature gasification, they concluded that corncoobs are a suitable material for gasification [20]. Wang et. investigated the conversion of corncoobs to furfural in a two-phase system (sulphuric acid–toluene) under extremely low water/solid ratios. A high furfural yield (65.67 mol%) was achieved in a very short time (10 min). It was confirmed that the production of furfural from lignocellulosic biomass was significantly improved by the addition of an immiscible organic solvent to the dilute acid solution [21]. Winarsih et al. studied the enzymatic hydrolysis of corncoobs for the production of bioethanol. The optimum time for the enzymatic hydrolysis of corncoobs was 72 h, resulting in an ethanol production of 6.4 g/L [22].

Environmentally friendly technologies have been developed to extract the valuable compounds [23], including the use of subcritical water [2]. Subcritical water is water with a temperature between 100 °C and its critical temperature (374 °C—the high critical temperature is due to the high polarity of the water) that is subjected to sufficient pressure (between 1 and 220 bar) to remain in the liquid state. In this state, water has unique physicochemical properties [24]. As the temperature increases, the dielectric constant, viscosity, and surface tension decrease uniformly, while the diffusivity and ionization constant increase. As the polarity of the water decreases, subcritical water behaves more like an organic solvent. Subcritical water dissociates into protons and hydroxide ions, allowing it to act as an acid or base catalyst. In addition, the solubility of organic compounds, gases, and other normally insoluble substances in water is increased. The increased molecular mobility of subcritical water can also lead to higher reaction rates [25]. Elevated temperatures accelerate chemical

processes and consequently shorten reaction times. The resulting products or extracted substances are pure and contain no toxic organic solvent residues [26]. In addition, the reaction conditions (temperature, pressure) can be controlled, enabling the high selectivity and targeted extraction of compounds. Due to its specific physicochemical properties, the use of subcritical water is very versatile, as it can be used for the extraction [27,28] and degradation of organic compounds [29–31] and enables the processing of biomass into valuable products, contributing to the circular economy. In addition, it effectively degrades organic pollutants such as dyes, pesticides, and pharmaceuticals in wastewater [32,33]. It can also depolymerize some types of (bio)plastic waste into monomers and other important secondary raw materials. However, subcritical water requires expensive high-pressure and high-temperature systems and corrosion-resistant materials (titanium, stainless steel), which increases costs [34]. Optimizing the conditions for specific applications also requires extensive research. Despite these challenges, hydrothermal processes often produce fewer by-products compared to conventional processes (reduction in organic solvents). As a result, hydrothermal processes have become increasingly popular in various applications in recent years. Subcritical water hydrolysis is a promising technology for converting biomass into fermentable sugars and sugar degradation products. Biomass derivatives, including sugars and sugar derivatives, are a sustainable source of a wide range of chemicals to reduce dependence on petroleum and play an important role in the chemical, food, cosmetics, and pharmaceutical industries [35,36]. This process has been studied for various biomasses to produce sugars and sugar derivatives, including rice husks [37], pecan wastes [38], coconut husks, defatted grape seeds, sugar cane bagasse and pressed palm fibers [39], cocoa shells [40], pistachio and walnut shells [29], and sweet blue lupin hulls [41]. Cellobiose, glucose, arabinose, galactose, xylose, mannose, fructose, rhamnose, 1,6-anhydroglucose, and also sugar derivatives, such as 5-HMF, furfural, 5-metil furfural, and organic acids (levulinic, formic and lactic acid) were identified in the hydrolysis extract from biomass. The hydrolysis of various sugars under subcritical conditions in water to obtain high-value compounds has also been investigated in various studies [42,43]. Gagić et al. found that aldohexoses such as glucose and galactose are more stable than keto- and furanose structures [42]. Various valuable products can be obtained from this process, including 5-HMF, furfural, and organic acids [42,43]. Several studies have been conducted on the extraction of value-added components or the production of energy and carbon from corncobs using sub- or supercritical water with or without catalysts. Lu et al. investigated the gasification of corncob biomass in a fluidized bed at up to 650 °C in supercritical water to produce hydrogen-rich fuel gas. The gas obtained was composed of H₂, CH₄, CO₂, CO, and small amounts of C₂H₄ and C₂H₆ [44]. Li et al. studied the catalytic hydrothermal pretreatment of corncob to xylose and furfural using a solid acid catalyst ((SO₄^{2−}/TiO₂–ZrO₂/La³⁺), where the maximal furfural yield (6.18 g/100 g) was obtained at 180 °C for 120 min when the corncob/water ratio was 1:10 [45]. In the work of Li et al., a two-stage process was used to obtain a high furfural yield from corncob (up to 57.80%), using microwave-assisted hydrothermal pretreatment in the first stage and heterogeneously catalyzed conversion in the second stage [12].

There are several techniques for the extraction of valuable components (sugars, furfurals) from biomass that are well established and generally recognized but have some disadvantages (use of organic solvents, addition of catalysts, long reaction times). The hydrolysis of corncobs with subcritical water offers the possibility to convert a low-value agricultural by-product into high-value compounds in a sustainable and efficient way. The method represents an important step forward in the utilization of biomass and supports the transition to a green and circular bioeconomy. Studies in which corncobs are degraded at moderate temperatures and reaction times without the addition of catalysts or organic sol-

vents to extract valuable components such as important sugars (xylose, arabinose, glucose), furfurals, and bioactive components are still lacking in the literature.

HPLC analysis was used to determine the presence of sugars (glucose, xylose, cellobiose) and sugar derivatives (5-HMF, furfural, levulinic acid), which are important components for the production of bioethanol as well as high-value-added chemicals that can be used in the food, cosmetics, and pharmaceutical industries and in biorefineries. Another new aspect of the study is that the content of total phenols, total carbohydrates, and the antioxidativity of the extracts were determined. Based on the obtained experimental data and data from the literature, a possible degradation mechanism of lignocellulosic biomass (corncoobs) in subcritical water is presented.

2. Materials and Methods

2.1. Materials

Corncoobs were obtained from a local market (Maribor, Slovenia). The corncoobs were ground to a size of 1–2 mm. D-(+)-glucose (99.5%), D-(–)-fructose ($\geq 98\%$), 5-hydroxymethylfurfural ($\geq 99\%$), levulinic acid (98%), 1,3-dihydroxyacetone dimer (97%), glycolaldehyde dimer, furfural (99%), 5-methylfurfural (99%), phenol ($\geq 96\%$), trifluoroacetic acid, Folin–Ciocalteu’s phenol reagent, sodium carbonate (Na_2CO_3), 2,2-diphenyl-1-picrylhydrazyl (DPPH), sodium acetate (CH_3COONa), gallic acid, and quercetin were purchased from Sigma Aldrich (Steinheim, Germany). Cellobiose (99%), D-(+) xylose ($\geq 99\%$), and aluminum chloride hexahydrate 98% ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Merck (Darmstadt, Germany). Absolute ethanol (EtOH , $\geq 99.9\%$), n-hexane ($\geq 98.5\%$), 96% sulphuric acid (H_2SO_4), and methanol (MeOH , $\geq 99.9\%$) were purchased from LabExpert Kefo (Ljubljana, Slovenia) and Carlo Erba Reagents (Val de Reuil, France). Nitrogen (99.5%) was supplied by Messer (Ruše, Slovenia).

2.2. Methods

2.2.1. Proximate and Ultimate Analysis of Corncoobs

The mass concentration (wt.%) of moisture, ash, volatiles, and fixed carbon in the raw material (corncoobs) was determined using the TGA method (Mettler Toledo TGA/DSC1 STAR, Columbus, OH, USA) described by Donahue and Rais [46]. The sample size was between 5 and 10 mg. Steps 1–4 were carried out in a nitrogen atmosphere. First, the sample was held at 25 °C for 4 min (1), then heated from 25 °C to 110 °C at 85 °C/min (2), held at 110 °C for 6 min (3), and then heated from 110 °C to 900 °C at 80 °C/min (4). The nitrogen atmosphere was then switched to air and held at 900 °C for 5 min. The moisture, volatile matter, and fixed carbon content were determined using the instrument software. The ash content was calculated by summing these quantities and subtracting the result from 100%. The elemental composition of the corncoobs was determined using a Perkin Elmer 2400 Series II System Analyzer (Waltham, MA, USA). The oxygen content (wt.%) was calculated from the difference between the sum of the C, H, N, S, and ash content and 100%.

