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Usability of Discarded Lignocellulosic Fibers in Paper for Secondary Green Packaging and Labeling

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Abstract: Packaging and labels are used for a variety of products and have become an indispensable part of daily life, while products without labels or packaging cause uncertainty among consumers. The global trend is to reduce the amount of packaging waste by recycling and reusing the same material or using other available waste raw materials. With large quantities of stalks remaining discarded in the fields after harvest each year, cereal straw is emerging as an alternative source of lignocellulosic fibers for secondary green packaging and labels. In this study, the usability of printed papers with discarded lignocellulosic fibers by offset and gravure printing processes for secondary green packaging and labels was observed based on the qualitative parameters of reproduction and ink penetration into the printing substrate. From the obtained results, it can be concluded that gravure prints have greater penetration of the ink into the printing substrate, resulting in more uneven surface coverage with printing ink, compared to offset prints, where the viscosity of the ink and the printing process itself have the greatest influence. Therefore, these substrates with discarded lignocellulosic fibers can be used for secondary green packaging and labeling printed by the offset printing process, while gravure printing requires an additional coating or a larger amount of filler in the paper structure.

Keywords: label; lignocellulosic fibers; printed paper; secondary packaging; straw; usability

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1. Introduction

Packaging is a material that has the function of wrapping or holding the product in order to protect the product or the environment. The function of packaging is also to identify and promote a product on the market [1]. A product without a label or packaging has an unsettling and distrustful effect on consumers. Printing on packaging and labels provides consumers with information about the product itself, the manufacturer of the product, the validity, and other important information required by certain regulations, for example EU Regulation 2283/2015 for food packaging, and legislation. Packaging and labels are used for a variety of products and are an indispensable part of everyday life. Almost 50% of printed products belong to packaging [2]. Nowadays, consumers are increasingly demanding packaging that is acceptable environmentally and health-wise with the aim of reducing, reusing and recycling (the Three Rs) the amount of waste worldwide [3].

With the growth and development of urbanization and industrialization, the consumption of packaging and labels is also increasing, causing the environment to be increasingly affected by soil, water and air pollution, global warming, etc. Annually, 1.3 billion tons of waste is produced, and it is expected to increase to 2.2 billion tons by 2025 and 27 billion tons per year by 2050. One-third of the waste comes from Asia, particularly China and India. Surprisingly, Asian countries produce up to one million tons of waste every day. Waste is the biggest problem of the present generation and a challenge for future generations [4]. The world is aware of this problem and is beginning to move towards a sustainable, biobased, circular economy. Thanks to initial government regulations against single-use plastic, up to

USD 26 trillion will be saved by 2030. Global environmental awareness has encouraged the development of biobased industries such as paper production, the graphic packaging industry, bioplastics, biocomposites, biofuels, biochar, bioenergy production (electricity and gas), biochemicals and renewable lubricants [5,6]. The increasing global demand for natural fiber materials is contributing to worldwide deforestation at an annual rate of 2%, meaning nonwood fibers for papermaking have become one of the most important alternative sources of fiber materials in the 21st century [7,8].

Nonwoody biomass also adds value to agricultural crops and food by utilizing their residues (traditionally discarded as waste). The wide variety of fiber properties and chemical composition of nonwood raw materials offers the potential for replacing wood raw materials in paper production. In addition, the pulp and paper industry is an excellent starting point for the development of lignocellulosic biorefineries, as it has the necessary technology and infrastructure as well as extensive experience in the conversion of lignocellulosic biomass. Lignocellulose is the main component of plants and by far the most abundant type of terrestrial biomass [9]. Lignocellulosic biomass consists mainly of cellulose (40–60%), hemicellulose (10–40%), and lignin (15–30%), with a smaller amount of extractive substances, proteins, and inorganic compounds [10]. Lignocellulosic components are found in both woody (e.g., spruce, pine, eucalyptus, poplar, etc.) and nonwoody biomass, the latter including plant (e.g., bamboo, tagasaste, kenaf, abaca, etc.) and agricultural crop residues (e.g., barley straw, wheat straw, orange trees pruning, olive trees pruning, etc.), and from the agrofood industry (e.g., bagasse, empty oil palm bunches EFB, etc.) [11].

The cellulose content in paper substrate has a positive effect on strength and makes the fiber strand susceptible to the binding of natural and synthetic inks, while hemicellulose is responsible for the water absorption of plant fibers and reduces the internal stresses of the fibers [12]. Cellulose is a linear and ordered polymer of D-anhydroglucopyranose units linked by β-1,4-glucoside bonds, with a degree of polymerization of 15 to 10,000–14,000. At the molecular level, cellulose is a glucose polymer and the number of glucose units in the cellulose molecule varies depending on the cellulose source material. Therefore, cellulose is the most abundant renewable polymer source available in the world today, which represents about 1.5×10^{12} tons in total per year of biomass production through photosynthesis [13]. Hemicellulose is a branched carbohydrate polymer that contains both pentoses (e.g., xylose and arabinose) and hexoses (e.g., galactose, mannose, and glucose) and often has uronic acids (e.g., glucuronic acid) and acetyl residues as pendant groups. Lignin is a three-dimensional network of dimethoxylated (syringyl, S), monomethoxylated (guaiacyl, G), and nonmethoxylated (p-hydroxyphenyl, H) phenylpropanoid units derived from the corresponding p-hydroxycinnamyl alcohols [11]. From a chemical composition perspective, plant fibers with a holocellulose content greater than 33% and a lignin content less than 30% are considered promising candidates for paper production [14,15].

Today, only a small percentage of paper (11%) is derived from nonwood fibers, also referred to as "tree-free" fiber, which are divided into two large groups: agricultural residues and primary crops [6]. The number of studies comparing the quality and usability of alternative fibers in paper production has increased in recent years. The use of alternative fibers depends on the region where a large amount can be collected and stored without degradation. Most of the nonwood sources used in research are straw, sugar cane bagasse, bamboo, kenaf, hemp, sisal, abaca, cotton linter and reeds, aquatic plants, tea waste, palm leaves, banana stems and invasive alien plant species (knotweed, goldenrod, and black locust) [16,17].

