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Article

Barley Straw Fiber Extraction in the Context of a Circular Economy

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Abstract: The potential for sustainable lignocellulosic agro-waste is immense, owing to the fact that it represents the most abundant organic compound on Earth. It is a valuable and desirable source for material production across numerous industries due to its abundance, renewability, and biodegradability. This paper explores the world of barley fibers, which are extracted from the straw of two different cultivars (old Rex or new Barun) and have tremendous potential for use, primarily for technical textiles. The quantity of the extracted fibers depends both on the type of barley used and on climate conditions that influence the plants' growth, resulting in fiber yields ranging from 14.82% to 19.59%. The chemical composition of isolated fibers revealed an optimal content of cellulose and lignin in barley fibers isolated from the Rex variety. Those results were confirmed with FTIR analysis, which revealed a lower intensity of peaks associated with hemicellulose and lignin and, therefore, indicated their better removal after the chemical maceration process. In terms of fiber density, the quality of the fibers was comparable to that of cotton fibers, but they differed significantly in moisture regain (10.37–11.01%), which was higher. Furthermore, sufficient fiber tenacity (20.31–23.08 cN/tex) was obtained in a case of old-variety Rex, indicating the possibility of spinning those fibers into yarns, followed by their extended usage for apparel. Additionally, our paper reveals the possibility of fulfilling the requirements of the zero waste principle due to the fact that a high percentage of solid waste left after the fiber extraction (26.3–32.3%) was afterwards successfully used for the production of biofuels, enabling the closing of the loop in a circular economy.

Keywords: straw fibers; agro-waste; fiber density; circular economy

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1. Introduction

We live in an era in which sustainable practices are at the core of all research. Scientists are searching for new biodegradable, sustainable, and renewable sources of textile fibers and materials. For this reason, the use of natural fiber sources has significantly increased in popularity. Furthermore, there is a rising trend of environmental awareness among people who are becoming more aware of the pollution of our planet and the disturbance it has caused to the balance of our planet's ecosystems. The manufacturing of synthetic fibers has also contributed to this imbalance, with about 60% of all fiber output worldwide being synthetic, and polyester (PET) and polyamide (PA) dominating.

Textiles made from synthetic materials have the potential to release microplastics (less than 5 mm in size) into the environment during production and cleaning processes [1]. This issue has become a hot topic, but at the same time, it is an inspiration to use natural resources in a more sustainable manner. Natural fibers have stood out among these resources as an affordable, healthy, and environmentally friendly option. The term "environmental sustainability" refers to finding a balance between human needs and nature preservation, and global concerns are oriented towards achieving this.

Due to the amount of pollution on our planet, innovative solutions are needed now more than ever before, and greener alternatives are taking place in various applications. Biowaste has now become a prominent raw material, and one such solution is biowaste from barley straw, which is considered a second-generation biomass. Barley is the fourth-largest grain crop in the world, grown in more than 100 countries, making it very interesting and widely available. In the last ten years, Europe generated over 60% of the world's production of barley, and Asia 15%, while North and South America produced 13%, respectively. Its distribution is worldwide, and it grows in different climate conditions. Today, thanks to its biowaste, its importance as a crop may rise even more [2,3].

People have been harvesting barley for 10,000 years, making it one of the earliest domesticated crop species in the world. Initially, humans consumed wild barley, which was later developed into a cultivated crop. Wild barley (*Hordeum spontaneum* L.) was discovered by the German botanist Carl Koch. Like all cereals and their ancestors, the barley we have been using nowadays and wild barley share the same genes [4–7].

1.1. Barley's Anatomy

Understanding the anatomy of plants and their different parts is essential for their cultivation and agricultural productivity [8]. Additionally, this knowledge is necessary for researchers and breeders attempting to improve barley varieties for diverse applications.

Barley (*Hordeum vulgare* L.) is a cereal crop that belongs to the family of Poaceae, which is economically the most important order of plants. This order contains more than 18,000 species of monocotyledons, meaning flowering plants characterized by a single seed leaf [8]. Barley differs in its grain arrangement. There are two main types of barley, based on the number and arrangement of barley kernels (seeds/grains) on the central stem (rachis): two-row barley and six-row barley (Figure 1) [8]. These two types have different characteristics, based on their plant anatomy and morphology.

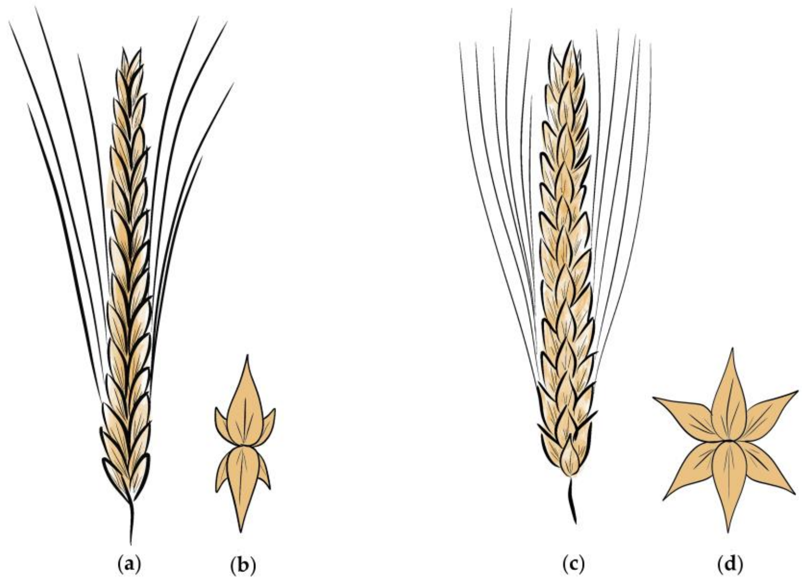


Figure 1. Two main types of barley, where: (**a**) Ear of two-row barley, (**b**) Arrangement of two-row barley grains, (**c**) Ear of six-row barley and (**d**) Arrangement of six-row barley grains.

Two-row barley grains are shorter and have a higher amount of starch content, while six-row barley grains are longer, containing less starch and more proteins. That is why the two-row barley is more desirable in the brewery industry.

1.2. Barley's Harvesting and Usage

The most common way of harvesting barley is by using a combine that cuts the barley and separates the grain from the straw. Thanks to its nutritional value, barley is widely used for food, animal feed, and the production of beer and other alcoholic beverages.

According to Zohary and Hopf [9], all parts of the barley plant, including the straw, grain derivatives, and hull, are classified as agro-residues [10]. After the harvest, huge amounts of agro-residues (barley straw) are usually left on the fields, burnt, and left unused.

This kind of disposal negatively impacts the environment and may endanger ecosystems, especially if left untreated. Such disposal of biowaste requires a more sustainable approach. Legal restrictions within the EU have made it illegal to burn agricultural waste in the field [11–14].

Since it is widely known that cereal straws are an important part of waste lignocellulosic biomass and they have a significant amount of cellulose (approx. 30–50%) their usage as a cellulose source is promising [15,16]. A more sustainable approach to reducing high amounts of agro-residue involves utilizing this source as a renewable source of lignocellulosic fibers. This kind of biomass represents a biomass of the second generation and stands out as a promising solution in our quest for a sustainable future. Additionally, it has huge potential for being a valuable raw material for various applications, such as textiles, pulp and paper production, bioplastics production, and as a source of thermal-electric power [5,17–20]. According to the literature presented in Table 1, barley straw is mainly used in its initial form of straw as reinforcements for construction materials [21–24]. Additionally, barley straw can be used as a source for biofuel production [23] or for aerogel production, which can consequently be used as a cleaner for spilled oil [25]. Barley cellulose fibers isolated from barley straw are commonly used in the composite and paper industry since the extracted fibers can be modified or combined with other materials and successfully enhance the properties of the final product [18,26–31].

Table 1. Literature review based on barley straw usage.

Lignocellulosic Biomass Source	Description	References
Barley straw	Barley thermomechanical fibers as reinforcements in composite material (length of fibers is 745 μm ± 21, diameter 19.6 μm ± 0.6)	[32,33]
Barley straw	Barley cellulose pulp for paper sheet production	[26]
Barley straw	Barley straw as reinforcements for earth-based construction materials (length of straw is 1–6 cm)	[21]
Barley straw	Barley cellulose pulp for paper sheet production	[27]
Barley straw	Barley fibers for various applications (length of fibers is 0.7–3.1 mm, diameter 7–24 μm)	[22]
Barley straw	Digestion of barley straw for biofuel production	[23]
Barley straw	Barley fibers for aerogel production for oil spillage clean-up (diameter of fibers is in the range of 5–12.5 μm)	[25]
Barley straw	Barley straw as reinforcements in composite materials	[28]
Barley straw	Barley cellulose pulp as reinforcements for nanocomposites	[18]
Barley straw	Barley cellulose pulp (length: 0.35–0.44 mm)	[34]
Barley straw	Barley crude and purified cellulose fibers	[35]
Barley straw	Barley cellulose fibers for sheet production	[15]
Barley straw	Barley fibers as reinforcements for composite materials	[29]
Barley straw	Barley straw as building insulation materials	[24]

Up to now, cellulose fibers have been isolated from the plant stem using different methods such as retting (Table 2), physical and/or mechanical procedures, and their combinations [36–39].