2.2.2. Hydrolysis of Corncoobs in Subcritical Water

The hydrolysis of corncoobs was performed in a 75 mL Parr batch reactor (series 4740 stainless steel, Parr instruments, Moline, IL, USA) at different temperatures (150, 170, 200, and 250 °C), reaction times (10, 30, and 60), and a water-to-corncob (solvent-to-material) ratio of 10 mL/g. The mixture of solvent and material and the magnetic stirrer were added to the reactor. The reaction mixture was stirred at 1000 rpm. Nitrogen was used as an inert gas to remove air and control the pressure (the initial pressure was 40 bar). The reactor was heated with an electric wire at a heating rate of around 28 °C/min. As soon as the

desired temperature was reached, the measurement of the reaction time began. After the reaction, the reactor was immediately exposed to rapid cooling. The post-reaction mixture, composed of aqueous solution and solid residue, was then filtered, and the small amount of liquid phase was evaporated to determine the yield of the water-soluble product obtained by corncob hydrolysis (Equation (1)).

$$\eta (\%) = \frac{m \text{ (dry extract)}}{m \text{ (initial material)}} \times 100 \quad (1)$$

where m (dry extract) is the mass of the dry matter in the liquid phase and m (initial material) is the initial mass of corncobs.

2.2.3. Determination of Total Carbohydrates (TCH)

The content of total carbohydrates in the liquid samples after the hydrolysis of the corncobs was determined using the phenol–sulfuric colorimetric method described in more detail in our previous work [29]. The absorbance was measured at 490 nm using a UV-VIS spectrophotometer (Cary 50, Varian, Palo Alto, CA, USA). The results were expressed in mg TCH/g dry extract.

2.2.4. Determination of Sugars and Sugar Derivatives

The content of glucose, xylose, cellobiose, galactose, fructose, arabinose, sucrose, 1,6-anhydroglucose, glycolaldehyde, 1,3-dihydroxyacetone, formic acid, and levulinic acid in the hydrolysates after the degradation of corncobs in subcritical water was determined using the Shimadzu Nexera HPLC system (Shimadzu, Kyoto, Japan), equipped with a DGU-20A SR degasser, a LC-20AD XR pump, a SIL-20AC XR autosampler, and a CTO-20AC column heater. The components were separated isocratically on the chromatography column Rezex RHM Monosaccharide H+, 300 × 7.8 mm, at an operating temperature below 80 °C. Sugars and sugar derivatives in the samples were detected using the refractive index. The mobile phase was 5 mM H₂SO₄ in water at a flow rate of 0.55 mL/min [29].

The content of sugar derivatives such as 5-HMF, furfural, and 5-MF was determined using an Agilent 1200 series HPLC system (Waldbronn, Germany). The compounds were separated using a ZORBAX Eclipse XBD C18 column (4.6 × 150 mm; 3.5 μm) at a temperature of 25 °C. The injection volume of the sample was 10 μL, the flow rate was 1 mL/min. The mobile phase consisted of methanol (solvent A) and a mixture of water and 0.1% trifluoroacetic acid (solvent B). The following gradient was set: 0 min 90% B, 18 min 65% B, and 20 min 90% B [29]. All measurements were carried out in triplicate. The quantification of the products was performed using the calibration curves of the standards. The results were expressed in mg compound/g dry extract.

2.2.5. Determination of the Total Phenol Content

The total phenolic content in the liquid phase after the degradation of the corncobs in subcritical water was determined using the Folin–Ciocalteu method described in our previous work [29]. The absorbance of the samples was measured at 760 nm using a UV-Vis spectrophotometer (Cary 50, Varian, Palo Alto, CA, USA). The total phenolic content was calculated using a standard curve for gallic acid and expressed in mg gallic acid (GA)/g dry extract.

2.2.6. Antioxidant Activity

The antioxidant activity of the products obtained after the hydrolysis of corncobs was determined by the DPPH free radical method. The sample was mixed with DPPH solution (conc. 6×10^{-5} M) and incubated for 15 min at room temperature in the dark.

The absorbance of the sample was measured at 515 nm [29]. The antioxidant activity was expressed in %.

2.2.7. Statistical Analysis

All experiments were performed in triplicate ($n = 3$) and the results are expressed as mean $\pm$ standard deviation (SD). The relative standard deviation (RSD) was calculated to assess the precision of the measurements and to ensure consistency between replicates. In all cases, the RSD was below 3%, indicating a high reproducibility of the experimental data.

3. Results

3.1. Characterization of Corncobs

The results of the proximate and ultimate analysis of the corncobs are presented in Table 1. The proximate analysis of lignocellulosic biomass is an efficient method for determining the quality of the biomass to be processed (Figure 1). The organic and inorganic composition provides information about the genetic composition of the material [47]. The proximate analysis showed the following composition: moisture: $5.39 \pm 0.12\%$, volatile matter: $71.46 \pm 1.47\%$, fixed carbon: $19.36 \pm 0.54\%$, and ash content: $3.79 \pm 0.10\%$. The moisture content is determined by mass loss when the sample is heated to $110\text{ }^{\circ}\text{C}$. As a result of the thermal decomposition of corncobs between 110 and $900\text{ }^{\circ}\text{C}$ in a nitrogen atmosphere, the volatile matter content was determined. Fixed carbon is a solid combustible material that is formed at $900\text{ }^{\circ}\text{C}$ when the nitrogen atmosphere changes to air, while ash is formed during combustion at $900\text{ }^{\circ}\text{C}$ in air.

Table 1. Proximate and ultimate analysis of corncobs.

Characteristics	Proximate Analysis
Moisture (wt.%)	5.39 ± 0.12
Volatile matter (wt.%)	71.46 ± 1.47
Fixed carbon (wt.%)	19.36 ± 0.54
Ash content (wt.%)	3.79 ± 0.10
Ultimate analysis	
Carbon (wt.%)	45.51 ± 1.16
Hydrogen (wt.%)	7.49 ± 0.13
Nitrogen (wt.%)	0.67 ± 0.02
Sulfur (wt.%)	0.26 ± 0.01
Oxygen (wt.%)	42.28 ± 0.97

3.2. The Yield of Water-Soluble Product

As can be seen from Figure 2, the lowest yield of the aqueous phase ($1.19 \pm 0.03\%$) was obtained at the mildest conditions of $150\text{ }^{\circ}\text{C}$ and 10 min. A large proportion of the corncobs therefore remained undecomposed ($98 \pm 0.86\%$) under these conditions. Increasing the temperature and extending the reaction time caused faster degradation of the material and an increase in the yield of water-soluble products. Thus, high yields of the water-soluble products were already achieved at a temperature of $170\text{ }^{\circ}\text{C}$ and times of 30 and 60 min, with yields between 34.8 ± 0.52 and $37.1 \pm 0.68\%$. The maximum value ($38.01 \pm 1.12\%$) was then achieved at $200\text{ }^{\circ}\text{C}$ and 10 min. A further increase in temperature and time led to a decrease in the yield of water-soluble products (the lowest yield at $250\text{ }^{\circ}\text{C}$ and 60 min was $12.6 \pm 0.28\%$). At higher processing conditions, the corncob biomass was most likely decomposed, and the further decomposition of the products in the aqueous phase to gas components began, and char formation also take place, which is also indicated by the black color of the solid residue. Similar optimal conditions for achieving the maximum yields of aqueous products as in this study were also determined for the hydrolysis of pistachio

shells (41.05% at 200 °C and 15 min) and walnut shells (31.61% at 200 °C and 60 min) with subcritical water [29]. In the study by Sultana et al. [48], the corncobs were extracted with various organic solvents (methanol, ethanol, ethyl acetate, acetone, and n-hexane) at room temperature overnight. They found that the extraction yield increased with the polarity of the solvents. The lowest yield was obtained with n-hexane (1.1%) and the highest with methanol (19.5%) [48]. However, in the case of subcritical water, the polarity of the water changes from highly polar (at ambient conditions) to much less polar. The dielectric constant of water at 200 °C, 250 °C, and 300 °C corresponds to that of acetonitrile, methanol, and ethanol, respectively, enabling the extraction of less polar compounds. This makes subcritical water a green extraction fluid used for a variety of organic materials [26].