In this research, crop straw was used as an alternative source of fiber for papermaking because it is discarded in the fields every year after harvest [18]. The analysis of the utilization of discarded lignocellulosic fibers in printed paper was carried out using qualitative parameters of reproduction and ink penetration into the substrate on prints produced by offset and gravure printing processes to obtain secondary green packaging and labels. Offset and gravure printing technologies were chosen for this research because they are the leading printing processes for packaging printing on absorbent substrates. Offset printing, which uses high-viscosity inks, differs in the way the ink is transferred from the ink application unit to the printing surface and in the way the printing plate itself holds the ink, achieving a very thin ink layer from 0.5 µm to 1.5 µm on a substrate, compared to gravure printing, which uses low-viscosity inks and achieves ink coverage from 8 µm to 12 µm. The largest area of gravure printing is printing on packaging, from thin films a (thickness of ≈200 µm) to thick cardboard (≈800 µm) [19,20]. Since the properties of the paper substrate are one of the factors that undoubtedly affect the overall quality of printing, this research focuses on analyzing the use of straw fiber in the composition of paper for the production of more environmentally friendly packaging and labels printed by offset and gravure printing processes.

2. Materials and Methods

The experimental part of this research was divided into the following phases: (1) the soda pulping of straw; (2) the production of paper substrates with straw pulp; (3) the printing of the paper substrates with offset and gravure techniques; (4) the evaluation of the printing quality based on: (4a) the analysis of the ink penetration depth; (4b) the analysis of the integral optical ink density; (4c) the analysis of the graininess value; (4d) the analysis of the mottling value.

2.1. Soda Pulping of Straw

Pure agricultural residues were collected in the continental part of Croatia after harvesting wheat, barley and triticale. The straw of wheat (*Triticum spp.*), barley (*Hordeum vulgare L.*) and triticale (*Triticale sp.*) was converted into lignocellulosic pulp using the process conditions summarized in Table 1 [18].

Table 1. Processes for converting straw into lignocellulosic pulp.

Soda Pulping–Cooking in Autoclave		Decantation and Pulp Washing	Defibration in Holländer Valley Mill	
NaOH charge	16%		Volume of added tap water	23 L
Alkali to straw ratio	10:1		Pulp consistency	1.5%
Pulping temperature	120 °C	In two stages using 10 L of tap water each	pH	8.5–9.0
			Temperature	24 °C
Pulping pressure	170 kPa		Speed of rotation	500 rpm
Pulping time	60 min		Time	40 min

Sodium hydroxide was used as the pulping liquor in this study as it is the main chemical used for the alkaline pulping of nonwood sources [21]. After the pulping process, the pulp was washed in two stages with tap water to remove soluble substances from the pulp. In the end, the straw pulp was beaten with a Valley Hollander.

Following the pulp production process described above, the fibers were separated from the water pulp suspension using a sheet former device.

2.2. Production of Paper Substrates with Straw Pulp

Laboratory-produced paper substrates weighing 42.5 ± 2.6 g/m^2 were prepared by mixing recycled wood pulp and unbleached wheat, barley or triticale straw pulp in a ratio of 3:7 with a Rapid-Köthen sheet former (FRANK-PTI) according to EN ISO 5269-2:2004 [18]. A laboratory paper substrate made from 100% recycled wood pulp was prepared in an identical manner and served as a reference sample (N) in this research.

The process of forming paper substrates under laboratory conditions is shown in Table 2 [18].

Table 2. Processes of forming paper substrates under laboratory conditions.

Disintegration		Homogenisation		Paper Substrate	
m (pulp)	80 g			Weight	42.5 g/m^2
V (H_2O)	1.6 l	V (H_2O)	10 L		
pH	8	pH	7.5		
Temperature	45 °C	Temperature	45 °C	Diameter	200 mm
Disintegration time	20 min	Homogenisation time	5 min		

Depending on the plant species, fibers may differ in terms of their length, width, fineness or microstructure, as well as chemical composition. Longer fibers provide greater strength to the paper substrate, while shorter fibers increase the opacity and smoothness of the paper surface. Softwood fibers (from coniferous trees) can be up to 5 mm long, while hardwood (from deciduous trees) is less homogeneous in its anatomical structure than softwood and contains fewer fibers with an average fiber length of about 1.5–2 mm [8]. From the presented values of fiber length range (Figure 1), it is evident that the length of the analyzed straw fibers was almost equal to the average length of hardwood fibers [22]. Wheat and barley straw consist of fibers that are very similar in length and shorter than triticale, which has a much wider range of fiber lengths.

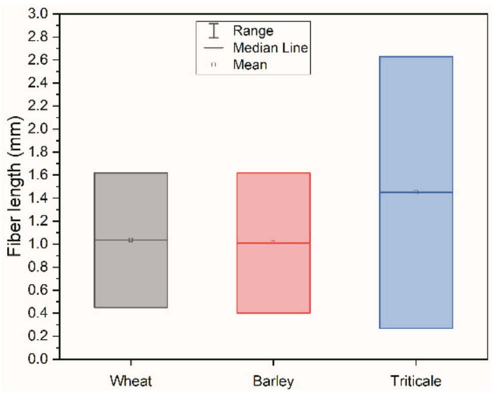
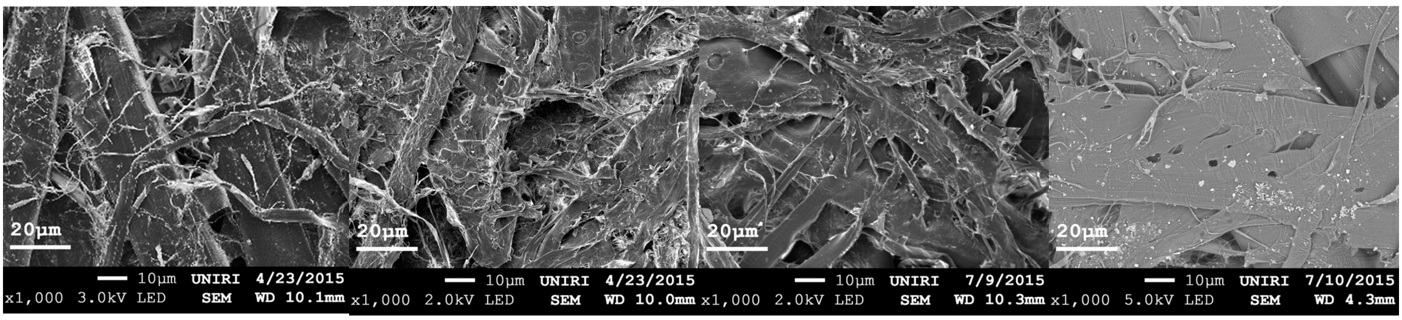


Figure 1. Fiber length of straw used in the production of laboratory paper.