Some of the most commonly used retting methods for fiber isolation from the plant stem can be applied to cereal straw [39].

Fibers from barley straw are most often extracted via chemical retting methods, followed by physical and mechanical processes, using extreme conditions in terms of temperature, pretreatment time, chemicals, etc., and in this way, fibers of relatively short lengths are isolated. The best usage of such short fibers is in the paper industry, but longer fibers could be more efficiently applied as reinforcements in the composite industry, or even in the clothing industry if their length is sufficient for spinning into yarn [40]. In this paper, reduced alkali concentration was applied for chemical retting in order to preserve the fiber quality as much as possible. Additionally, this entire process of isolating the fibers from the barley straw and gathering solid and liquid waste during the chemical maceration process contributes to the generation of a circular economy. After the use of barley grain for food, agro-waste in the form of straw becomes a raw material for fiber production, while solid waste from fiber production, together with evaporated waste chemicals (filtrates), becomes an input raw material for solid biofuel production.

Table 2. Retting methods for fiber isolation.

Methods	Medium	Advantages	Disadvantages	Retting Duration
Biological retting	Water	Fibers of great uniformity and high quality	Ecological unacceptability because this method creates chemical compounds such as CO_2, H_2, CH_4, NH_3, and H_2S that can affect the health of living organisms from the water	7–14 days
	Dew	Easier pectin removal	Fibers are contaminated with soil, inconsistent quality, and reduced strength	2–3 weeks
	Enzymes	Cleaner and faster process that enables specific properties of fibers	Higher cost and lower fiber strength	12–24 h
Chemical retting	Acid, alkali, etc.	Cleaner and smoother surface of the fibers within a short period	Deterioration of fiber strength and other important properties if aggressive and highly concentrated chemicals are used	1–3 h

Our research investigated the potential of different two-row barley varieties (Barun and Rex) for fiber production, and the determination of fiber quality was determined from the perspective of their possible application for apparel or technical textiles.

The successful isolation of barley fibers from straw and their usage in the clothing industry or for technical textiles presents a novel and sustainable solution.

2. Materials and Methods

2.1. Barley Variety

Barun barley is one of the primary varieties of winter two-row barley from the selection program of the Osijek Agricultural Institute. It has a low, firm, and elastic stem that is resistant to lodging and a large and uniform grain. Additionally, it is tolerant of the most common diseases [41]. Rex barley is also a winter two-row cultivar, having a well-formed, round grain. It is low-growing and highly resistant to diseases [42]. The barley straw used in this study was obtained from the experimental field set up by the Osijek Agricultural Institute.

2.2. Biomass Pretreatments and Fiber Extraction

A chemical retting process was applied according to a slight modification of a method found in the literature review [43]. The barley biomass was cut into lengths of approximately 10 to 12 cm and subjected to chemical treatment in three parallel baths containing 3% sodium hydroxide (NaOH). The bath ratio was 1:20, and the processing time was 90 min. The fibers and residues were removed from the liquid and washed first with hot water and then with cold water. The next steps involved neutralization with acetic acid (CH_3COOH) and washing with cold water. The liquid in which the extraction took place was filtered and separated to become black liquor. The mixture of fibers and residue was then dried overnight at 60 °C. The next step was the separation of the fibers from the residue, followed by weighing both the fibers and residue. In order to better explain the experimental processes in this paper, an experimental flow chart is presented in Figure 2.

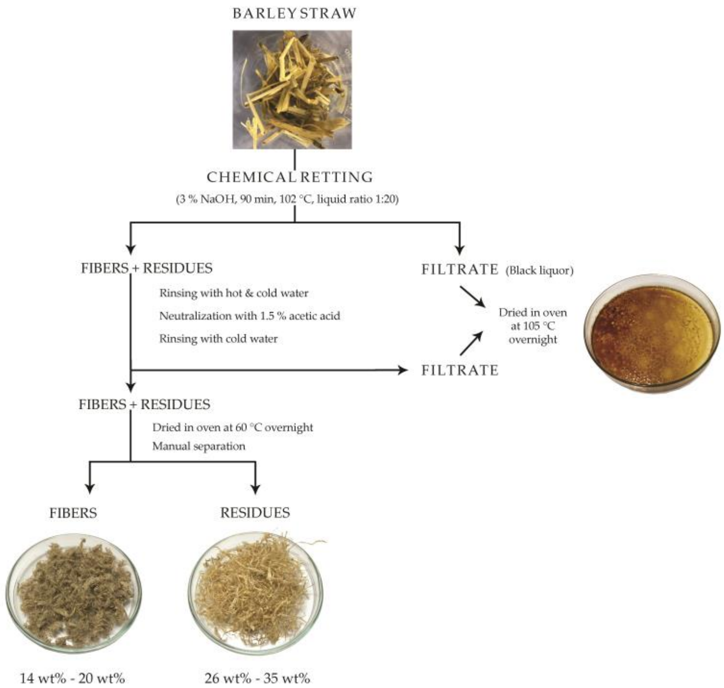


Figure 2. Experimental flow chart.

2.3. Fiber Testing

The following tests were performed: the determination of fiber and residue yields, tensile properties, the length of the fibers, the moisture content, the moisture regain, and density. Additionally, fiber morphology and chemical composition testing were determined on both the initial and extracted barley straw.

Fiber and residue yield percentages (*Yf*% and *Yr*%) were determined via the gravimetric method using Equations (1) and (2) [44]. All measurements were performed in triplicate.

$$Yf\% = \left(\frac{mf}{mi}\right) \times 100 \tag{1}$$

$$Yr\% = \left(\frac{mr}{mi}\right) \times 100 \tag{2}$$

where *Yf*% = fiber yield percentage, *mf* = the mass of barley fibers extracted from the barley straw, *mi* = the initial mass of the barley straw, *Yr*% = the residue yield percentage, and *mr* = the mass of barley residues after the fibers' extraction.

The tensile properties of 50 individual fibers of each variety were examined using the Vibroskop 500 and Vibrodyn 500 devices (Lenzing Instruments, Gampern, Austria). The preload, testing speed, and gauge length values were 1500 mg, 3 mm/min, and 5 mm, respectively.

The fiber length of 100 individual fibers of each variety was determined using a measuring scale placed parallel to the straightened but unstretched fiber.

To determine the moisture content and moisture regain, the mass of the air-dried sample was first calculated. The same sample was then placed in a climate chamber and conditioned for 24 h under standard atmosphere conditions. The mass of the conditioned sample was determined, and the sample was then dried for 24 h. Finally, the mass of the absolutely dried sample was calculated. The following Equations (3) and (4) were then used to determine the moisture content and moisture regain, respectively. All measurements were performed in triplicate.

$$MC\% = \left(\frac{m1 - m2}{m1}\right) \times 100 \tag{3}$$

$$MR\% = \left(\frac{m3 - m2}{m2}\right) \times 100 \quad (4)$$

where $MC\%$ = moisture content, $m1$ = the mass of an air-dried sample, $m2$ = the mass of an absolute dried sample, $MR\%$ = the moisture regain, and $m3$ = the mass of a conditioned sample.

The density was measured using the gas pycnometer Ultrapyc 1200e (Anton Paar, Vernon Hills, IL, USA). The actual density of the barley fibers was determined under atmospheric conditions according to the ASTM D8171-18 standard [45]. High-purity nitrogen (N_2) gas was used because of its ability to penetrate the smallest pores, allowing for the highest measurement precision. All measurements were performed in triplicate.

The morphology of the fibers was analyzed using a scanning electron microscope, Mira II LMU (Tescan, Brno, Czech Republic). Prior to SEM examination, the fibers were coated with chrome to achieve better sample conductivity.

The major chemical constituents (cellulose, hemicellulose, and lignin) of the barley straw, fibers, and residues were determined using an automatic fiber analyzer, the ANKOM Delta Fiber Analyzer (ANKOM Technology, New York, NY, USA). According to the manufacturer's methods, the mass fractions of neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) were determined using F57 filter bags. Hemicellulose content was calculated by subtracting ADF from NDF and cellulose content by subtracting ADL from ADF. NDF represents the residue after digestion of the sample in the detergent solution and was mainly composed of hemicellulose, cellulose, and lignin. ADF represents the residue after digestion using sulfuric acid (H_2SO_4) and detergent and consists mainly of cellulose and lignin, while ADL represents lignin. All measurements were performed in triplicate.

The evaluation of the barley straw's and fibers' surface chemistry was performed with a Spectrum 100 FTIR spectrometer (Perkin Elmer, Buckinghamshire, UK) using the attenuated total reflection method. Five different measurements for each fiber were evaluated, and the average value was considered. All spectra were registered from 4000 cm^{-1} to 380 cm^{-1}, with a resolution of 4 cm^{-1} and four scans.

3. Results and Discussion

The first part of the experiment involved determining the fiber and residue yields. The experiment included two series of results: one for the old-variety Barun and another for the new-variety Rex. The influence of climate conditions was investigated over a two-year period (2021 and 2022).