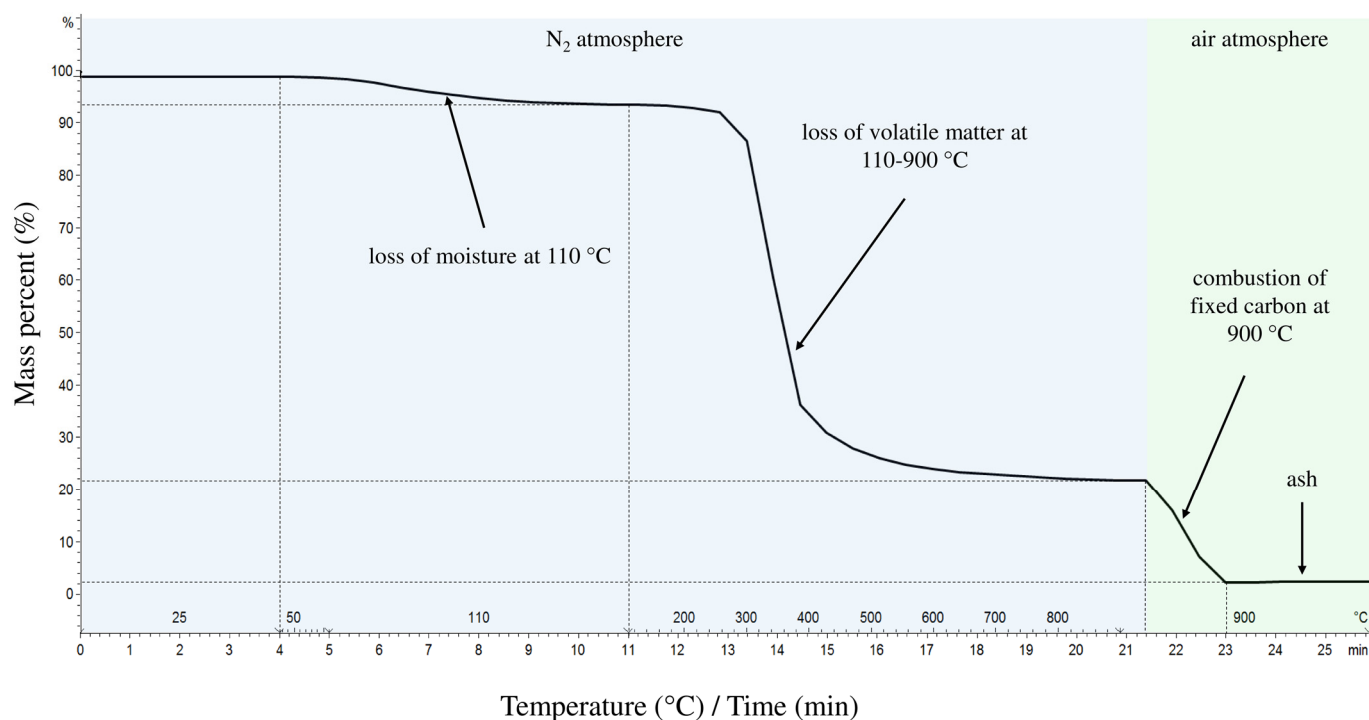


Figure 1. The TGA thermogram of corncobs showing the weight loss (%) as a function of temperature.

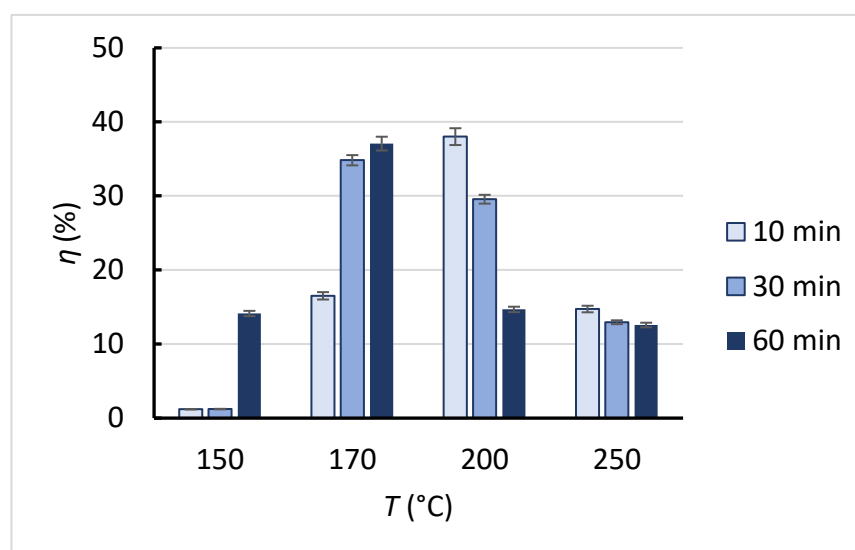


Figure 2. Yield of water-soluble product after corncob hydrolysis in subcritical water as a function of temperature and time.

3.3. Content of Sugars and Sugar Derivatives

The content of sugars and sugar derivatives in the water-soluble product obtained from corncobs with subcritical water is shown in Figures 3 and 4. As already mentioned, corncobs are lignocellulosic biomass composed of hemicellulose, cellulose, and lignin. When corncobs decompose at low temperatures (150 °C), the hemicellulose is most likely the first to decompose. Hemicellulose is a branched and amorphous polymer with a low molecular weight. It is composed of C5 and C6 atoms, known as pentoses and hexoses [49]. Consequently, in this case, glucose (between 11.76 ± 0.31 and 3.48 ± 0.08 mg/g dry extract) and galactose (between 21.05 ± 0.51 and 25.10 ± 0.67 mg/g dry extract), which are the representatives of hexoses, and arabinose (between 20.84 ± 0.31 and 25.89 ± 0.71 mg/g dry extract), which is a representative of pentoses, were formed first during the hydrolysis of corncobs in the aqueous phase at 150 °C and all reaction times. When the temperature increased to 170 °C, xylose (representative of pentoses) also began to form, and the yield of galactose and arabinose in the aqueous phase also increased, reaching a maximum content of 33.80 ± 0.87 mg/g dry extract for galactose and 56.68 ± 1.26 mg/g dry extract for arabinose after 10 min. The glucose content at a temperature of 170 °C was about 4 mg/g dry extract, independent of the reaction time. Under these conditions, 1,3-dihydroxyacetone and furfural (Figure 4) were also detected in the aqueous phase, which are most likely due to the further decomposition of the pentoses (arabinose, xylose). Water in the subcritical range has an increased ion product, which slightly increases its acidity and consequently accelerates the degradation of hemicellulose and cellulose in the biomass [24,50]. When the temperature increased to 200 °C, the cellulose (consisting of glucose molecules linked by 1–4 β glycosidic bonds [49]) also began to decompose, as the glucose concentration increased again (from 6.46 ± 0.14 mg/g dry extract at 200 and 10 min to 28.95 ± 0.76 mg/g dry extract at 200 °C and 60 min). In the aqueous phase, 1,6-anhydroglucose also appeared as a result of the dehydration of the glucose and also increased with time.

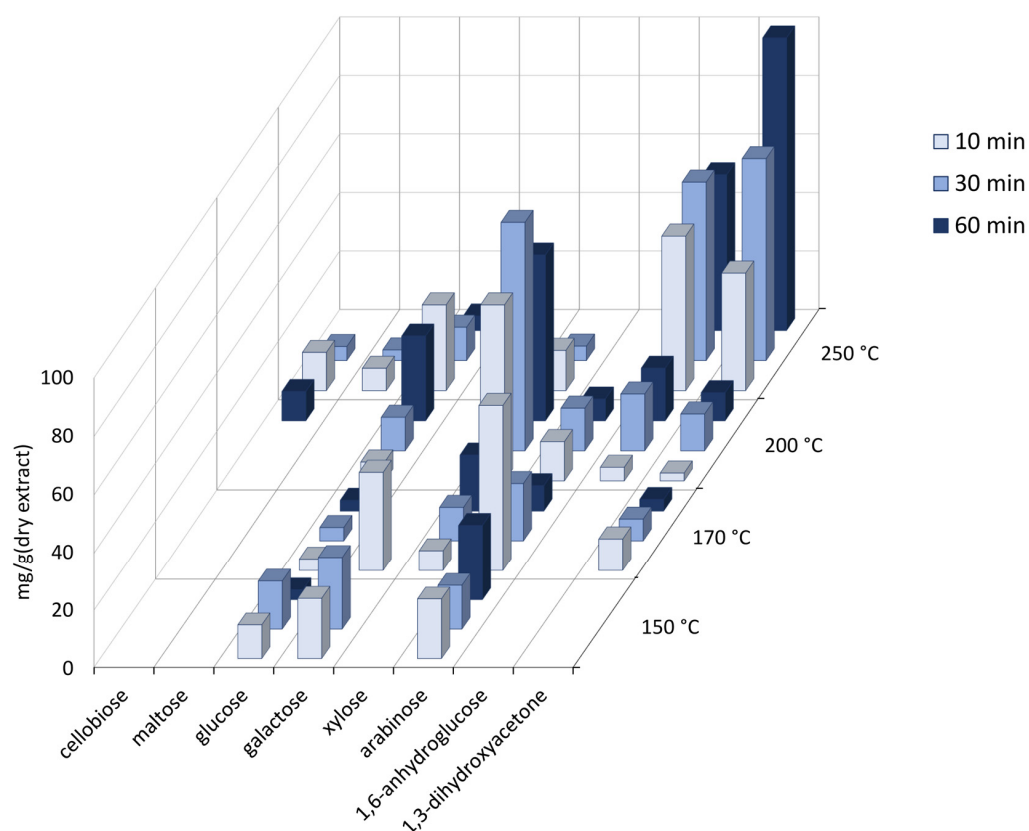


Figure 3. Sugar content in the extract obtained by hydrolysis of corncobs in subcritical water.