To gain a better insight into the structure of the laboratory papers, SEM images of all the analyzed paper substrates are included in Figure 2 [23].



(**a**) (**b**) (**c**) (**d**)

Figure 2. SEM images (magnification 1000×) of laboratory papers of different composition: (**a**) N; (**b**) 30W; (**c**) 30B; (**d**) 30TR.

Table 3 presents the properties of laboratory-produced paper substrates, where the paper marked N is a laboratory paper made from 100% recycled cellulose fibers from newsprint and was used as the reference sample in this research. The papers marked 30W, 30B, and 30TR are laboratory papers consisting of 30% straw pulp (wheat, barley, and triticale, respectively) and 70% recycled wood pulp.

Table 3. Characteristics of laboratory paper substrates [18,24].

Paper Substrate	Thickness (μm)	Air Permeability (mL/min)	Ash (%)	Roughness, R_a (μm)	Surface Free Energy, σ_s (mN/m)
N	90.10 ± 2.13	221.12 ± 0.90	4.73 ± 0.22	4.15 ± 0.34	40.92
30W	101.67 ± 17.22	406.92 ± 2.28	3.64 ± 0.07	4.59 ± 0.51	40.70
30B	91.67 ± 4.08	426.88 ± 2.47	3.32 ± 0.67	4.24 ± 0.41	41.38
30TR	101.67 ± 14.72	371.25 ± 5.44	3.99 ± 0.15	4.40 ± 0.39	43.55

The absorption of water inside the printing substrate and the surface free energy of each laboratory substrate were determined using a Goniometer CCD video camera instrument with a resolution of 768 × 576 pixels, producing 50 frames per second. To calculate the surface free energies, 10 contact angle measurements of standardized liquids (glycerol, water, formamide and methyl dioxide) with a volume of 1 μL and dosing rate of 5 μL/s were used according to the OWRK method [25].

2.3. Printing Paper Substrates with Offset and Gravure Techniques

Since the printing of packaging and labels experiences the largest annual growth (over 4%), this research analyzed the usability of paper with discarded lignocellulosic fibers by applying the main techniques for printing secondary packaging on absorbent substrates (offset and gravure) [2]. Offset printing, the predominant printing technique, is mainly used for printing publications and packaging, while gravure printing is mainly used for printing luxury products, publications, and packaging in very long runs.

Printing on laboratory-produced paper substrates was performed using laboratory equipment that simulates offset and gravure printing processes. Offset printing was carried out at a speed of 0.5 m/s and a pressure of 600 N in full tone with the conventional ink Express (manufacturer Sun Chemicals) using a test building multipurpose testing machine at a temperature of 23 °C and a relative humidity of 50%. Gravure printing was carried out with a laboratory KPP Gravure System using a printing cylinder with a mechanical hardness (HS) of 65 Shore and an engraved printing plate at an angle of 37° with a diamond needle at an angle of 130° with a screen frequency of 100 lines/inch (equivalent to 40 lines/cm). Printing was carried out in full tone using Sunprop inks (manufacturer Sun Chemicals) at a speed of 20 m/min at a temperature of 23 °C and a relative humidity of 52%. Printing with both printing techniques was carried out in full tone with a layer of cyan (C), magenta (M), yellow (Y) and black (K) ink on laboratory-produced paper substrates.

Table 4 shows the viscosity values of offset and gravure process inks (C, M, Y and K) measured at a temperature of 23 °C and a relative humidity of 50% using an automatic Laray viscometer and a DIN 4 cup. Viscosity is a property of a liquid that describes the tension in the liquid flow caused by the different speeds of movement of a liquid layer or its ability to adhere to a surface. In other words, viscosity indicates the degree to which the ink resists movement or flow. A liquid with high viscosity is also sticky and does not flow easily. The property of viscosity can be described in two ways: dynamic viscosity and kinetic viscosity. Dynamic viscosity is determined by the coefficient η, which is defined by the force (F) per unit area (A) required to achieve a unit velocity difference between two parallel layers at a distance (x), while kinematic viscosity (ν) in Newtonian fluids is the ratio between dynamic viscosity (η) and fluid density (ρ) [26].

The kinematic viscosity is determined from the flow time and calculated using the following Equation (1) based on the standard DIN 53211 [27].

$$\nu = 4.57t - \frac{452}{t} \tag{1}$$

Figure 3 presents microscopic images of magenta prints on N, 30W, 30B, and 30TR paper substrates to observe the obtained reproduction quality achieved by offset and gravure printing techniques.

Table 4. Viscosity of C, M, Y and K offset and gravure printing inks.