3.1. Biomass Pretreatment

Up to this point, the most frequently used chemical agent in the pretreatment process has been sodium hydroxide (NaOH), also known as caustic soda. It is a versatile chemical compound used in various sectors, including the textile industry, where it is one of the key agents in textile processing. Its main usage in textiles is related to the mercerization procedure, but it is frequently used for dyeing, printing, neutralization, cleaning, and alkali scouring to remove all remaining impurities from the fibers [46–48]. Apart from that, NaOH is often used as an active agent in the process of the chemical extraction of textile fibers from lignocellulosic biomass. It is generally known that alkaline treatment with caustic soda removes hemicellulose and lignin, simultaneously releasing cellulose fibers and improving their physico-chemical and mechanical properties [49–52].

However, the negative aspect of NaOH lies in its character, as it is a strong base and hazardous to the environment. Therefore, its concentration should be minimized [53]. In our research, its quantity was reduced to 3%. The results revealed that the application of a more environmentally friendly option still results in a high fiber yield, ranging from 14.82% to 19.59%.

3.2. Fiber and Residue Yield

One of the goals of our project was to investigate how strongly different varieties of barley (the "old" and "new" cultivars) influence the fiber yield. The extracted fibers were intended for technical textile usage, while the remaining solid residues, ranging from 26.03% to 32.90%, were intended for biofuel production and were tested accordingly.

The results revealed that the old barley variety (Rex) harvested in 2021 had the highest fiber yield of 19.59% (Figure 3a), while its residue yield was 26.03% (Figure 3b). The lowest fiber yield of 14.82% was obtained from the new variety, Barun, collected in 2021, while its residue yield was 28.50%. An opposite trend was detected in the 2022 harvest, where the fiber yield of the Rex variety was slightly lower than that of the Barun variety (15.25% compared to 16.07%). The residue yield for the Rex variety was 28.03%, compared to the higher value of 32.90% for Barun.

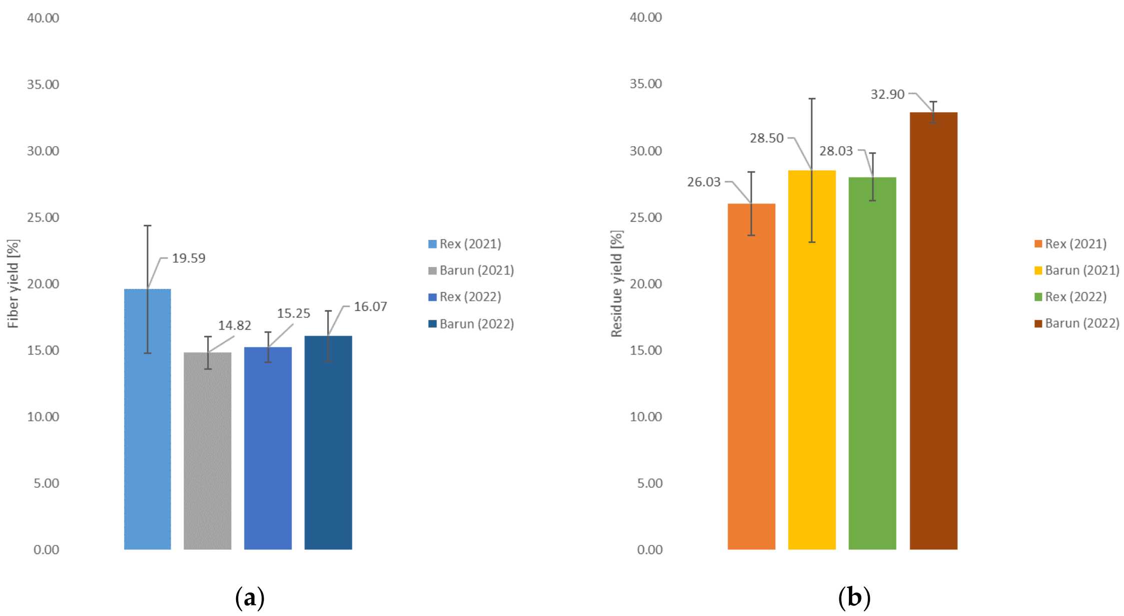


Figure 3. (**a**) Fiber yield and (**b**) residual yield of the Rex and Barun varieties (2021 and 2022).

The total amount of precipitation from sowing to harvest is presented in Table 3. It is noticeable that the amount of precipitation for the 2021 harvest was much higher, at 433.7 mm, compared to 363.1 mm for the 2022 harvest, indicating that the year 2022 was characterized by more drought [54].

Table 3. Total amount of precipitation from October 2020 to May 2022.

	X	XI	XII	I	II	III	IV	V
2020	86.5	18.0	61.4	/	/	/	/	/
2021	72.9	71.0	75.6	77.5	36.3	34.4	60.7	58.9
2022	/	/	/	7.5	28.7	6.4	35.0	66.0

The total amount of precipitation for the 2021 harvest is the gray area, while for the 2022 harvest, it is the yellow area.

Considering that the descriptive statistical analysis indicated higher variability in the fiber yield results for the 2021 Rex variety, it can be concluded, from the perspective of different barley varieties and the climatological data in the 2020–2022 period (Table 3), that the new barley variety, Barun, showed a positive trend of higher fiber and residue yields despite the negative effect of climate change, specifically the increase in drought.

3.3. Tensile Properties

The investigation of the mechanical properties of different varieties of barley fibers consisted of breaking tenacity, Young's modulus, and elongation measurements (Table 4). It can be concluded that the fiber breaking tenacity for the varieties from 2021 was slightly higher than the fiber tenacity of varieties from 2022. The Barun variety from 2021 showed the highest fiber tenacity of 25.63 cN/tex, indicating the spinning possibility of these fibers into yarn [40]. Fibers are spinnable into yarn if their minimal tenacity is within the range of 10 cN/tex–25 cN/tex but with the indication that fibers whose strength corresponds to the lower limit of the minimum range must show a good ability to withstand deformation [40]. All the tested samples fulfilled the minimal requirements for tenacity and had sufficient resistance to deformation. Although both varieties of fibers from 2022 had lower Young's modulus values in comparison to the 2021 varieties, they were still spinnable due to their characteristics of softness and high cohesion forces [55] and a rough surface (confirmed via SEM).

Table 4. Tensile properties of barley fibers.

	Rex (2021)			Rex (2022)			Barun (2021)			Barun (2022)		
	T [cN/tex]	YM [cN/tex]	E [%]	T [cN/tex]	YM [cN/tex]	E [%]	T [cN/tex]	YM [cN/tex]	E [%]	T [cN/tex]	YM [cN/tex]	E [%]
Average	23.08	440.30	4.51	20.31	298.39	6.11	25.63	619.30	3.89	13.07	243.76	5.40
SD	9.96	245.85	1.60	14.74	278.66	2.22	13.35	490.88	1.13	9.29	239.15	1.94
CV [%]	43.16	55.84	35.44	72.56	93.39	36.29	52.10	79.26	28.90	71.07	98.11	35.85
SE [%]	2.76	68.15	0.44	4.09	77.24	0.62	3.70	136.06	0.31	2.58	66.23	0.54

T—breaking tenacity; YM—Young's modulus; E—elongation; SD—standard deviation; CV—coefficient of variation, and SE—standard error.

Natural fibers, though very attractive in the means of their low density and environmental compatibility, show non-uniformity in their properties. That is especially noticeable within the variability of the diameter along their length [56]. This property, together with other factors such as the retting method used for fiber isolation, pore size distribution, fiber type and variety, gauge length, strain rate, average number of tested fibers, etc., have been found to affect tensile properties, which explains the high values of statistical parameters (SD and CV) and, thus, the high variability of the results. The tensile properties of cellulose fiber representatives in each category (seed fibers, stem (bast) fibers, and leaf and fruit fibers) are presented in Table 5.

Table 5. Tensile properties of some of the most commonly used fibers from the seed, stem, leaf, and fruit categories in comparison to the barley fibers from this study.

Fiber Category	Fiber	Tensile Strength (MPa)	Young's Modulus (Gpa)	Elongation (%)	Reference
Seed fiber	Cotton	287–597	5.5–12.6	3–10	[57]
Stem fiber	Flax	345–900	27–80	1.2–1.6	[58]
	Hemp	300–800	30–70	1.3–1.6	
	Jute	200–800	10–55	1.4–1.8	
	Spanish broom	500–1100	15–20	3–9	[55]
Straw/stem fiber	Barley	190–380	3–10	3–7	This study
Leaf fiber	Sisal	100–800	9–28	2–3	[58]
Fruit fiber	Coir	13–220	4–6	15–40	

Values regarding strength and modulus were calculated from the results presented in Table 4 and approximated on the basis of a circular cross section of the barley fibers.

It was noticeable that the tensile properties of barley fibers corresponded to the lower range of given properties in the case of strength but fit very well with cotton fibers, according to the deformation parameters (Young's modulus and elongation).

3.4. Fiber Length

As part of the project "Production of food, bio-composites, and biofuels from cereals in the circular bioeconomy KK.05.1.1.02.0016", the possibility of isolating cellulose fibers from barley straw and their quality for usage in the production of technical textiles, specifically biocomposites and biofilters, was investigated. The chosen barley varieties, Rex and Barun, had stems growing up to 80 cm in height [59]. In the fiber extraction process, a chemical maceration procedure was carried out in an alkaline medium using a 3% sodium hydroxide solution. Although the literature often mentions the production of cellulose pulp from barley, which is then used to produce biofilters [18,26,33,60], there are almost no scientific papers on the extraction of long barley fibers, which would be even more suitable for the reinforcement of composite materials [15]. Natural fibers, used as reinforcements in composites, have been categorized by Djafari Petroudy into two groups based on their length: short fibers (1–5 mm) and long fibers (5–50 mm) [61].