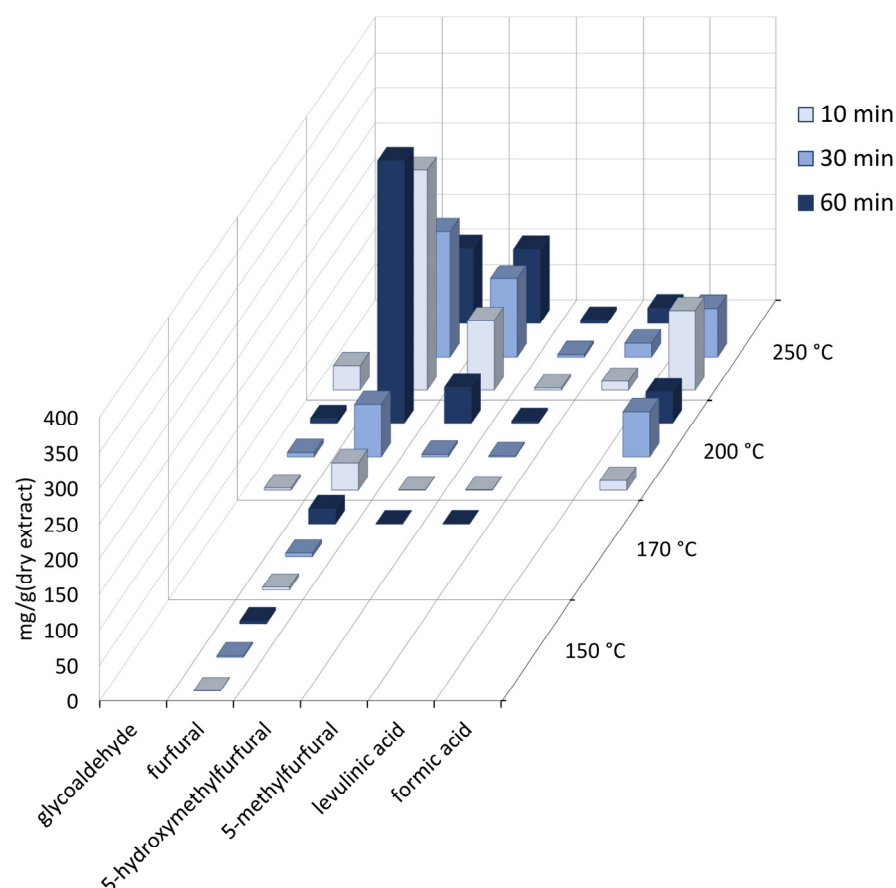


Figure 4. Sugar derivatives in the extract obtained by hydrolysis of corncobs in subcritical water.

At a temperature of 200 °C, some other sugar derivatives (formic acid, 5-HMF, 5-methylfurfural, furfural, glycolaldehyde), the content of which is shown in Figure 4, began to form intensively due to the decomposition of glucose and other monomeric sugars by various reactions (dehydration, fragmentation) [51]. The concentration of decomposition products generally increased over time. Thus, a significant increase in furfural was observed, rising from 38.54 ± 1.09 mg/g dry extract at 200 °C and 10 min to 472.01 ± 5.64 mg/g dry extract at 200 °C and 60 min. Furfural was probably formed in large quantities from pentose sugars (mainly from arabinose and xylose) by various cyclic and alicyclic mechanisms. Furfural can also be formed from the cellulose portion of lignocellulosic biomass by the isomerization of glucose to fructose, forming 5-HMF, which loses the $-\text{CH}_2\text{O}$ group and then forms furfural [42]. By increasing the temperature to 250 °C, the decomposition rate became even more pronounced. As the temperature rises, the water becomes even more reactive, as it probably contains more hydroxonium ions, which immediately break the linking bonds of the hemicellulose and cellulose, abruptly accelerating the formation of C5 and C6 sugars, their further decomposition, and the formation of new products [52,53].

The maximum yield of formic acid (112.19 ± 3.71 mg/g dry extract), glucose (29.31 ± 0.57 mg/g dry extract), glycolaldehyde (maximum yield 35.13 ± 0.94 mg/g dry extract), cellobiose (13.07 ± 0.34 mg/g dry extract), and maltose (7.64 ± 0.18 mg/g dry extract) were determined at 250 °C and 10 min. Under these conditions, levulinic acid also began to form, which also increased with the extension of the reaction time (from 12.93 ± 0.21 to 21.4 ± 0.31 mg/g dry extract). The content of 5-HMF, 5-MF, 1,6-anhydroglucose, and 1,3-dihydroxyacetone also increased at 250 °C, and the maximum concentrations of these components were reached at 30 min for 5-HMF (109.82 ± 1.85 mg/g dry extract) and

1,6-anhydroglucose (61.01 ± 0.95 mg/g dry extract), and at 60 min for 1,3-dihydroxyacetone (100.55 ± 1.63 mg/g dry extract) and 5-MF (4.42 ± 0.08 mg/g dry extract). If the temperature was increased further and the reaction time extended, further reactions (repolymerization, fragmentation, condensation, etc.) would lead to the formation of bio-oil, biogas and charcoal [51]. In the work of Yu et al. [54], the liquefaction of corncobs with supercritical water was studied. The liquid phase obtained from corncobs at high temperatures (300–400 °C) consisted of various chemical compounds, including polycyclic aromatic hydrocarbons, ketones, aldehydes, carboxylic acids, esters, and nitrogen-containing compounds, while the main compounds in the gas phase were carbon dioxide, carbon monoxide, hydrogen, methane, and a small amount of C₂–C₄ hydrocarbons [54].

3.4. Total Carbohydrates

The total carbohydrate content in the water-soluble phase depends on the reaction conditions. In addition to the free sugars, furfurals are also detected with the phenol–sulfuric colorimetric method used, as the phenol added to the sample binds to furfurals and thus forms a yellowish complex [29]. At temperatures of 150 °C to 200 °C, the concentration of total carbohydrates in the water-soluble product increases with increasing temperature and time (Figure 5). The lowest concentrations of total carbohydrates were determined at 150 °C and 10 min, where they amounted to 58.33 ± 0.82 mg TCH/g dry extract. Under these conditions, glucose, arabinose, and galactose were detected in the aqueous phase (Figure 3), which is consistent with the results obtained. The carbohydrate content began to increase more intensively at 200 °C and increased significantly when the reaction time was extended to 60 min, where it amounted to 715.28 ± 10.73 mg TCH/g dry extract. A similar degradation behavior was observed in a previous study in which the hydrolysis of pistachio and walnut shells was carried out in subcritical water. The total carbohydrate content was quite high and at 200 °C and 60 min amounted to 595 mg TCH/g dry extract in the case of pistachio shells and 602 mg TCH/g dry extract in the case of walnut shell waste [29]. The reason for the increase in carbohydrate content is probably the complete degradation of hemicellulose, which is usually achieved when the lignocellulosic material is treated at temperatures between 190 and 210 °C [55], and the initial degradation of cellulose and lignin [52,56]. The yield of total carbohydrates consequently increased with the further degradation of cellulose and lignin, and a maximum content of 744.31 ± 11.08 mg TCH/g dry extract was achieved at 250 °C and 10 min. However, with an increasing reaction time at 250 °C, the total carbohydrate content started to decrease as the content of sugars and furfurals decreased due to their further decomposition. The decrease in carbohydrate content in the water-soluble phase is also confirmed by the results in Figures 3 and 4, where at 250 °C and 60 min, the sugars cellobiose, maltose, and xylose disappear completely, while the content of glucose and 1,6-anhydroglucose decreases. A significant decrease was also observed in the content of furfural and 5-HMF. It can be concluded that the sugars and furfurals probably started to convert into oil, gaseous components, and a solid residue under these reaction conditions, which confirms the decrease in the carbohydrate content in the aqueous phase [52].