Printing Ink		Dynamic Viscosity (Pa·s) (Laray Viscometer)	Printing Ink		Kinematic Viscosity (mm^2/s) (DIN 4 Cup)
Offset	C_o	48.70 ± 3.64	Gravure	C_g	146.54 ± 5.29
	M_o	62.85 ± 9.85		M_g	143.62 ± 8.11
	Y_o	33.69 ± 2.27		Y_g	135.61 ± 4.13
	K_o	87.47 ± 2.74		K_g	288.23 ± 8.35

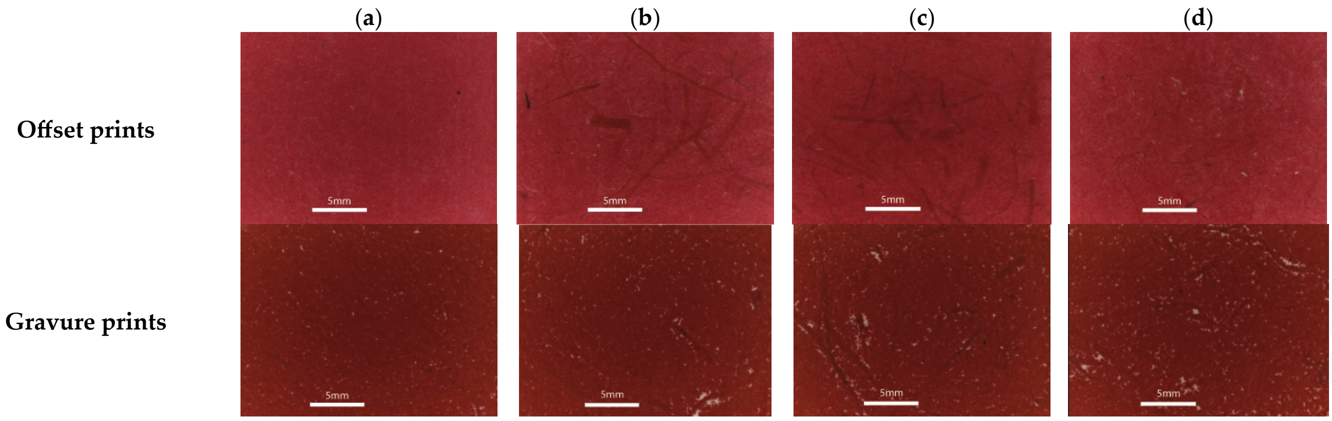


Figure 3. Microscopic images of magenta prints made with offset and gravure inks: (**a**) N; (**b**) 30W; (**c**) 30B; (**d**) 30TR.

2.4. Evaluation of the Printing Quality

The usability of discarded lignocellulosic fibers in paper for secondary green packaging and labeling was defined in this study by evaluating print quality, comparing reproductions on innovative laboratory-produced papers with straw pulp to laboratory-produced papers made exclusively from recycled wood pulp. The evaluation of the print quality was based on several analytical parameters: the ink penetration depth, the integral optical ink density, the graininess, and mottling values.

2.4.1. Analysis of Ink Penetration Depth

Ink penetration into the paper substrate is a complex issue; therefore, there are several methods for determining ink penetration into the interior of the paper, which can be distinguished according to the following criteria: sample preparation, image capture, sample size and resolution, and with nondestructive or destructive methods. The most common destructive methods are based on microtomy and microscopic analysis using scanning electron microscopy (SEM) or secondary ion mass spectroscopy (SIMS) or a focused ion beam instrument (FIB) or a confocal laser scanning microscope (CLSM). The most common nondestructive method for determining ink penetration depth is based on the Kubelka–Munk theory using spectral reflectance [28].

Microscopic methods are not reliable enough due to additional factors that may affect the accuracy of the results, as well as the limited observation range [23].

Therefore, in this research, the ink penetration depth was determined using a non-destructive method by analyzing the print surface using reflectance values based on the Kubelka–Munk theory according to Equation (2) [29]:

$$H_p = \frac{ln\frac{(1-R_0\times R_\infty)(1-R_p\times R_\infty)(1-R_q/R_\infty)}{(1-R_0/R_\infty)(1-R_p/R_\infty)(1-R_q\times R_\infty)}}{ln\frac{1-R_0\times R_\infty}{1-R_0/R_\infty}} \times D \quad (2)$$

where R_∞ is the reflectance value of unprinted laboratory paper over an opaque pad of unprinted laboratory papers, Ro is the reflectance value of unprinted laboratory paper over a standard black background, R_p is the reflectance value of printed laboratory paper over an opaque pad of unprinted laboratory papers, R_q is the reflectance value of the reverse side of printed laboratory paper placed over an opaque pad of unprinted laboratory papers, and D is an average value of the thickness of the unprinted laboratory paper.

The required reflectance values (R) were measured with a spectrophotometer eXact, X-Rite (D65/10°) at 457 nm (brightness). The ink penetration depth (H_p) was summarized from the average reflectance value of 50 spectrophotometric measurements of each print.

2.4.2. Analysis of Integral Optical Ink Density

The integral optical ink density (D_i) parameter was also considered in this research to describe the thickness of the ink film on the laboratory-produced paper substrates. The integral optical ink density was measured on all offset and gravure prints using a Techkon SpectroDens densitometer (manufactured by Techkon GmbH) through a 3 mm aperture (measurement status E, illumination D50, standard observer 2°, without a polarizing filter, calibrated on sample paper). Since the ink layer on the print is opaque, the optical density of the ink can be calculated from the value of the intensity of the light reflected from the ink layer (I) in relation to the intensity of the light transmitted and reflected from the unprinted paper substrates (I_0) according to the following Equation (3). A higher optical ink density value means a higher ink coverage, or a higher pigment concentration and a higher optical contrast compared to the substrate [19].

$$D_i = log\frac{I_0}{I} \quad (3)$$

2.4.3. Analysis of Graininess Value

Various models have been developed to define the uneven coverage of the substrate with printing ink, and all models are based on similar or the same factors. The main factors that lead to uneven coverage of the substrate with printing ink are the interaction between the printing press and the ink, the interaction between the printing press and the substrate, the interaction between the printing ink and the printing substrate, and the interaction between the substrate, the printing ink and the printing press. The causes of uneven coverage of the substrate with printing ink can be different, and are most often related to surface roughness, porosity, absorption, the surface free energy of the substrate, ink viscosity, printing pressure, printing speed and ambient conditions [30].

The graininess of the solid surface in the specified printing area refers to irregular optical density variations with a spatial frequency smaller than a specified tile size. It is calculated according to the international print quality protocol ISO-13660, which uses a tile size of 42.3 μm × 42.3 μm [31].

According to ISO 13660, the image area under examination is divided into 100 equal tiles (1.27 mm × 1.27 mm), where 900 reflectance measurements were made in small nonoverlapping square areas (42.3 μm × 42.3 μm) to obtain the magnitude of the optical density variation. Graininess is defined by the following Equation (4):

$$Graininess = \sqrt{\frac{\sum_{i=1}^{n} {\sigma_i}^2}{n}} \quad (4)$$

where σ_i is the standard deviation within a tile, i is the tile number, and n is the total number of tiles.