One of the most important properties of fiber-reinforced composites that affects the strength of the final product is the critical fiber length, which differs based on the type of fiber [62]. If the fiber reinforcements are shorter than the critical length, the composite will not have satisfactory strength because the necessary stress transfer between the fiber and the polymer matrix will not occur. The ends of the fibers act as the points where stress concentration is the highest and where cracking occurs. Therefore, a large volume of short fibers inside the composite will cause a high concentration of free fiber ends, leading to a high possibility of cracks occurring inside the composite when it is exposed to stress forces [32]. In cases where the fiber's length is greater than the critical length, and the strength of the composite is still not satisfactory, the reason is the entanglement of too-long fibers during processing, causing the deterioration of the mechanical properties due to the poor dispersion of fibers in the matrix [61].

The fibers used in this research were obtained from barley straw via an alkaline maceration process with a low NaOH concentration, resulting in technical fibers (bundles of fibers consisting of elementary or ultimate fibers, as presented in SEM images below in a text). The straw was chopped to a length of 10–12 cm before the chemical maceration process, which also affected the length of the isolated fibers. The isolated fiber length is presented in Table 6, and the distribution of their lengths in Figure 4. The Rex variety harvested in 2021 showed the greatest fiber length—4.03 cm—but also the highest variability in results. According to a two-way ANOVA, there was a significant difference in the length means within the following variables: barley variety and harvesting year (Fcritical < Fstatistical and p-value < 0.05 for each variable). The length of cellulose fibers is influenced by many factors, such as a combination of the genetic factors of the plant, its anatomy and composition, environmental conditions, the growth stage, stress factors, pretreatment, and the stem processing procedures used to isolate the fibers, etc. [63]. From these results, it can be concluded that the old-variety Rex produces fibers of longer length than the new-variety Barun. Also, weather conditions during growth and the fact that 2022 was drier compared to 2021 negatively affected the length of the fibers.

Table 6. Length of technical fibers isolated from different barley varieties collected within a 2-year period.

	Rex (2021)	Rex (2022)	Barun (2021)	Barun (2022)
Average [cm]	4.03	2.40	3.20	2.26
Standard deviation [cm]	1.35	0.77	1.05	0.66
Coefficient of variation [%]	33.56	31.98	32.68	29.26
Standard error [%]	0.27	0.15	0.20	0.13

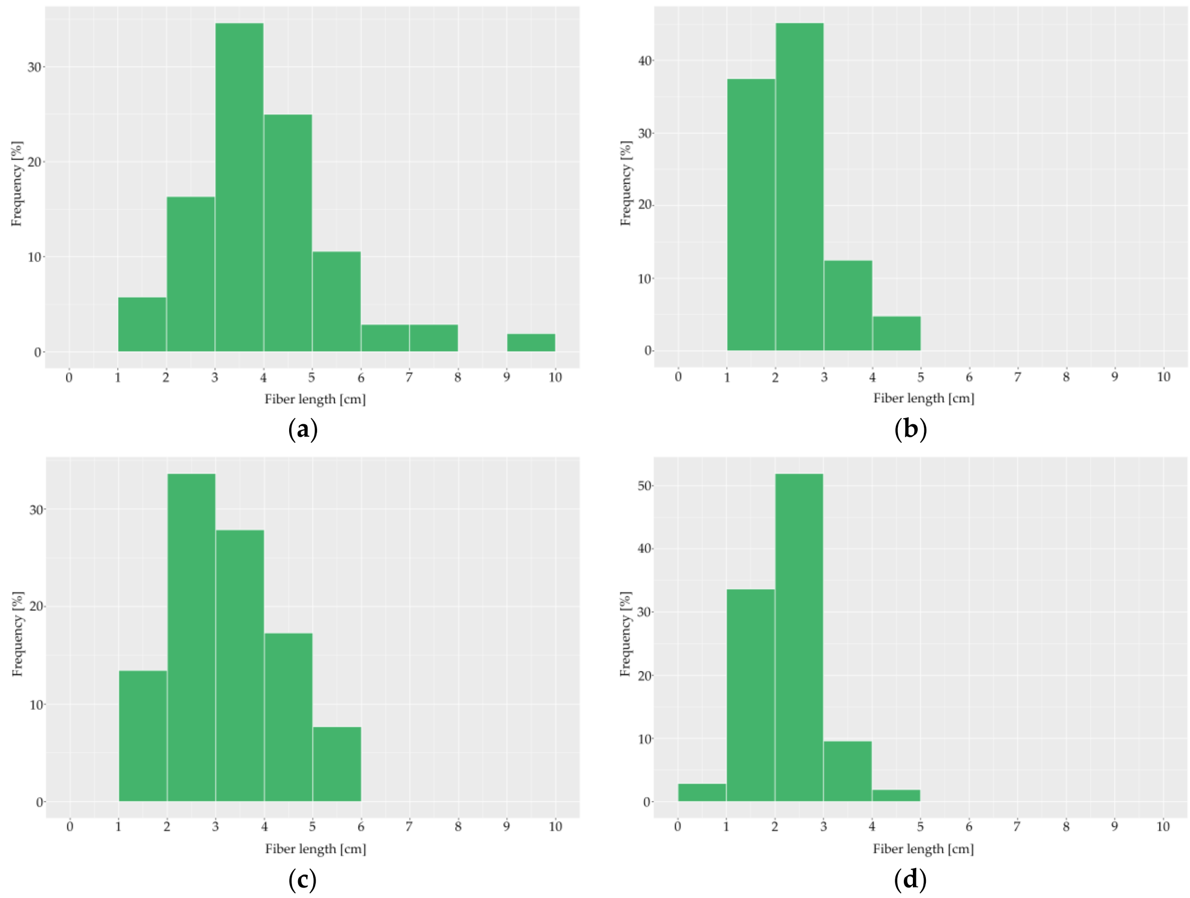


Figure 4. Fiber length distribution of the varieties: (**a**) Rex (2021), (**b**) Rex (2022), (**c**) Barun (2021), and (**d**) Barun (2022).

3.5. Moisture Content and Moisture Regain

Natural fibers are hygroscopic and rich in hydroxyl groups, which has a great influence on the moisture content and water absorption of the fibers [64]. The processes of water sorption and the swelling of natural fibers are complex due to their biochemical, structural, and morphological features. In this sense, these processes are influenced by several factors, such as lumen size, microfibrillar angle, cellulose crystallinity, accessibility to hydroxyl groups, amounts of amorphous biopolymers, and their relative hydrophilic/hydrophobic character [65]. The amount of moisture in the fibers is related not only to the amount of hemicellulose and lignin but also to the proportion of non-crystalline cellulose parts in the fiber [61,66]. In summary, the hemicellulose content in natural fibers is influenced by a combination of genetic, environmental, and process factors [67]. Understanding and controlling these factors can be essential for optimizing the hemicellulose content in natural fibers so that they can be used for various industrial and commercial applications.

One of the main deficiencies in the properties of natural fibers is their high moisture content, caused by the large amount of hydroxyl and other polar functional groups found in natural fibers. The negative aspect of this property is that it can have a detrimental effect on the mechanical properties of the fiber, as well as its dimensional stability. The positive aspect is biodegradability, which is improved by increasing the water content in the fiber [61].

Table 7 presents the moisture content of isolated barley fibers. The moisture content was the lowest in 2022 for both barley varieties—Rex and Barun—at 7.12% and 6.75%, respectively. A significant difference among the mean values of moisture content was confirmed with a two-way ANOVA, where Fcritical < Fstatistical and the p-value for both variables (variety and harvesting year) was lower than 0.05. Moisture content below

10% is a positive property, as drying such fibers would consume less energy, and storage conditions would be easier to maintain [68,69].

Table 7. Moisture content of barley fibers.

	Moisture Content [%]			
	Rex (2021)	**Rex (2022)**	**Barun (2021)**	**Barun (2022)**
Average [%]	9.45	7.12	9.52	6.75
Standard deviation [%]	0.04	0.07	0.06	0.15
Coefficient of variation [%]	0.41	0.99	0.65	2.26
Standard error [%]	0.04	0.08	0.07	0.17

Table 8 presents the standard moisture regain of isolated barley fibers. The lowest moisture regain was observed in both varieties of barley fibers—Rex and Barun—from 2021, i.e., 10.37% and 10.41%, respectively. The new-variety Barun from 2022 showed a slightly higher moisture regain of 11.01%, but all the values of the tested barley fibers met the moisture regain characteristic for natural fibers (Table 9). A significant difference among the mean values of moisture regain was confirmed with a two-way ANOVA, where Fcritical < Fstatistical and the *p*-value for both variables (variety and harvesting year) was lower than 0.05.

Table 8. Moisture regain of barley fibers.