3.5. Antioxidant Activity and Content of Total Phenols

During the degradation of corncobs in subcritical water, bioactive components were also formed in the water-soluble phase. Figure 6 shows the antioxidant activity (6a) and the amount of total phenols (6b) (mg GA/g dry extract) isolated from corncobs as a function of temperature at different reaction times. The antioxidant activity and the content of total phenols in the extracts increase with increasing temperature. The lowest antioxidant activity ($2.98 \pm 0.05\%$) and total phenolic content (1.79 ± 0.03 mg GA/g dry extract) were detected at

the lowest temperature (150 °C) and the shortest reaction time (10 min). The content of total phenols increased significantly at a temperature of 200 °C, from 7.79 ± 0.14 mg GA/g dry extract at 10 min to 67.25 ± 1.24 mg GA/g dry extract at 60 min. Similarly, the antioxidant activity also increased from $11.24 \pm 0.22\%$ to $34.03 \pm 0.68\%$ under these conditions. This behavior can be attributed to the initial thermal degradation of the lignin, which starts at around 200 °C, which is confirmed by the increase in antioxidant capacity and total phenolic content (due to the phenolic structure of the lignin) [56]. Phytochemicals such as phenols, flavonoids, and tannins generally have an antioxidant effect [57]. Dong et al. determined the phenolic components in corncob extracts obtained with an ultrasonic cleaner at 40 °C for 30 min (three times). They used different extraction solvents: water, 50% ethanol, 80% ethanol, 50% methanol, 80% methanol, and ethyl acetate. They found that only a few phenolic components were present in the extracts. The highest yield of gallic acid (13.47 ± 0.40 mg/100 g dry weight) was obtained with ethyl acetate, resveratrol (11.01 ± 0.50 mg/100 g dry weight) with 80% ethanol, caffeic acid (3.73 ± 0.11 mg/100 g dry weight) with 50% methanol, and femlic acid (1.72 ± 0.09 mg/100 g dry weight) with 80% methanol. In the aqueous extract, the highest content of gallic acid (8.58 ± 0.56 mg/100 g dry weight) was determined, followed by femlic acid (1.25 ± 0.06 mg/100 g dry weight), caffeic acid (1.09 ± 0.03 mg/100 g dry weight), and resveratrol (0.94 ± 0.05 mg/100 g dry weight) with the lowest concentration [58].

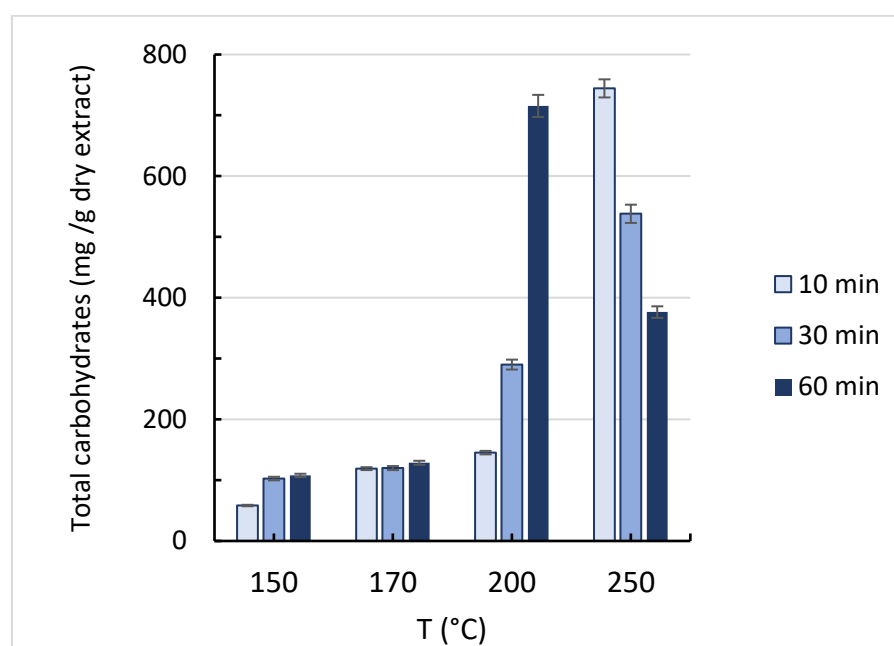


Figure 5. Total carbohydrate content in the extract obtained by hydrolysis of corncobs in subcritical water.

In this study, the highest number of total phenols that are isolated was found at a temperature of 250 °C and a time of 30 min and was 72.94 ± 1.45 mg GA/g dry extract, while the highest antioxidant activity ($48.66 \pm 0.97\%$) was found after 250 °C and 60 min. In previous studies by Sultana et al. [48], corncob extracts were prepared with hexane (42.1%) and acetone (34.2%) and were found to have slightly lower antioxidant activity than the water-soluble corncob product obtained in this study [48]. When the reaction time was further extended and the temperature was increased, the phenolic compounds from corncobs were further degraded to other organic compounds (aldehydes, alkanes, ketones, alkenes, etc.) [31,54].

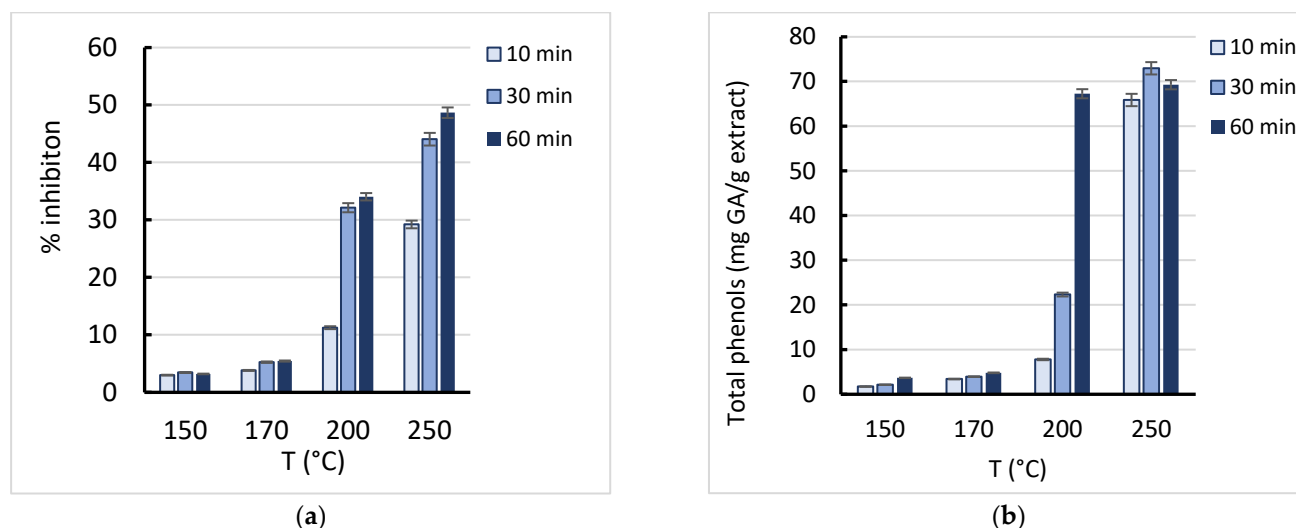


Figure 6. Antioxidant activity (a) and total phenol content (b) in extract after decomposition of corncob biomass in subcritical water.

4. Degradation Mechanisms of Corncobs (Lignocellulosic Biomass) in Subcritical Water

The degradation mechanism of lignocellulosic biomass in subcritical water (Figure 7) was proposed based on data from the current study on the decomposition of corncobs in subcritical water and data from the literature.

Lignocellulosic biomass consists of three main components: hemicellulose, cellulose, and lignin. Each of these components reacts differently to the reaction conditions in subcritical water. Hemicellulose is the most thermally labile component of lignocellulose, which is why it is the first to decompose at low temperatures (around 150 °C). Subcritical water easily hydrolyses the glycosidic bonds and breaks it down into the monosaccharides (xylose, glucose, xylose, and arabinose) [59]. As the temperature rises, the sugars are dehydrated and form compounds such as furfurals. Furfurals are thought to be formed exclusively from C5 sugars, mainly xylose and arabinose due to various cyclic and alicyclic mechanisms [60]. Notably, 5-HMF is also formed by the isomerization of glucose to fructose and the subsequent dehydration of fructose [29]. During decomposition at elevated temperatures (200–250 °C), some organic acids (e.g., levulinic acid, acetic acid, and formic acid) are also formed, which lower the pH value and also catalyze the decomposition of hemicellulose. Levulinic acid and formic acid are formed by the hydrolysis of 5-HMF and furfural [53]. The breakdown of sugars (glucose, xylose, and arabinose) also produces some phenolic compounds [60]. Crystalline cellulose requires higher temperatures and longer reaction times (higher energy) for degradation. During hydrolysis, the β -1,4-glycosidic bonds in the cellulose are broken and converted into glucose [52]. Glucose is dehydrated or isomerized, resulting in the formation of 5-HMF [61]. Notably, 5-HMF is broken down into levulinic acid and formic acid at higher temperatures and longer reaction times, as already mentioned for the degradation of hemicellulose [29]. Lignin is the most resistant component due to its amorphous and cross-linked aromatic structure. Subcritical water breaks the ether and ester bonds between the phenylpropanoid units of lignin. Monomeric phenols are released during depolymerization (phenol, vanillin, syringol, guaiacol, eugenol, guaiacetyl acetone) [62,63].

