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The effect of pulp production times on the characteristics and properties of hemp-based paper

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ABSTRACT

The aim of this study was to determine if the pulping process (*i.e.*, beating) time of hemp cellulose fibers significantly affected the characteristics and mechanical properties of hand-made hemp paper. Hemp stalk were beaten using different pulping sequences, and two pulp groups were used to make the different hemp paper (under beaten, UB, and over beaten, OB). The hemp pulp and paper groups were analyzed using visual, chemical, physical, and mechanical tests. This study revealed that the characteristics of the hemp paper groups correlated with beating time. Ideal paper was produced from OB pulp, as it was stiffer, stronger, and tougher. The enhanced mechanical properties of the OB paper were the result of fibers with smaller diameters, from increased fibrillation, which resulted in a more amorphous, uniform paper product. The outcomes of this study will help with standardizing the hemp paper production process, obtaining more repeatable and desirable results for manufacturing, allowing for more widespread use of hemp while reducing the environmental impacts of the paper industry.

1. Introduction

Hemp, a member of the Cannabis sativa cultivar, is a versatile material used in an array of industries, including textiles, biofuels, and nutrition. [1] Hemp is an extremely viable fiber source for papermaking due to its composition and structure. [2] Hemp paper is regarded as a more sustainable option compared to conventional wood-based paper products. For instance, it requires less energy to pulp hemp fibers than it is to pulp wood-based products. Hemp paper can be recycled for more cycles compared to wood-based paper can, due to the resilience and elastoplastic behavior of the long hemp cellular fibers. [3] Additionally, hemp plants yield more biomass than forestry, lowering the acreage necessary to cultivate source materials, reducing the pressure on primary forests and their biodiversity. [3].

Hemp plant stalks are composed of two fiber sources, an inner hurd layer and an outer bast layer, in which each fiber source has the potential to serve multiple applications. [4] Fiber characteristics, such as diameter, length, coarseness, stiffness, and flexibility, need to be considered when optimizing the strength of paper products. Often, the strength is dependent on the effect of pulp production on the fiber characteristics. [5] The longest fibers come from the outer bast layer of the stalk, which consists of cellulose, lignin, pectin, and various other components. [6] The bast layer is processed prior to utilization, leaving primarily the cellulose component behind for mechanical pulping. [7] Mechanical pulping, or beating, cuts and macerates the cellulose fibers, encouraging hydration, flocculation, and fibrillation. [5,7] Fibrillation has been described as the gradual unravelling of fibrils, in the secondary wall layer of pulp fibers, characterized as slender fibrillar segments branching off of the larger, multi-layered fibers. [5] Internal and external fibrillation increase fiber flexibility and are key to the ability for pulp fibers to bond. To cleave these fibrils, shear forces are applied using a beater. [8] As the fibers circulate in the Hollander beater, they are drawn between the beater roll and the bedplate, each consisting of stainless-steel blades. By controlling the variables of the beating process

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(*e.g.*, time and roller height), one can affect the characteristics of the pulp and ultimately the qualities of the resulting paper. [9] In the current study, the amount of beating time and blade pressure were altered in the last stages of the pulping process; however, sequences of the pulping process are analogous to the specific techniques used in the art studio.

New pathways toward hemp fiber adoption necessitates an understanding of the fiber qualities expressed by various cultivars and pulp processing. Identifying fiber characteristics and properties are essential to maximize producer yield towards a desired product. Indeed, consistency in fiber performance regarding manufacturing is lacking in the field. Gaining an understanding of the intrinsic characteristics of individual hemp fiber cultivars, agricultural producers can target specific markets, processors can create material streams for industries, and manufacturers can rely on consistent material properties for various bioproduct applications. In this study, two repeatable operating techniques were analyzed to determine the effect of fiber diameter and processing methodologies on the physical and mechanical properties of the final hemp paper product. The information gained in this study can be utilized to help standardize hemp paper processing, allowing for more widespread use of hemp while reducing the environmental impact of the paper industry.

2. Methods and materials

2.1. Pulp preparation

Hemp cultivar Futura 75 was acquired from The University of Vermont Extension, Northwest Crops & Soils Program 2021 hemp fiber trials at Borderview Farm in Alburgh, Vermont. All processed samples for this study were prepared using the bast section of the hemp plant. Harvested hemp bundles were steamed for 8 h, allowing bast fiber to be hand separated from the stalk. Once the bast layer was isolated, it was delignified prior to utilization, leaving primarily the cellulose component behind. [7] Each pulped batch of dry hemp bast was cut to length (1–3") and soaked in water for 24 h. Then sodium carbonate (20% dry fiber weight, Carriage House Paper)) was diluted into 2 L of water, added to the soaking fibers, and cooked at 98.4 °C for 3 h. The fibers were subsequently rinsed with water to remove any sodium carbonate and released lignin. Next, the fibers were prepared using a 2 lb Hollander beater (Reina Designs 2 lb. Stainless Steel Beater) for mechanical pulping. The beater was filled with 15 L water, then fibers were fed in over a 5-minute period. The beaten pulp was classified as over beaten (OB) or under beaten (UB) based on the processing method (*i.e.,* different sequences of roller height and processing times) listed in Table 1. The pulp samples were stored in water and refrigerated at 4 °C until use.