2.4.4. Analysis of Mottling Value

According to the standard ISO 13660, the analysis of uneven coverage of the printing substrate with printing ink is divided into two levels: at the micro level, from 42 μm to 1270 μm, which is called graininess; and at the macro level, above 1270 μm, which is called mottling of the full tone. Mottling is defined as the standard deviation of the average reflectance values on 100 uniform tiles, i.e., the variation in optical density from tile to tile, which is calculated based on Equation (5):

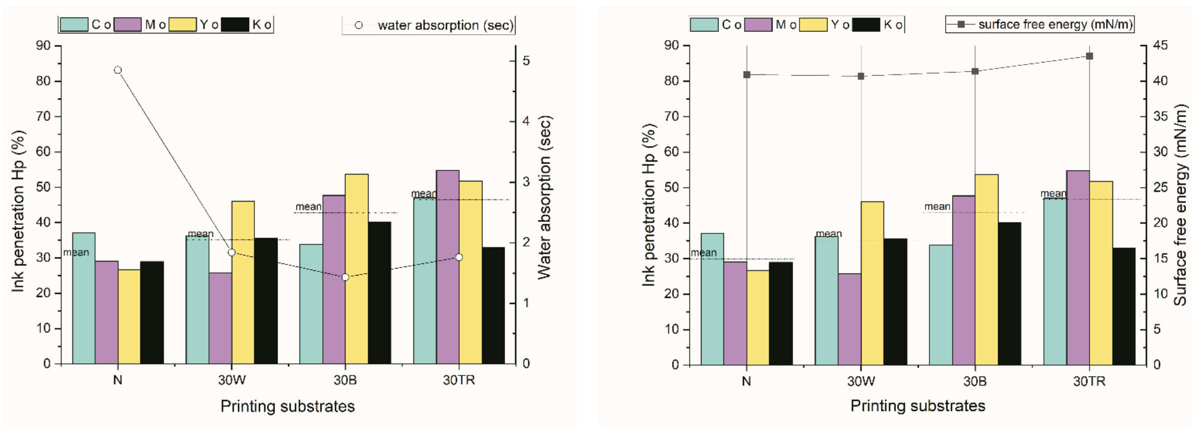
$$Mottling = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(m_i - \left(\frac{1}{n}\sum_{i=1}^{n} m_i\right)\right)^2} \tag{5}$$

where m_i is the mean value of the reflection coefficient, i is the tile number, and n is the total number of tiles.

The analysis of graininess and mottling was performed with a digital microscope PIAS-II using software that complies with the standard ISO 13660 [31].

3. Results

The usability of discarded lignocellulosic fibers in paper for secondary green packaging and labeling was analyzed using the parameter of ink penetration depth, which was compared with the characteristics of the printing substrate and the properties of the ink (water absorption, surface tension, and ink viscosity) and with the qualitative parameters of the prints (graininess values and mottling values) to evaluate the reproduction quality of offset prints (Figures 4–6) and gravure prints (Figures 7–9). Tables 5 and 6 show the properties of offset and gravure prints with the integral optical density.



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

Figure 4. Ink penetration depth on offset prints compared to the characteristics of the printing substrate: (**a**) water absorption and (**b**) surface free energy. Note: the mean penetration values of cyan, magenta, yellow and black printing inks on the same substrate are shown and labeled "mean".

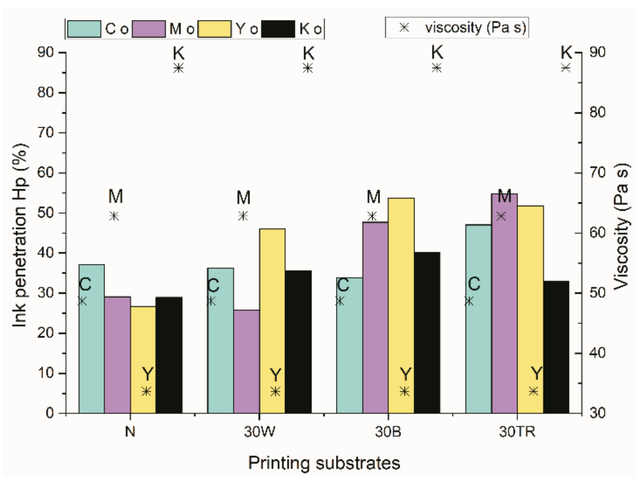
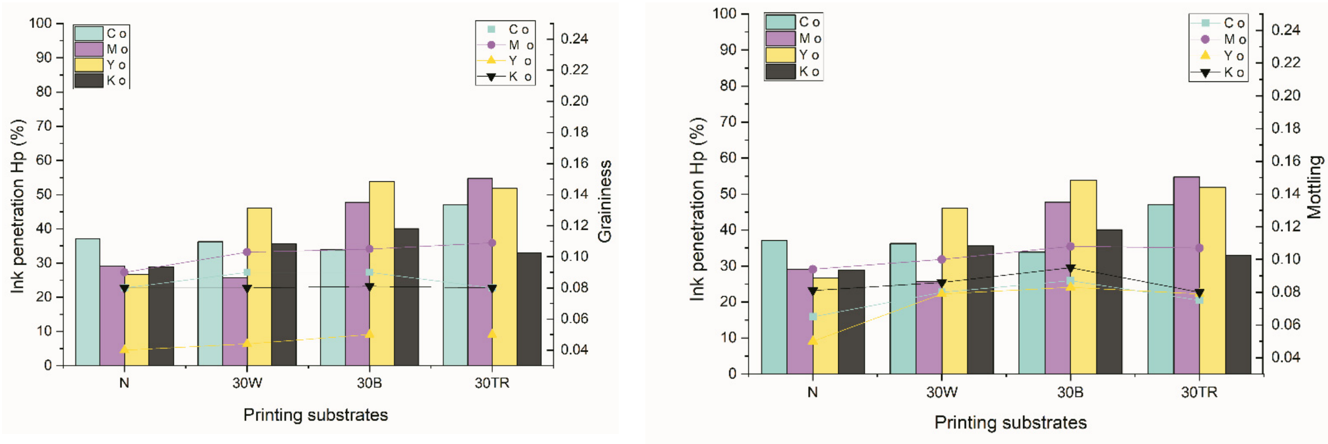
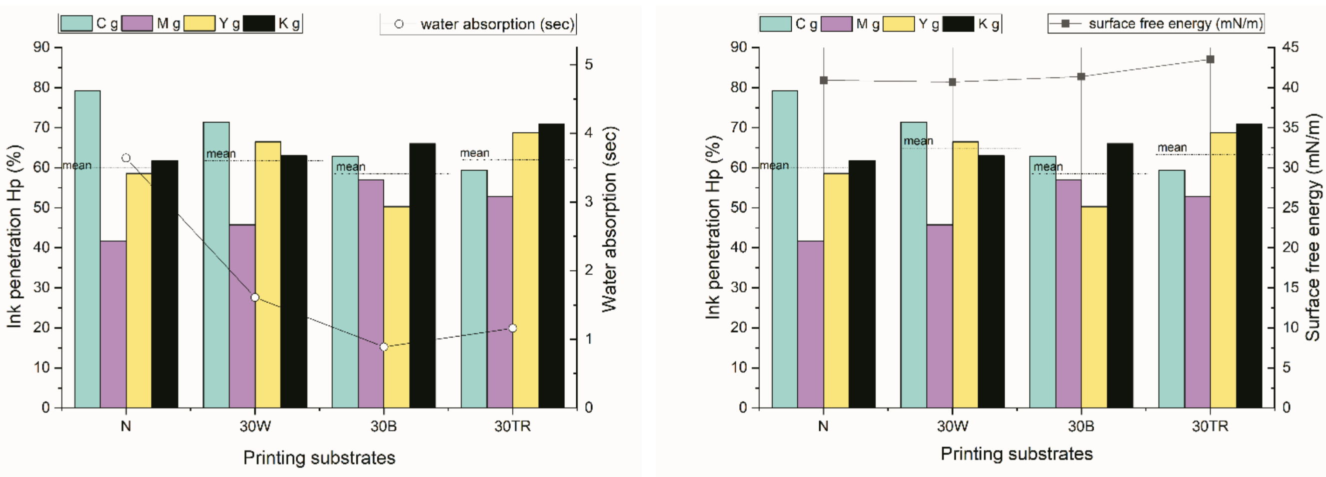