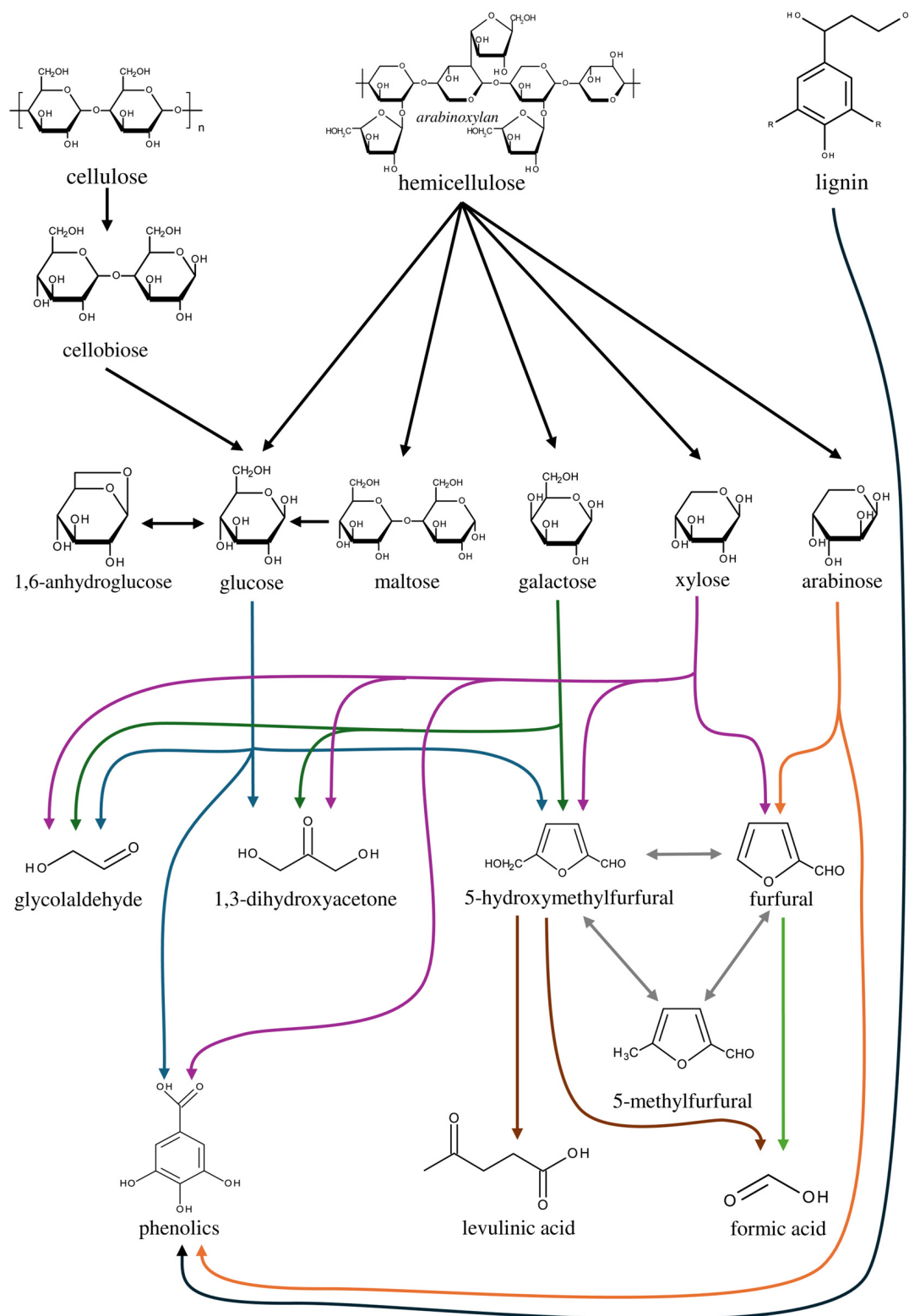


Figure 7. The potential degradation mechanisms of lignocellulosic biomass in subcritical water.

5. Conclusions

The subcritical water hydrolysis of corncobs was investigated at temperatures of 150 °C to 250 °C and reaction times of 10 min to 60 min. It was found that at low temperatures, only small amounts of corncobs were degraded, as the yield of hydrolysis was quite low (at 150 °C it ranged from 1.19 ± 0.03 to $14.12 \pm 0.41\%$). As the temperature increased, the degradation of hemicellulose and cellulose became more intense, lead-

ing to an increase in the hydrolysis yield, which at 200 °C and 10 min amounted to a maximum value ($38.01 \pm 1.12\%$). Under these reaction conditions, numerous high-value-added products were formed in the aqueous phase. During the degradation of cellulose and hemicellulose, important sugars were formed, with the highest content of galactose (33.80 ± 0.87 mg/g dry extract) and arabinose (56.68 ± 1.26 mg/g dry extract) at 170 °C and 10 min, of xylose (78.11 ± 1.29 mg/g dry extract) at 200 °C and 30 min, and of glucose (29.31 ± 0.57 mg/g dry extract) at 250 °C and 10 min. At the same time, the degradation products of sugars (1,6-anhydroglucose, 1,3-dihydroxyacetone, furfural, formic acid, levulinic acid) were also formed. Among these desired products, furfural clearly stands out with 472.01 ± 5.64 mg/g dry extract (or 6.9 ± 0.09 g/100 g material) at 200 °C and 60 min. Compared to the literature, where the catalytic hydrothermal pretreatment of corncobs with a solid acid catalyst was used to obtain maximum furfural yield (6.18 g/100 g), our results are very encouraging as no additional catalysts or organic solvents were used.

In addition, phenolic compounds were also formed in the aqueous phase due to the decomposition of lignin (maximum content of total phenols was 72.94 ± 1.45 mg/g dry extract at 250 °C and 30 min), which probably influenced the antioxidant activity of the aqueous solution, which reached almost 50% at 250 °C and 60 min.

All compounds detected in the water-soluble product, i.e., carbohydrates, furfurals, and phenols, have great potential for the further synthesis of commodity chemicals, but it is necessary in the future to optimize the process parameters (temperature, pressure, time, material/water ratio, etc.) more precisely in order to maximize the yield of desired compounds and to develop efficient separation and fractionation methods for the water-soluble product in order to obtain specific compounds with the desired purity.

Although working with subcritical water can involve high equipment costs (special reactors made of corrosion-resistant materials such as stainless steel or titanium) and difficulties in optimization, its environmental benefits, versatility, and potential for selective extraction free of organic solvents and harmful chemicals make it a valuable alternative to established methods (solvent extraction or supercritical CO₂ extraction). For larger scale applications, overcoming these limitations through advances in reactor design, energy efficiency, and process integration will be key to widespread adoption.

Author Contributions: M.Č.: Writing—Original Draft, Writing—Review and Editing, Visualization, Investigation, Formal analysis, and Conceptualization. M.I.: Writing—Original Draft, Writing—Review and Editing, Investigation, and Formal Analysis. A.P.: Formal Analysis. M.Š.: Writing—Review and Editing, Supervision, Investigation, Conceptualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Slovenian Research and Innovation Agency Programme (research core funding No. P2-0421 and No. P2-0046).

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors would like to acknowledge financial support from the Slovenian Research Agency (research core funding No. P2-0421 and No. P2-0046). The authors also acknowledge the funding within the project “Upgrading National Research Infrastructures—RIUM”, which was co-financed by the Republic of Slovenia, the Ministry of Higher Education, Science and Innovation, and the European Union from the European Regional Development Fund.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Mujtaba, M.; Fernandes Fraceto, L.; Fazeli, M.; Mukherjee, S.; Savassa, S.M.; Araujo de Medeiros, G.; do Espírito Santo Pereira, A.; Mancini, S.D.; Lipponen, J.; Vilaplana, F. Lignocellulosic Biomass from Agricultural Waste to the Circular Economy: A Review with Focus on Biofuels, Biocomposites and Bioplastics. *J. Clean. Prod.* **2023**, *402*, 136815. [\[CrossRef\]](#)