	Moisture Regain [%]			
	Rex (2021)	**Rex (2022)**	**Barun (2021)**	**Barun (2022)**
Average [%]	10.37	10.66	10.41	11.01
Standard deviation [%]	0.19	0.18	0.01	0.11
Coefficient of variation [%]	1.87	1.71	0.10	1.04
Standard error [%]	0.22	0.21	0.01	0.13

Table 9. Physical properties of some of the most commonly used fibers from the seed, stem, leaf, and fruit categories in comparison to the barley fibers from this study.

Fiber Category	Fiber	Diameter (µm)	Length (mm)	Moisture Regain (%)	Density (g/cm^3)	Reference
Seed fiber	Cotton	10–22	12–64	8.5	1.55	[70,71]
Stem fiber	Flax	40–600	5–900	7	1.4–1.5	[55,58]
	Hemp	10–500	5–56	8	1.3–1.6	
	Jute	25–200	1.5–120	12	1.4–1.8	
	Spanish broom	10–200	5–900	8	1.55–1.6	[55]
Straw/stem fiber	Barley	10–350	5–100	10–11	1.4–1.5	This study
Leaf fiber	Sisal	8–200	900	11	1.2–1.5	[58,70]
Fruit fiber	Coir	10–460	20–150	13	1.1–1.4	

When considering the application of barley straw fibers as reinforcements in composite materials, it should be noted that their hygroscopic character will affect the overall mechanical properties of the composite material. Moisture penetrates the cellulose structure through the amorphous regions, leading to fiber swelling and microcracks within the composite [72]. The amount of moisture in the fibers has a negative effect on the adhesion between the hydrophobic matrix and the hydrophilic fibers, thus negatively affecting the mechanical properties of such a composite [69,72]. The lower the regain, the better the adhesion between the fibers and the polymer matrix. Additionally, the regain affects other properties of the material, such as dimensions, thermal effects, and electrical properties [73,74].

3.6. Fiber Density

Fiber density is an important property of textile fibers that affects their further application. When used as a reinforcement in composite materials, such as those used in the automotive industry, it is crucial that the product is lightweight, as its use reduces fuel consumption and expenses [75].

The mean value of fiber density was determined as a result of 45 parallel measurements per variety (Figure 5). The tested barley fibers showed density values ranging from 1.4761 g/cm^3 (new-variety-from-2022 Barun) to 1.4972 g/cm^3 (old-variety-from-2021 Rex). Natural fibers typically have a density range from 1.2 g/cm^3 to 1.6 g/cm^3 [76], so the investigated barley fibers fell within this range. Statistical analysis revealed a significant difference in the density mean values for fibers from different varieties of barley collected from two consecutive years (Fcritical = 2.656 < Fstatistical = 5.486 and p-value = 0.001 < 0.05). We could rank the tested fibers in order of lightest to heaviest as follows: Barun (2022) < Barun (2021) < Rex (2022) < Rex (2021). After the two-way ANOVA, it was concluded that there was a statistically significant difference in fiber density between the different varieties (p-value < 0.05), but fiber density did not depend on the year in which the straw was collected from which the fibers were isolated (p-value > 0.05).

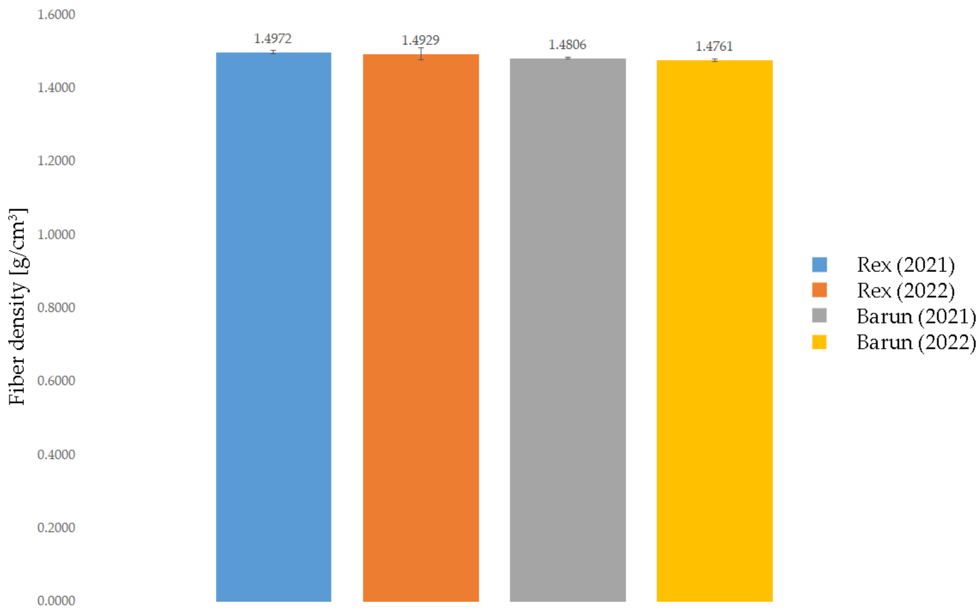


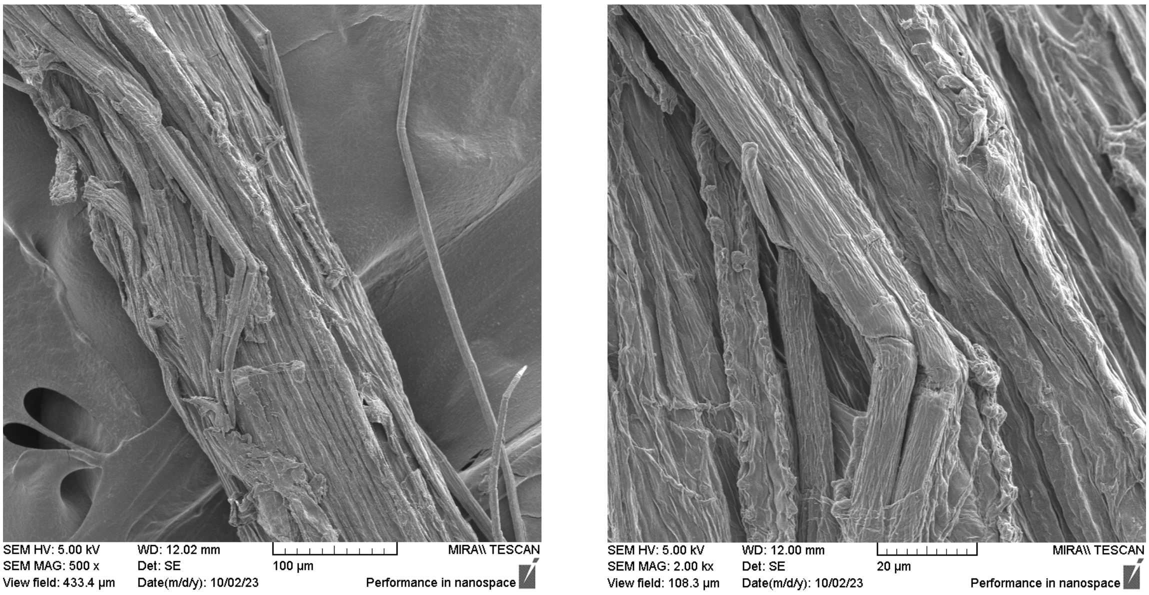
Figure 5. Density of barley fibers.

The density of fibers was inversely proportional to their volume, and the volume depended on the chemical structure of the fiber, including the content of hemicellulose, lignin, and cellulose, as well as their amorphous or crystalline nature. Therefore, it could be concluded that the old-variety Rex had a smaller volume of fibers due to fiber shrinkage caused by the better removal of hemicellulose and lignin, which was not the case with the fibers from the Barun variety (the new variety). Additionally, the alkaline treatment of barley straw and the subsequently isolated fibers with NaOH affected the filling of micropores on the surface of the fibers, resulting in a reduction in the fiber volume and an increase in its density [56,77–79]. Although fibers from both varieties of barley are suitable as reinforcements in composite materials, fibers from the new Barun variety would enable a slightly lower mass of the final product, resulting in better energy and economic efficiency, for example, in the automotive industry.

Table 9 presents the physical properties of fiber representatives in each category of cellulose fibers (seed fibers, stem (bast) fibers, and leaf and fruit fibers). The results revealed the correspondence of barley fibers' characteristics to most of the stem or fruit fibers.