Figure 5. Ink penetration depth on offset prints compared to the property of printing ink viscosity.



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

Figure 6. Ink penetration depth on offset prints correlated with print quality parameters: (**a**) graininess and (**b**) mottling.



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

Figure 7. Ink penetration depth on gravure prints compared to the characteristics of the printing substrate: (**a**) water absorption and (**b**) surface free energy. Note: the mean penetration values of cyan, magenta, yellow and black printing inks on the same substrate are shown and labeled "mean".

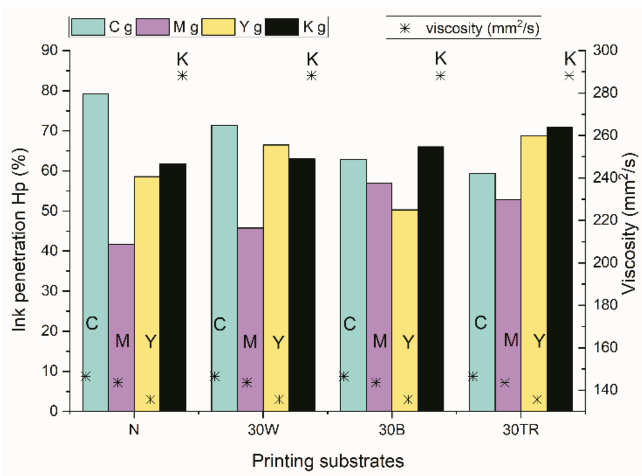


Figure 8. Ink penetration depth on gravure prints compared to the property of printing ink viscosity.

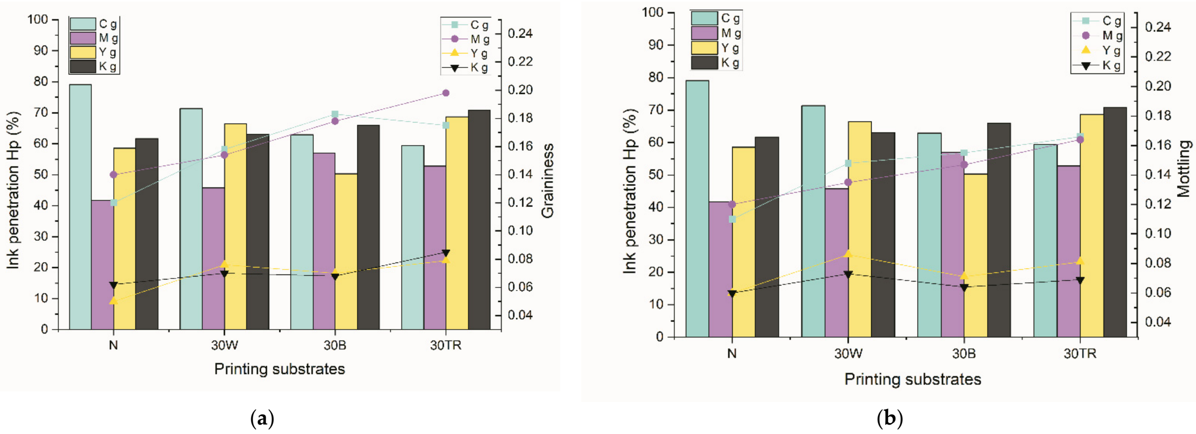


Figure 9. Ink penetration depth on gravure prints correlated with print quality parameters: (**a**) graininess and (**b**) mottling.

Table 5. Integral optical density of cyan, magenta, yellow and black offset prints.