2. Knez, Ž.; Hrnčič, M.K.; Čolnik, M.; Škerget, M. Chemicals and Value Added Compounds from Biomass Using Sub- and Supercritical Water. *J. Supercrit. Fluids* **2018**, *133*, 591–602. [\[CrossRef\]](#)
3. Bergamasco, S.; Zikeli, F.; Vinciguerra, V.; Sobolev, A.P.; Scarnati, L.; Tofani, G.; Scarascia Mugnozza, G.; Romagnoli, M. Extraction and Characterization of Acidolysis Lignin from Turkey Oak (*Quercus cerris* L.) and Eucalypt (*Eucalyptus camaldulensis* Dehnh.) Wood from Population Stands in Italy. *Polymers* **2023**, *15*, 3591. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Perera, S.M.H.D.; Wickramasinghe, C.; Samarasiri, B.K.T.; Narayana, M. Modeling of Thermochemical Conversion of Waste Biomass—A Comprehensive Review. *Biofuel Res. J.* **2021**, *8*, 1481–1528. [\[CrossRef\]](#)
5. Govumoni, S.P.; Koti, S.; Kothagouni, S.Y.; Venkateshwar, S.; Linga, V.R. Evaluation of Pretreatment Methods for Enzymatic Saccharification of Wheat Straw for Bioethanol Production. *Carbohydr. Polym.* **2013**, *91*, 646–650. [\[CrossRef\]](#)
6. Tshikovhi, A.; Motaung, T.E. Technologies and Innovations for Biomass Energy Production. *Sustainability* **2023**, *15*, 12121. [\[CrossRef\]](#)
7. Sarkar, N.; Ghosh, S.K.; Bannerjee, S.; Aikat, K. Bioethanol Production from Agricultural Wastes: An Overview. *Renew. Energy* **2012**, *37*, 19–27. [\[CrossRef\]](#)
8. Zielińska, M.; Bułkowska, K. Agricultural Wastes and Their By-Products for the Energy Market. *Energies* **2024**, *17*, 2099. [\[CrossRef\]](#)
9. Corn Production Worldwide 2023/24. Available online: <https://www.statista.com/statistics/1156213/global-corn-production/> (accessed on 2 December 2024).
10. Samanta, A.K.; Senani, S.; Kolte, A.P.; Sridhar, M.; Sampath, K.T.; Jayapal, N.; Devi, A. Production and *in Vitro* Evaluation of Xylooligosaccharides Generated from Corn Cobs. *Food Bioprod. Process.* **2012**, *90*, 466–474. [\[CrossRef\]](#)
11. Ayeni, A.O.; Daramola, M.O. Lignocellulosic Biomass Waste Beneficiation: Evaluation of Oxidative and Non-Oxidative Pretreatment Methodologies of South African Corn Cob. *J. Environ. Chem. Eng.* **2017**, *5*, 1771–1779. [\[CrossRef\]](#)
12. Li, H.; Chen, X.; Ren, J.; Deng, H.; Peng, F.; Sun, R. Functional Relationship of Furfural Yields and the Hemicellulose-Derived Sugars in the Hydrolysates from Corncob by Microwave-Assisted Hydrothermal Pretreatment. *Biotechnol. Biofuels* **2015**, *8*, 127. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Oni, O.; Olajuyigbe, F.; Fatokun, C. Effective Substrate Loading for Saccharification of Corn Cob and Concurrent Production of Lignocellulolytic Enzymes by *Fusarium Oxysporum* and *Sporothrix Carnis*. *Curr. Biotechnol.* **2019**, *8*, 109–115. [\[CrossRef\]](#)
14. Pointner, M.; Kuttner, P.; Obrlik, T.; Jäger, A.; Kahr, H. Composition of Corncobs as a Substrate for Fermentation of Biofuels. *Agron. Res.* **2014**, *12*, 391–396.
15. Ranilla, L.G.; Rios-Gonzales, B.A.; Ramírez-Pinto, M.F.; Fuentealba, C.; Pedreschi, R.; Shetty, K. Primary and Phenolic Metabolites Analyses, *In Vitro* Health-Relevant Bioactivity and Physical Characteristics of Purple Corn (*Zea mays* L.) Grown at Two Andean Geographical Locations. *Metabolites* **2021**, *11*, 722. [\[CrossRef\]](#)
16. Ramos-Escudero, F.; Muñoz, A.M.; Alvarado-Ortiz, C.; Alvarado, Á.; Yáñez, J.A. Purple Corn (*Zea mays* L.) Phenolic Compounds Profile and Its Assessment as an Agent against Oxidative Stress in Isolated Mouse Organs. *J. Med. Food.* **2012**, *15*, 206–215. [\[CrossRef\]](#)
17. Harakotr, B.; Suriharn, B.; Tangwongchai, R.; Scott, M.P.; Lertrat, K. Anthocyanin, Phenolics and Antioxidant Activity Changes in Purple Waxy Corn as Affected by Traditional Cooking. *Food Chem.* **2014**, *164*, 510–517. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Yong, K.J.; Wu, T.Y.; Lee, C.B.T.L.; Lee, Z.J.; Liu, Q.; Jahim, J.M.; Zhou, Q.; Zhang, L. Furfural Production from Biomass Residues: Current Technologies, Challenges and Future Prospects. *Biomass Bioenergy* **2022**, *161*, 106458. [\[CrossRef\]](#)
19. Qu, W.-H.; Xu, Y.-Y.; Lu, A.-H.; Zhang, X.-Q.; Li, W.-C. Converting Biowaste Corncob Residue into High Value Added Porous Carbon for Supercapacitor Electrodes. *Bioresour. Technol.* **2015**, *189*, 285–291. [\[CrossRef\]](#)
20. Anukam, A.I.; Goso, B.P.; Okoh, O.O.; Mamphweli, S.N. Studies on Characterization of Corn Cob for Application in a Gasification Process for Energy Production. *J. Chem.* **2017**, *2017*, 6478389. [\[CrossRef\]](#)
21. Wang, Q.; Qi, W.; Wang, W.; Zhang, Y.; Leksawasdi, N.; Zhuang, X.; Yu, Q.; Yuan, Z. Production of Furfural with High Yields from Corncob under Extremely Low Water/Solid Ratios. *Renew. Energy* **2019**, *144*, 139–146. [\[CrossRef\]](#)
22. Winarsih, S.; Siskawardani, D.D. Hydrolysis of Corncobs Using a Mixture of Crude Enzymes from *Trichoderma Reesei* and *Aspergillus Niger* for Bioethanol Production. *Energy Rep.* **2020**, *6*, 256–262. [\[CrossRef\]](#)
23. Soquetta, M.B.; Terra, L.d.M.; Bastos, C.P. Green Technologies for the Extraction of Bioactive Compounds in Fruits and Vegetables. *CyTA—J. Food* **2018**, *16*, 400–412. [\[CrossRef\]](#)
24. Pavlovič, I.; Knez, Ž.; Škerget, M. Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research. *J. Agric. Food Chem.* **2013**, *61*, 8003–8025. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Mohammadi, H.S.; Haghighi Asl, A.; Khajenoori, M. Production of Pharmaceutical Micro and Nano Particles by Subcritical Water Based Technologies: A Review. *J. Drug Deliv. Sci. Technol.* **2023**, *85*, 104621. [\[CrossRef\]](#)
26. Cheng, Y.; Xue, F.; Yu, S.; Du, S.; Yang, Y. Subcritical Water Extraction of Natural Products. *Molecules* **2021**, *26*, 4004. [\[CrossRef\]](#) [\[PubMed\]](#)