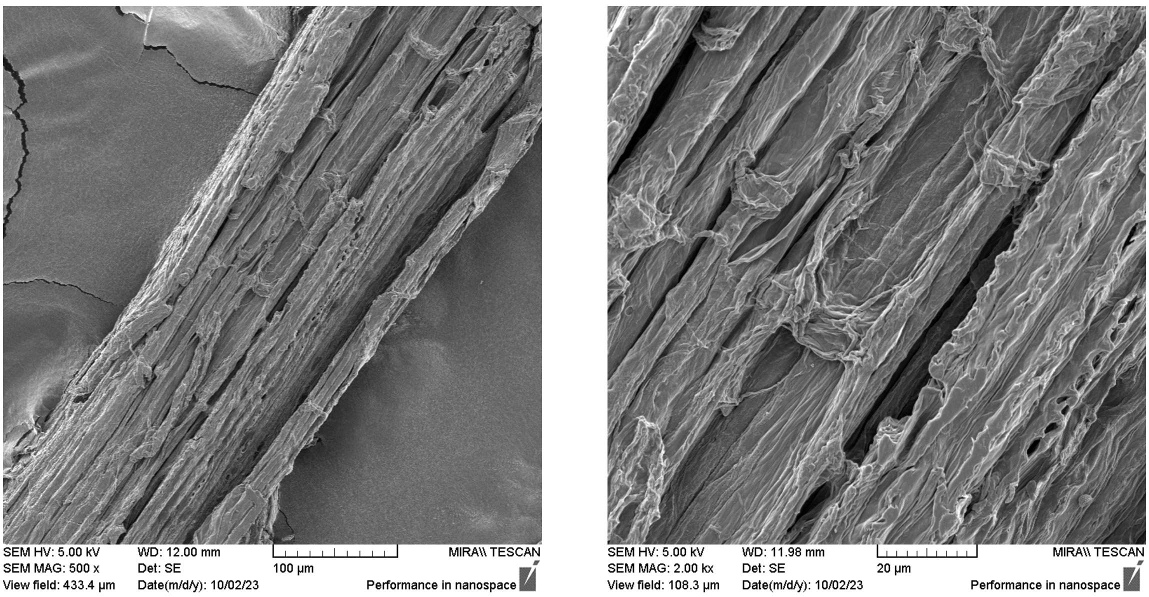
3.7. Fiber Morphology

Figures 6–9 depict SEM micrographs of fibers that were isolated from different varieties of barley. The micrographs, captured at 500× magnification, reveal technical fibers (fiber bundles) that consist of elementary fibers (ultimate fibers), which were isolated from barley straw. It is observable that all the fibers were isolated using the same alkaline process with the use of low-concentration NaOH, which resulted in the incomplete delignification and solubilization of hemicellulose.



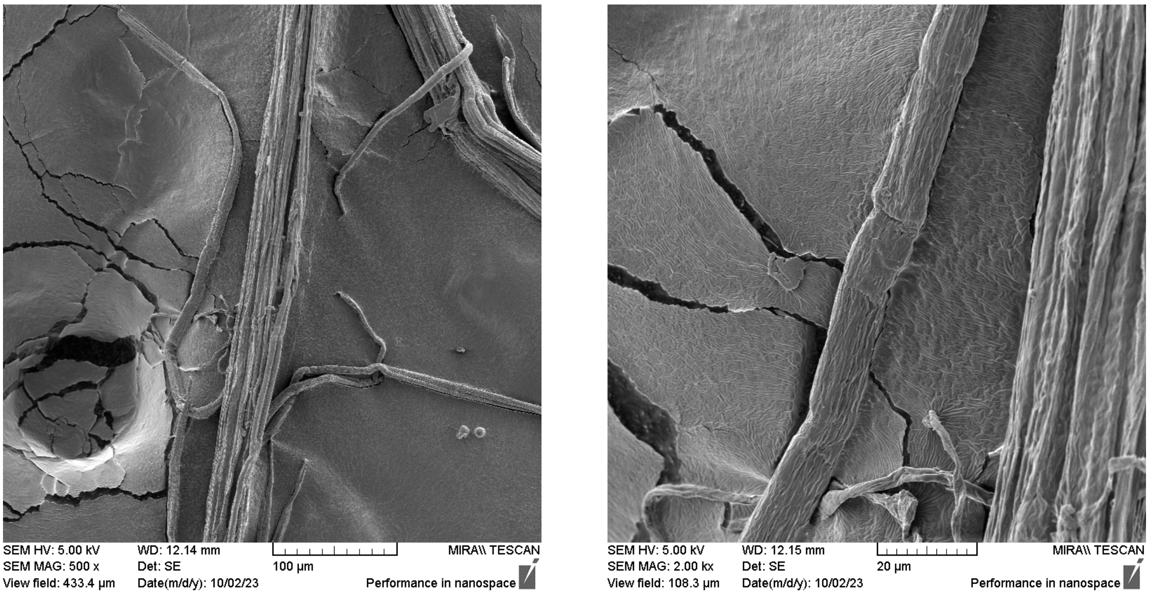
(**a**) (**b**)

Figure 6. SEM micrographs of barley fiber isolated from the straw of the REX variety from 2021: (**a**) technical fiber under magnification of 500× and (**b**) the ultimate fiber as part of the technical fiber under magnification of 2000×.



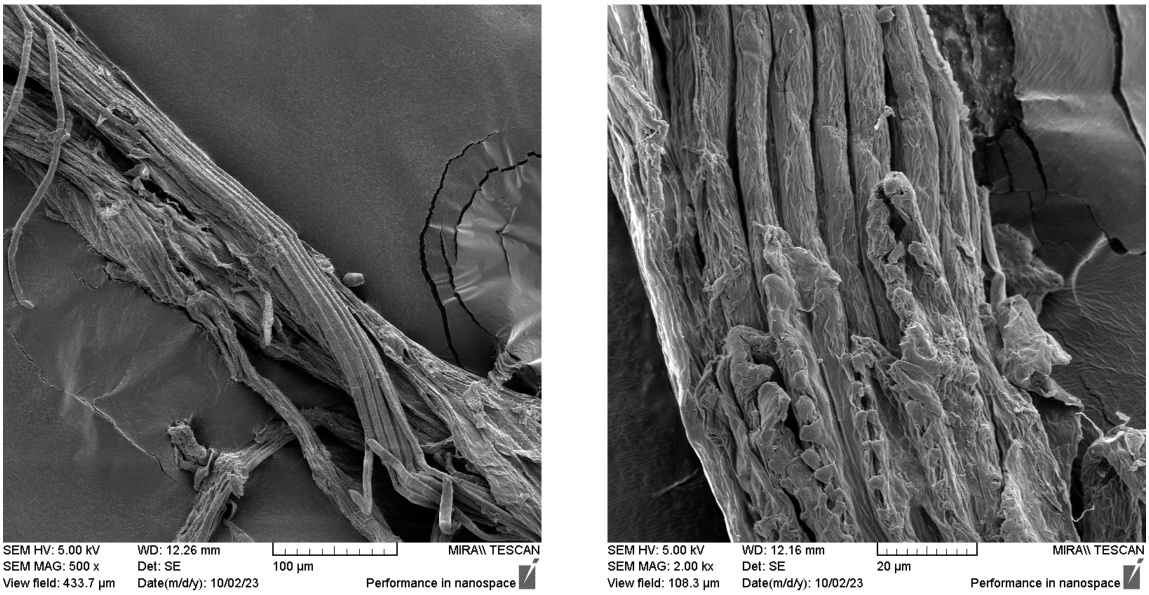
(**a**) (**b**)

Figure 7. SEM micrographs of barley fiber isolated from the straw of the REX variety from 2022: (**a**) technical fiber under magnification of 500× (**b**) the ultimate fiber as part of the technical fiber under magnification of 2000×.



(**a**) (**b**)

Figure 8. SEM micrographs of barley fiber isolated from the straw of the Barun variety from 2021: (**a**) technical fiber under magnification of 500× and (**b**) the ultimate fiber as part of the technical fiber under magnification of 2000×.



(**a**) (**b**)

Figure 9. SEM micrographs of barley fiber isolated from the straw of the Barun variety from 2022: (**a**) technical fiber under magnification of 500× and (**b**) the ultimate fiber as part of the technical fiber under magnification of 2000×.

Chen et al. [80] investigated the effect of different concentrations of sodium alkali on the microstructure of fibers. They concluded that the concentration of alkali lower than 5% has a relatively small effect on the microstructure of fibers.

In the case of the Barun variety from 2021, a more significant separation of the elementary fibers from the technical fibers was visible. In Figure 8b, at a magnification of 2000×, the rough surface made of cellulose microfibrils is visible, along with nodes along the elementary fibers. Such a surface with non-uniform geometrical characteristics is typical of most natural fibers isolated from plant stems [67].

The irregular surface of the fibers is a beneficial feature when such fibers are used as a reinforcement in composite materials. It can lead to a better adhesion and interlock effect between the polymer matrix and the fiber, which, in turn, affects the composite's mechanical properties. The transfer of stress between the polymer matrix and fibers determines the effectiveness of the reinforcement [67,81].

3.8. Chemical Composition

3.8.1. Cellulose, Hemicellulose, and Lignin Content

The chemical composition of barley straw before and after fiber isolation, as well as the chemical composition of the solid residue (Figure 2), are presented in Figure 10.