Paper Substrate	Cyan Offset Print (C_o)	Magenta Offset Print (M_o)	Yellow Offset Print (Y_o)	Black Offset Print (K_o)
N	0.78 ± 0.03	0.82 ± 0.02	0.68 ± 0.01	1.02 ± 0.01
30W	0.86 ± 0.03	0.85 ± 0.04	0.77 ± 0.01	0.96 ± 0.04
30B	0.88 ± 0.03	0.85 ± 0.02	0.85 ± 0.02	1.02 ± 0.03
30TR	0.87 ± 0.02	0.86 ± 0.03	0.77 ± 0.02	0.91 ± 0.04

Table 6. Integral optical density of cyan, magenta, yellow and black gravure prints.

Paper Substrate	Cyan Gravure Print (C_g)	Magenta Gravure Print (M_g)	Yellow Gravure Print (Y_g)	Black Gravure Print (K_g)
N	1.06 ± 0.01	1.01 ± 0.02	0.91 ± 0.01	1.01 ± 0.01
30W	1.04 ± 0.02	0.97 ± 0.04	0.82 ± 0.03	0.98 ± 0.04
30B	1.03 ± 0.02	0.98 ± 0.02	0.84 ± 0.01	0.99 ± 0.02
30TR	1.03 ± 0.03	0.94 ± 0.03	0.81 ± 0.02	0.99 ± 0.01

The analysis of the amount of fiber within the printing substrates was additionally performed using a Spec*Scan 2000/2001 image analysis scanner based on the TAPPI T437 standard, which uses a statistical method to quantify the differences in the quality of the formation by analyzing the frequency distribution of the grayscale values of each pixel in the image of the analyzed sample. The results of the analysis obtained on 10 samples of each printing substrate are shown in Figure 10.

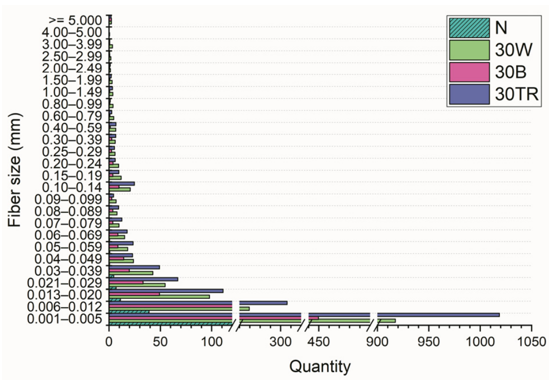


Figure 10. The quantity of fibers within each printing substrate in relation to the fiber size.

4. Discussion

The composition and surface properties of the printing substrate significantly affect the ability of the ink to penetrate the structure of the substrate. For example, coated papers absorb the ink harder than uncoated papers because they are less porous and less permeable, so the ink spreads more over the surface of the substrate and makes the ink layer on the printing surface more uniform [32]. Uncoated papers are more porous (which is confirmed by Figure 2) and rougher, which explains why, with these papers, the printing ink penetrates into the pores of the paper and does not remain on the surface, so the print will be less glossy, and the patterns will have low density values [33]. The results in this study also confirm that the addition of nonwood fibers to paper pulp increases the air permeability by up to 93%, the roughness value by up to 10.6% and the water absorption by up to 70.5% of laboratory-produced papers (Table 3 and Figures 4a and 7a).

From Figure 4, which shows the penetration depth values of offset inks into the printing substrate determined using the nondestructive method based on the Kubelka–Munk theory, it is visible that the ink penetration depth values are very similar and differ only slightly from ink to ink. To better compare the prints on printing substrates with and without discarded lignocellulosic fibers, the mean penetration values of cyan, magenta, yellow and black printing inks on the same substrate were calculated. The lowest mean value of the ink penetration depth (30.44%) was for the printing substrate without discarded lignocellulosic fibers (N), while the mean value of ink penetration depth gradually increased for the prints with discarded lignocellulosic fibers added, respectively, with 30% wheat, 30% barley and 30% triticale pulp (35.89%, 43.85% and 46.66%). This increase in the penetration depth of offset inks in printing substrates with discarded lignocellulosic fibers can be additionally explained by the ash amount (Table 3), which is lower by up to 30% for papers with straw pulp. Namely, in these printing substrates, which have approximately equal thickness, the amount of hydrophilic lignocellulosic fibers is increased. This behavior can be confirmed by the results of water absorption within the printing substrate where the printing substrate N showed a lower absorption capacity (4.85 s), compared to the substrates with discarded lignocellulosic fibers which had a water absorption capacity ranging from 1.43 to 1.84 s (Figure 4a).

Figure 4b shows a correlation between the ink penetration depth value and the surface free energy values for printing substrates. With an increase in the value of the surface free energy, a greater penetration depth of the offset ink was achieved. As with the addition of discarded lignocellulosic fibers in the pulp, the surface free energy of the substrate increased by up to 6.43% and the mean penetration value of the inks increased by up to 53.29%. Printing inks that contain a lower surface energy than the printing substrate will be accepted with the printing substrates; therefore, the high surface free energy of the printing substrates, which is a measure of the cohesive energy of the material's surface molecules, enables good ink absorption on the surface, i.e., these substrates have good wetting properties [34]. These results indicate that discarded lignocellulosic fibers from crop straw have potential as a raw material in the production of paper for printing.

From the comparison of the offset ink viscosity with ink penetration depth shown in Figure 5, it can be concluded that there is a wide range of ink viscosity from 34 to 87 Pa·s, and its influence on ink penetration depth was noticed only for low-viscosity yellow ink and high-viscosity black ink. Ink with low viscosity had a greater penetration depth compared to ink with higher viscosity, which is consistent with the results of Yong's research [35]. Based on the optical density variation value indicated by the graininess and mottling parameter, it was determined that the prints with the smallest integral optical density values (N substrate) had the best coverage of the printing substrate with the ink (Figure 6). It was evident that the mottling values were very similar for all prints (ranging from 0.05 to 0.11), regardless of the type of printing substrate and printing offset ink (Figure 6b), while the graininess values were in a similar range (0.04–0.11) and were more influenced by the type of printing ink.