27. Jokić, S.; Gagić, T.; Knez, Ž.; Banožić, M.; Škerget, M. Separation of Active Compounds from Tobacco Waste Using Subcritical Water Extraction. *J. Supercrit. Fluids* **2019**, *153*, 104593. [\[CrossRef\]](#)
28. Erşan, S.; Güçlü Üstündağ, Ö.; Carle, R.; Schweiggert, R.M. Subcritical Water Extraction of Phenolic and Antioxidant Constituents from Pistachio (*Pistacia vera* L.) Hulls. *Food Chem.* **2018**, *253*, 46–54. [\[CrossRef\]](#)
29. Čolnik, M.; Irgolič, M.; Perva, A.; Škerget, M. The Conversion of Pistachio and Walnut Shell Waste into Valuable Components with Subcritical Water. *Processes* **2024**, *12*, 195. [\[CrossRef\]](#)
30. Ravber, M.; Knez, Ž.; Škerget, M. Isolation of Phenolic Compounds from Larch Wood Waste Using Pressurized Hot Water: Extraction, Analysis and Economic Evaluation. *Cellulose* **2015**, *22*, 3359–3375. [\[CrossRef\]](#)
31. Gagić, T.; Knez, Ž.; Škerget, M. Subcritical Water Extraction of Chestnut Bark and Optimization of Process Parameters. *Molecules* **2020**, *25*, 2774. [\[CrossRef\]](#)
32. Daneshvar, S.; Hidemi, N.; Salak, F.; Mahinpey, N. Degradation of Textile Dyes under Subcritical Water Conditions in the Presence of Hydrogen Peroxide. *Can. J. Chem. Eng.* **2014**, *92*, 615–622. [\[CrossRef\]](#)
33. Jones, A.D.; Morehead, A.T.; Yang, Y. Degradation and Extraction of Organochlorine Pollutants from Environmental Solids under Subcritical Water Conditions. *Molecules* **2023**, *28*, 5445. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Son, S.-H.; Lee, J.-H.; Lee, C.-H. Corrosion Phenomena of Alloys by Subcritical and Supercritical Water Oxidation of 2-Chlorophenol. *J. Supercrit. Fluids* **2008**, *44*, 370–378. [\[CrossRef\]](#)
35. Jing, Y.; Guo, Y.; Xia, Q.; Liu, X.; Wang, Y. Catalytic Production of Value-Added Chemicals and Liquid Fuels from Lignocellulosic Biomass. *Chem* **2019**, *5*, 2520–2546. [\[CrossRef\]](#)
36. Brown, J.; Lindstrom, J.K.; Ghosh, A.; Rollag, S.A.; Brown, R.C. Production of Sugars from Lignocellulosic Biomass via Biochemical and Thermochemical Routes. *Front. Energy Res.* **2024**, *12*, 1347373. [\[CrossRef\]](#)
37. Abaide, E.R.; Ugalde, G.; Di Luccio, M.; de FPM Moreira, R.; Tres, M.V.; Zabot, G.L.; Mazutti, M.A. Obtaining Fermentable Sugars and Bioproducts from Rice Husks by Subcritical Water Hydrolysis in a Semi-Continuous Mode. *Bioresour. Technol.* **2019**, *272*, 510–520. [\[CrossRef\]](#) [\[PubMed\]](#)
38. Dos Santos, M.S.N.; Zabot, G.L.; Mazutti, M.A.; Ugalde, G.A.; Rezzadori, K.; Tres, M.V. Optimization of Subcritical Water Hydrolysis of Pecan Wastes Biomasses in a Semi-Continuous Mode. *Bioresour. Technol.* **2020**, *306*, 123129. [\[CrossRef\]](#) [\[PubMed\]](#)
39. Prado, J.M.; Vardanega, R.; Nogueira, G.C.; Forster-Carneiro, T.; Rostagno, M.A.; Maugeri Filho, F.; Meireles, M.A.A. Valorization of Residual Biomasses from the Agri-Food Industry by Subcritical Water Hydrolysis Assisted by CO₂. *Energy Fuels* **2017**, *31*, 2838–2846. [\[CrossRef\]](#)
40. Jokić, S.; Gagić, T.; Knez, Ž.; Šubarić, D.; Škerget, M. Separation of Active Compounds from Food By-Product (Cocoa Shell) Using Subcritical Water Extraction. *Molecules* **2018**, *23*, 1408. [\[CrossRef\]](#)
41. Ciftci, D.; Saldaña, M.D.A. Hydrolysis of Sweet Blue Lupin Hull Using Subcritical Water Technology. *Bioresour. Technol.* **2015**, *194*, 75–82. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Gagić, T.; Perva-Uzunalić, A.; Knez, Ž.; Škerget, M. Hydrothermal Treatment of Sugars to Obtain High-Value Products. *J. Serbian Chem. Soc.* **2020**, *85*, 97–109. [\[CrossRef\]](#)
43. Alonso-Riaño, P.; Illera, A.E.; Benito-Román, O.; Melgosa, R.; Bermejo-López, A.; Beltrán, S.; Sanz, M.T. Degradation Kinetics of Sugars (Glucose and Xylose), Amino Acids (Proline and Aspartic Acid) and Their Binary Mixtures in Subcritical Water: Effect of Maillard Reaction. *Food Chem.* **2024**, *442*, 138421. [\[CrossRef\]](#)
44. Lu, Y.J.; Jin, H.; Guo, L.J.; Zhang, X.M.; Cao, C.Q.; Guo, X. Hydrogen Production by Biomass Gasification in Supercritical Water with a Fluidized Bed Reactor. *Int. J. Hydrog. Energy* **2008**, *33*, 6066–6075. [\[CrossRef\]](#)
45. Li, H.; Deng, A.; Ren, J.; Liu, C.; Lu, Q.; Zhong, L.; Peng, F.; Sun, R. Catalytic Hydrothermal Pretreatment of Corn cob into Xylose and Furfural via Solid Acid Catalyst. *Bioresour. Technol.* **2014**, *158*, 313–320. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Donahue, C.J.; Rais, E.A. Proximate Analysis of Coal. *J. Chem. Educ.* **2009**, *86*, 222. [\[CrossRef\]](#)
47. Gani, A.; Adisalamun; Arkan, D.M.R.; Suhendrayatna; Reza, M.; Erdiwansyah; Saiful; Desvita, H. Proximate and Ultimate Analysis of Corn cob Biomass Waste as Raw Material for Biocoke Fuel Production. *Case Stud. Chem. Environ. Eng.* **2023**, *8*, 100525. [\[CrossRef\]](#)
48. Sultana, B.; Anwar, F.; Przybylski, R. Antioxidant Potential of Corn cob Extracts for Stabilization of Corn Oil Subjected to Microwave Heating. *Food Chem.* **2007**, *104*, 997–1005. [\[CrossRef\]](#)
49. Brandt, A.; Gräsvik, J.; Hallett, J.P.; Welton, T. Deconstruction of Lignocellulosic Biomass with Ionic Liquids. *Green Chem.* **2013**, *15*, 550–583. [\[CrossRef\]](#)
50. Knierim, L.; Uhl, A.; Schmidt, A.; Flemming, M.; Höß, T.; Treutwein, J.; Strube, J. Pressurized Hot Water Extraction as Green Technology for Natural Products as Key Technology with Regard to Hydrodistillation and Solid–Liquid Extraction. *ACS Omega* **2024**, *9*, 31998–32010. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Lü, X.; Saka, S. New Insights on Monosaccharides' Isomerization, Dehydration and Fragmentation in Hot-Compressed Water. *J. Supercrit. Fluids* **2012**, *61*, 146–156. [\[CrossRef\]](#)

52. Gagić, T.; Perva-Uzunalić, A.; Knez, Ž.; Škerget, M. Hydrothermal Degradation of Cellulose at Temperature from 200 to 300 °C. *Ind. Eng. Chem. Res.* **2018**, *57*, 6576–6584. [\[CrossRef\]](#)
53. Delbecq, F.; Wang, Y.; Muralidhara, A.; El Ouardi, K.; Marlair, G.; Len, C. Hydrolysis of Hemicellulose and Derivatives—A Review of Recent Advances in the Production of Furfural. *Front. Chem.* **2018**, *6*, 146. [\[CrossRef\]](#)
54. Yu, F.; Ruan, R.; Chen, P.; Deng, S.; Liu, Y.; Lin, X.; Deng, S.; Paul, S.; Liu, Y. Liquefaction of Corn Cobs with Supercritical Water Treatment. *Trans. ASABE* **2007**, *50*, 175–180. [\[CrossRef\]](#)
55. Mok, W.S.L.; Antal, M.J., Jr. Uncatalyzed Solvolysis of Whole Biomass Hemicellulose by Hot Compressed Liquid Water. *Ind. Eng. Chem. Res.* **1992**, *31*, 1157–1161. [\[CrossRef\]](#)
56. Brebu, M.; Vasile, C. Thermal Degradation of Lignin—A Review. *Cellul. Chem. Technol.* **2010**, *44*, 353–363.
57. Škerget, M.; Kotnik, P.; Hadolin, M.; Hraš, A.R.; Simonič, M.; Knez, Ž. Phenols, Proanthocyanidins, Flavones and Flavonols in Some Plant Materials and Their Antioxidant Activities. *Food Chem.* **2005**, *89*, 191–198. [\[CrossRef\]](#)
58. Dong, J.; Cai, L.; Zhu, X.; Huang, X.; Yin, T.; Fang, H.; Ding, Z. Antioxidant Activities and Phenolic Compounds of Cornhusk, Corncob and Stigma Maydis. *J. Braz. Chem. Soc.* **2014**, *25*, 1956–1964. [\[CrossRef\]](#)
59. Wolf, M.; Berger, F.; Hanstein, S.; Weidenkaff, A.; Endreß, H.-U.; Oestreich, A.M.; Ebrahimi, M.; Czermak, P. Hot-Water Hemicellulose Extraction from Fruit Processing Residues. *ACS Omega* **2022**, *7*, 13436–13447. [\[CrossRef\]](#)
60. Rasmussen, H.; Sørensen, H.R.; Meyer, A.S. Formation of Degradation Compounds from Lignocellulosic Biomass in the Biorefinery: Sugar Reaction Mechanisms. *Carbohydr. Res.* **2014**, *385*, 45–57. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Tongtummachat, T.; Akkarawatkhoosith, N.; Kaewchada, A.; Jaree, A. Conversion of Glucose to 5-Hydroxymethylfurfural in a Microreactor. *Front. Chem.* **2020**, *7*, 951. [\[CrossRef\]](#)
62. Roy, R.; Rahman, M.S.; Amit, T.A.; Jadhav, B. Recent Advances in Lignin Depolymerization Techniques: A Comparative Overview of Traditional and Greener Approaches. *Biomass* **2022**, *2*, 130–154. [\[CrossRef\]](#)
63. Yong, T.L.-K.; Matsumura, Y. Kinetic Analysis of Lignin Hydrothermal Conversion in Sub- and Supercritical Water. *Ind. Eng. Chem. Res.* **2013**, *52*, 5626–5639. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.