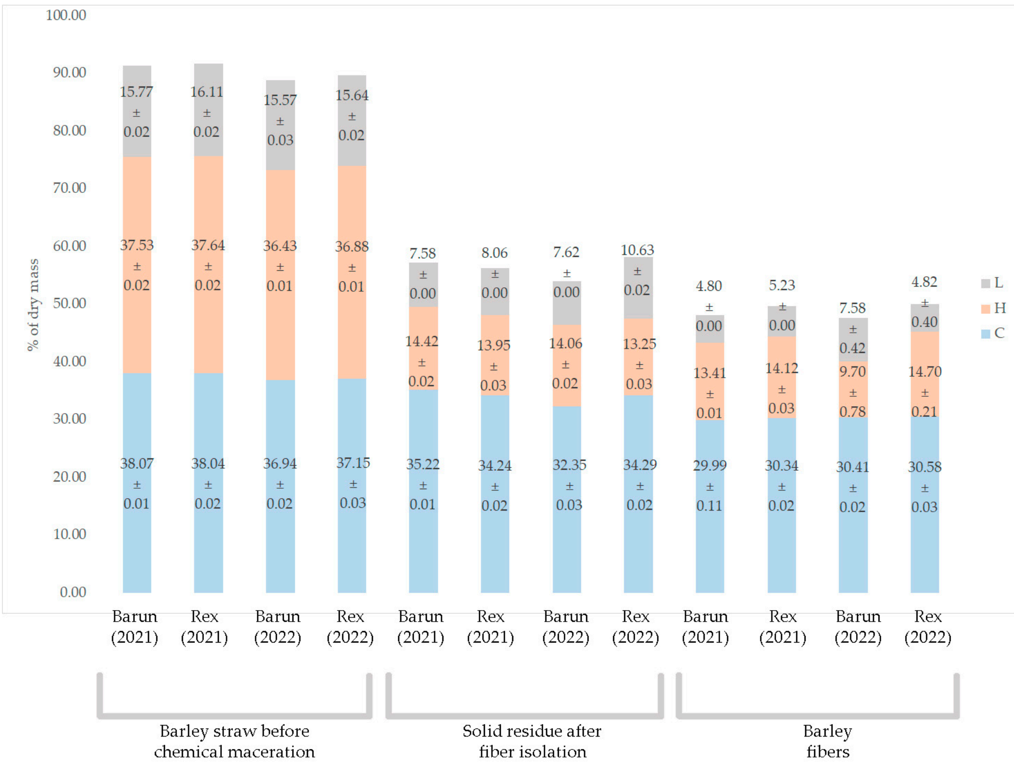


Figure 10. Chemical composition of barley straw before chemical maceration, solid residue after fiber isolation, and barley fibers, where L is the lignin content (wt.%), H is the hemicellulose content (wt.%), and C is the cellulose content (wt.%).

The barley fibers isolated from the Rex variety (2022) straw showed the highest content of cellulose among all the tested fibers—30.58%—and lignin content below 5%. All the tested fibers showed very similar properties regarding cellulose, hemicellulose, and lignin content, except fibers isolated from the straw of the Barun variety (2022), which showed 58% higher lignin content compared to the lowest value.

Table 10 presents the chemical composition of some of the most commonly used fibers expressed as the content of cellulose, hemicellulose, and lignin. The barley fibers investigated in this paper showed very low cellulose content, which was also confirmed via tensile testing. Comparing the results from Table 10, the barley fibers can be categorized as bast and leaf fibers.

Table 10. Chemical properties of some of the most commonly used fibers from the seed, stem, leaf, and fruit categories in comparison to the barley fibers from this study.

Fiber Category	Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Seed fiber	Cotton	82–96	2–6.4	0–5	[70]
Stem fiber	Flax	70–75	9–21	2–5	[71]
	Hemp	7–75	2–22	4–8	
	Jute	61–76	14–20	5–13	
	Spanish broom	90–92	2–6	3–4	[80]
Straw/stem fiber	Barley	30–31	9–15	4–8	This study
Leaf fiber	Sisal	48–78	10–18	8–14	[71]
Fruit fiber	Coir	32–43	<1	40–50	

3.8.2. FTIR

The ATR-FTIR spectra of the investigated fibers isolated from the barley varieties Rex and Barun are presented in Figures 11 and 12. The effect of chemical maceration was evaluated according to characteristic peaks of lignin, cellulose, and hemicellulose (Table 11).

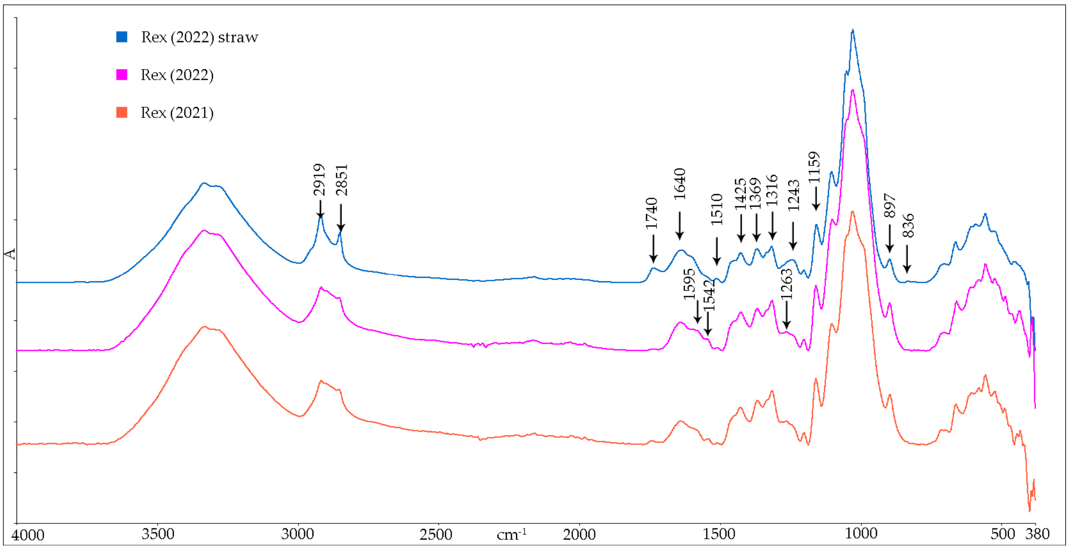


Figure 11. FTIR spectra of barley fibers isolated from straw of the old Rex variety.

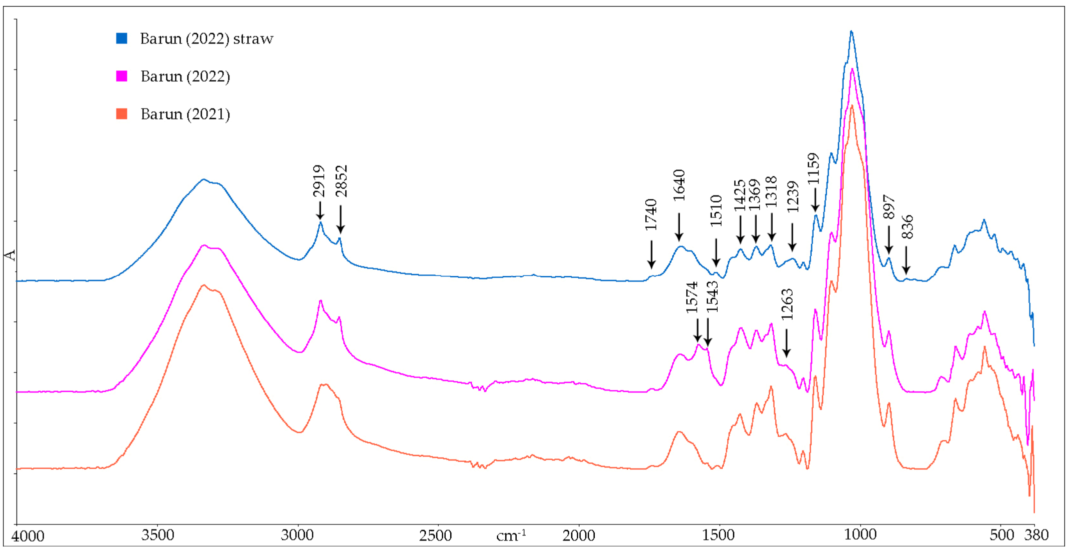


Figure 12. FTIR spectra of barley fibers isolated from straw of the new Barun variety.

A large absorption band visible within the range of 3200–3400 cm^{-1} was attributed to the -OH group, while bands at 2919 cm^{-1} and 2850–2852 cm^{-1} were attributed to the -CH_2 and -CH groups of cellulose, hemicellulose, pectin, fats, and waxes [55]. The barley straw of the Rex variety exhibited the highest intensity of its band at 1740 cm^{-1}. This peak was associated with free -COOH groups of polygalacturonic acid, which is the main constituent of pectins, and therefore, the lower intensity of this peak observed within barley fibers indicates the successful removal of pectin and the positive effect of chemical maceration [82,83]. The absorption band at 1640 cm^{-1} corresponded to the adsorbed water and derived from hydrogen bonding in the amorphous region of the cellulose macromolecules [84]. Fibers from the Rex variety (2021) showed a lower intensity of this peak, which was due to the removal of hemicellulose after chemical maceration, thus improving the internal organization of cellulose chains in more crystalline regions and, consequently, allowing better fiber strength [55]. The barley straws and fibers from both varieties showed characteristic bands for lignin at 1574–1595 cm^{-1}, 1542 cm^{-1}, and 1510 cm^{-1}. In Figures 11 and 12, the lower intensity of those peaks is noticeable in the case of the barley fibers, indicating lignin removal after the chemical maceration process [85,86]. The same observations were captured for lignin bands at 1239 cm^{-1} and 836 cm^{-1}. The absence of these peaks in the barley fibers in comparison to the straw indicated good efficiency of chemical maceration and confirmed the elimination of lignin. The peaks at 1239–1243 cm^{-1} and 1263 cm^{-1} correspond to syringyl (S) and guaiacyl (G) units in lignin, respectively. Therefore, it could be concluded that the fibers contained more guaiacyl moieties, which are characteristic of softwood species, while syringyl moieties were reduced after chemical maceration [87]. The absorption band at around 1420–1430 cm^{-1} corresponds to the cellulose crystalline structure, while the band at 897 cm^{-1} is associated with the amorphous structure of the cellulose [55,88]. The bands at 1369 cm^{-1}, 1335 cm^{-1}, 1318 cm^{-1}, and 1204 cm^{-1} are associated with the stretching and bending of -CH2, -CH, -OH, and C-O-C bonds in cellulose and hemicellulose [88]. In comparison to the FTIR spectra from Figures 11 and 12, the spectra from Figure 13 indicates that the fibers isolated from barley straw correspond well with the other cellulose fibers, showing the same peaks at 1159 cm^{-1}, 1105 cm^{-1}, 1050 cm^{-1}, 1030 cm^{-1}, 1000 cm^{-1}, and 985 cm^{-1}. These peaks are assigned to C-O-C glycosidic ether, -CO stretching vibrations of acetyl xylan, and -CO stretching vibrations of the polysaccharide components, mainly cellulose. The bands at 1050 cm^{-1}, 1000 cm^{-1}, and 985 cm^{-1} are visible only as shoulders in the barley fiber FTIR spectra, pointing to the less developed secondary cell wall of these fibers that influences the mechanical strength of barley fibers [55].