Observing Table 5, the achieved integral optical density of process inks on offset prints was very similar on all printing substrates. The highest values being achieved were with black offset ink (from 1.02 for N and 30B substrates), and the lowest values belonged to yellow offset ink (0.68 for N substrate). In comparison with the ink penetration depth, it is evident that offset prints with yellow ink had a higher ink penetration depth and the smallest integral optical density, while those prints with high-viscosity black ink had the highest integral optical density (Table 5), which was also reported in the research by Krainer et al. [36].

When looking at prints obtained by using the gravure printing technique (Figure 7), it was noticeable that the ink penetrated deeper into the printing substrate (the mean penetration values ranged from 59.05% for 30B substrate to 62.94% for 30TR substrate) compared to offset inks which mean penetration values ranged from 30.44% for the N substrate to 46.66 for the 30TR substrate. The values of ink penetration depth differed the most depending on the ink used for printing, especially for substrates without discarded lignocellulosic fibers (N) and with an addition of 30% wheat pulp (30W), while the values mentioned were very similar for gravure prints on printing substrates with an addition of 30% barley (30B) and 30% triticale pulp (30TR). The same observation of greater ink penetration inside the printing substrate was obtained in gravure prints with UV-curing inks when using inks with higher viscosity and dried by UV radiation, from which it can be concluded that the principle of printing itself causes greater ink penetration inside the substrate [37].

Observing the mean value of the ink penetration depth of all process gravure inks on the substrate, it can be concluded that the ink penetration depth on all printing substrates was nearly the same and did not differ regarding water absorption and free energy of the substrate (Figure 7a,b), which was due to the lower viscosity of gravure ink compared to offset ink.

The viscosity values of cyan, magenta, and yellow gravure inks were very similar to each other (from 146.54 to 135.61 mm^2/s), while the higher viscosity values of black ink (288.23 mm^2/s) did not significantly affect the ink penetration into the printing substrate (Figure 8), regardless of the measured values of ink viscosity. A deep penetration of the ink into the substrate was observed in all prints, indicating that laboratory papers with discarded lignocellulosic fibers are permeable to liquid gravure inks. Intense ink penetration appeared when low-viscosity printing ink was applied on an uncoated porous paper substrate [38].

A very similar value of integral optical density was measured for all gravure prints with variations between prints and substrates of 0.08, with the highest value obtained for prints on a printing substrate consisting only of recycled wood pulp (from 0.90 for yellow print to 1.06 for cyan print) (Table 6), which indicates that the high penetration of the low-viscosity gravure ink did not significantly affect the retained ink layer on the surface of the printing substrate.

Prints made with magenta and cyan inks were found to have higher values for graininess (the magenta prints were between 0.14 and 0.20 and the cyan prints were between 0.12 and 0.18) and for mottling (the magenta prints were between 0.12 and 0.13 and the cyan prints were between 0.11 and 0.17) compared to prints made with other inks (whose values for graininess of yellow prints ranged from 0.05 to 0.08 and for black prints from 0.06 to 0.09, while mottling values for yellow prints ranged from 0.06 to 0.09 and for black prints from 0.06 to 0.09). As stated in the research by Karlovits et al. [39], different surface free energies and different values of ink penetration depth do not directly affect the uneven ink coverage on the substrate when printing is conducted with low-viscosity ink. Both analyzed values of uneven ink coverage on the printing substrate presented in Figure 9a,b were increased by up to 0.20 for gravure prints compared to offset prints (by up to 0.11) indicating that a greater depth of ink penetration into the printing substrate results in greater uneven surface coverage with ink.

Since the chemical composition of printing substrates plays a key role in the penetration depth of the ink into the uncoated printing substrate, the amount of filler and cellulose fibers determines the permeability in the substrate itself. From Figure 10, which shows the quantity of fibers within the printing substrate in relation to the fiber size, it was evident that printing substrates with the addition of 30% triticale pulp, as well as other substrates with the addition of discarded lignocellulosic fibers, contained fibers larger than 0.14 mm compared to printing substrates consisting of recycled wood fibers only. Considering the number of fibers and the length of the fiber in our analyzed papers, the penetration of the ink, which first moves along the cellulose fibers and then fills the pores between the fibers [40], was deeper to the substrates with discarded lignocellulose fibers. Hence, the highest ink penetration was achieved on printing substrates with triticale pulp which consisted of the longest cellulose fibers (Figure 1).

From the research conducted, it appears that prints on paper substrates with the addition of discarded lignocellulosic fibers can be used for secondary green packaging and labeling printed with an offset printing technique, where low values of ink penetration depth were obtained, while these substrates need to be additionally coated or the amount of filler inside the pulp should be increased so that they can be used for secondary green packaging and labeling printed with the gravure printing technique.

5. Conclusions

Based on the results, the following conclusions were drawn:

- The addition of discarded lignocellulosic fibers to the pulp of printing substrates increased the surface free energy of the substrate by up to 6.43% and the mean penetration value of ink inside the printing substrate by up to 53.29% compared to printing substrates without the addition of lignocellulosic fibers.
- The increase in the depth of penetration of offset inks into printing substrates with discarded lignocellulosic fibers was due to a smaller amount of ash, i.e., an increased amount of hydrophilic lignocellulosic fibers inside the printing substrate, which was also confirmed by the results of water absorption inside the printing substrate.
- In the case of prints obtained with offset thick-paste ink, it was proven that the ink with low viscosity had a greater penetration depth than the ink with higher viscosity.
- Gravure prints contain more significant ink penetration into the printing substrate compared to offset inks, where the viscosity of the ink and the printing process itself have the greatest influence.
- Both types of printing processes produced prints with nearly the same values of integral optical density, from which it can be concluded that the same reproduction of the ink application on the printing substrates was achieved.
- In gravure printing, the greater penetration depth of the printing ink into the substrate leads to uneven surface coverage with printing ink.
- It was proven that the highest ink penetration was achieved on printing substrates with a triticale pulp which consists of the longest cellulose fibers.

Based on the results of this study, it is concluded that discarded lignocellulosic fibers from crop straw have potential as a raw material for the production of paper for printing secondary packaging and labels with the offset printing technique, while these substrates require additional coating or higher filler composition to be used for printing with the gravure printing technique.

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