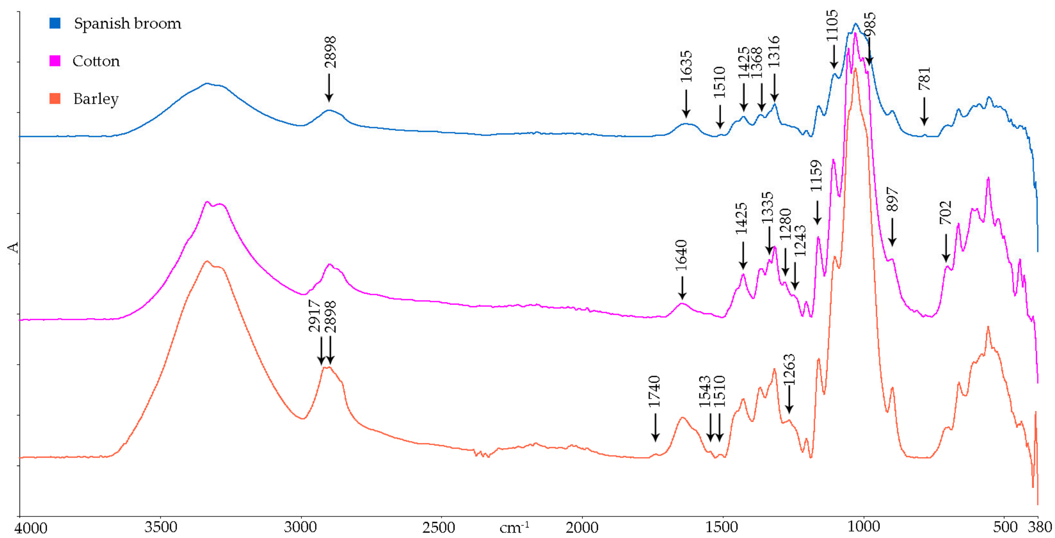


Figure 13. FTIR spectra of barley fibers compared to Spanish broom and cotton fibers.

Table 11. Main infrared (IR) transitions of cellulose fibers [55,85,86].

Wavenumber (cm^{-1})	Vibration	Sources
3200–3400	OH stretching	Cellulose and hemicellulose
2917–2919, 2850–2852	C-H symmetrical stretching	Cellulose and hemicellulose
1740	C=O stretching vibration	Pectin and waxes
1640	OH bending of absorbed water	Water
1574–1605	Aromatic skeletal vibrations and C=O stretch	Lignin
1543 and 1510–1515	C=C aromatic symmetrical stretching	Lignin
1456	C-H and C-O deformations, bending or stretching vibrations in lignin and carbohydrates	Cellulose, hemicellulose, and lignin
1425	HCH and OCH in-plane bending vibration	Cellulose
1368	In-plane CH bending	Cellulose and hemicellulose
1335	C-H vibrations and O-H in-plane bending	Cellulose and hemicellulose
1316–1318	CH_2 rocking vibration	Cellulose
1230–1263	C=O and S and G ring stretching	Lignin
1204	C-O-C symmetric stretching	Cellulose and hemicellulose
1159	C-O-C asymmetrical stretching	Cellulose and hemicellulose
1105	C-O-C glycosidic ether	Cellulose
1051, 1030, and 1000	C-C, C-OH, C-H ring, and side group vibrations	Cellulose and hemicellulose
985	C-O valence vibrations	Cellulose
897	COC, CCO, and CCH deformation and stretching	Cellulose
836	Out-of-plane aromatic CH	Lignin
781	Deformation vibrations of C-H bonds associated with aromatic rings	Lignin

4. Conclusions

Despite today's enormous potential for information flow, the media's influence, higher rates of education, and the significant impact of social networks, people still consider textiles to be fabrics and clothes used in daily life. However, the use of textiles extends far beyond the fashion and clothing industry, with applications in various fields, including automotive and construction, maritime and aerospace, composites, nanotechnology, and biomedicine. The properties of textile products depend on the properties of their basic components, i.e., textile fibers.

This research aimed to promote the circular bioeconomy by examining the properties of textile fibers obtained from the straw of two varieties of barley. These fibers will be used to produce technical textiles, specifically biocomposite materials. The fiber extraction process was accomplished via chemical maceration under milder alkali conditions using a low concentration of NaOH to achieve more environmentally friendly conditions.

Although the Rex variety harvested in 2021 showed the best fiber yield results (23.98%), due to the significant variability in the results, it can be concluded that the new Barun variety harvested in 2022 has a positive tendency in fiber (16.07%) and residue (32.90%) yield, considering the negative effects of climate change, such as an increase in drought.

The fiber breaking tenacity for the varieties from 2021 was slightly higher compared to the varieties from 2022. Both barley varieties from 2021 showed high fiber tenacity of 25.63 cN/tex and 23.08 cN/tex, respectively, indicating the possibility of spinning such fibers into yarn.

Our results confirmed that the parameter of fiber length is influenced by the barley variety and harvest year. The longest fiber length was observed for the Rex variety from the 2021 harvest year (average length: 4.03 cm). According to the length distribution analysis, most of the investigated fibers showed the highest frequency in the range 2–3 cm, except for the Rex variety from 2021, which showed the highest frequency in the length range of 3–4 cm. Both fiber lengths had satisfactory values to be used as reinforcements in composite materials.

Moisture content and moisture regain were strongly influenced by the feedstock variety and its harvest year. The moisture content of fibers isolated from straw harvested in 2022 was low, approx. 7%, which is positive from the perspective of storage maintenance conditions and lower energy consumption. All the tested fibers showed moisture regain in the range of 10.37% to 11.01%, which is in line with conventional bast fibers. Furthermore, fibers with a low moisture regain perform better when used for reinforcement in composite material due to the better adhesion between the polymer matrix and the fiber.

The density of all the tested fibers fell within the range of 1.4761 g/cm^3 to 1.4972 g/cm^3, which is consistent with the densities of natural fibers. Although fibers from both varieties of barley are suitable as reinforcements in composite materials, fibers from the new Barun variety would enable a slightly lower mass of the final product and, thus, better energy and economic efficiency if used, for example, in the automotive industry.

Morphology analysis revealed non-uniform geometrical characteristics on the fiber surfaces, which are typical for most natural fibers isolated from plant stems. The roughness of the fiber surface is a positive characteristic if such fibers are used as reinforcements in composite material since its relief topography has a positive effect on adhesion between a polymer matrix and natural fibers.

The chemical composition of isolated fibers showed that the optimal content of cellulose and lignin was observed in the barley fibers isolated from the straw of the old Rex variety (2021 and 2022). They showed a higher content of cellulose in comparison to the Barun variety within the same harvesting year—30.34% and 30.58%, respectively. Those results were confirmed via FTIR analysis since the spectra of the Rex fibers showed lower intensities of peak characteristics for hemicellulose and lignin, which proved their better removal after the performed chemical pretreatment.

The results concerning fiber density confirmed low values (lower than 1.5 g/cm^3), which are favorable for their usage as light reinforcements of a composite matrix designed for the automotive industry. Another possible usage of barley fibers derived from old cultivars is in the clothing industry due to the fact that the obtained fiber tenacity of 20.31–23.08 cN/tex fulfills minimal spinning requirements. This research presents only part of the very broad investigation of the possible usage of cereal biomass for the dual production of fibers and biofuels. Our results revealed the possibility of the usage of a very high percentage of solid waste left after the fiber isolation for the production of high-quality biofuels.

Author Contributions: Conceptualization, S.S. and Z.K.; methodology, Z.K.; software, Z.K.; validation, Z.K. and S.B.; formal analysis, Z.K. and S.S.; investigation, Z.K. and S.S.; resources, Z.K. and S.B.; data curation, Z.K.; writing—original draft preparation, S.S. and S.B.; writing—review and editing, Z.K. and S.B.; visualization, S.S. and Z.K.; supervision, S.B.; project administration, S.B.; funding acquisition, S.B. All authors have read and agreed to the published version of the manuscript.

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

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