Table 1
Beater roll height setting and time for macerating fibers to generate pulp.

	Roll Height (inches)	Time (minutes)
Under Beaten (UB) Pulp	0	5
	10	5
	7	10
	4	15
	3	15
	2	15
	1.5	30
	1	25
	30	5
Over Beaten (OB) Pulp	0	5
	10	5
	7	10
	4	15
	3	15
	2	30
	1	30
	0.5	25
	30	5

2.2. Pulp characterization

To observe the morphology and variability of beaten hemp fibers, a contrast microscope (Olympus IX51) was used. UB and OB hemp fibers were examined at 40x, 200x and 400x magnification. Microscopy samples were prepared by diluting 3 mL of pulp with 7 mL of water. The pulp sample was vortexed for 30 s to disperse suspended fibers. An aliquot of the fiber suspension was placed on a slide with 1-mm scale bar. Fiber diameter and fibrilization were examined using the image analysis program ImageJ (n = 25) and qualitative evaluation. [10].

2.3. Paper preparation

After pulping (*vide supra*), sheets were formed using the deckle box method for a controlled volume of pulped fibers. [11] Briefly, 4 L of water and 1 L of pulp were thoroughly combined, poured into a custom deckle box, and gravity drained through a mesh screen mold (30/30 mesh, phosphor bronze screen) for 15 min. After draining, the sheet was transferred from the mold and pressed at 2500 lbs/restraint using a hydraulic platen press (Reina Designs 50-Ton Hydraulic Press), and dried for 24 h under pressure at ambient temperature. The paper samples were stored at ambient conditions.

2.4. Paper characterization

2.4.1. Scanning electron microscopy

For scanning electron microscopy (SEM), pulp samples were lyophilized and stored in an airtight container until characterization. The dried samples were sputter-coated with 10 nm of Au–Pd prior to imaging. SEM (Zeiss Sigma 300 VP Field-Emission SEM) was used to image the pulp fibers at a magnification of 500x and an aperture size of 30 μm. [12–14].

2.4.2. Grammage

Twenty rectangle paper samples (51 mm × 42 mm) were obtained for each material group and were stored in ambient conditions prior to recording the mass. Each sample was weighed in the same atmospheric conditions. Test samples were weighed and the grammage was determined by the following formula, where g is grammage, m is mass, and A is area, following standard ISO 536: $g = m/A$ (g/m^2). [15,16].

2.4.3. Water retention

To determine swell ratio and percent weight loss, water retention was calculated. One square sample (26 mm^2) was taken from each sheet of paper. The initial dry weight (W_I) of each sample was recorded, then the sample was placed in 20 mL of DI water for 24 h. Next, samples were weighed to obtain the wet weight (W_W), the samples were frozen and lyophilized, then weighed a final time to obtain the final dry weight (W_D). The swell ratio and weight loss were calculated according to the following formulae: swell ratio (%) = $(W_W\text{-}W_D)/W_D$* 100; weight loss (%) = $(W_I - W_D)/W_I$* 100. The swell ratio is an absolute value, indicating how much weight the material took on as it was swollen.

2.4.4. Contact angle

Prior to contact angle measurements, 15 square samples (25 mm^2) were prepared for each paper type. Five hundred μL of DI water were placed on paper samples. The water contact angle was measured at five seconds (Theta C) and 60 s (Theta Ć) to determine wettability following standard ISO 186. [17,18] The contact angle of the droplet was determined using the Contact Angle plugin in ImageJ.

2.5. Paper mechanical testing

Tensile testing was performed using a benchtop axial testing

machine (Test Resources Force Transducer SM-5000 N 294) to calculate tensile strength and stiffness following ASTM D828. [19] Paper samples were cut into rectangles with a gauge length of 80 mm and a gauge width of 14 mm. Cross sectional areas (A_C) were measured and recorded prior to testing. The axial tensile displacement rate was constant at 25 mm/min. All tests were performed in ambient conditions on the same day (n = 11). Normalized force (F) and displacement (L) data were exported and processed in Microsoft Excel. Stress (σ) and strain (ε) were calculated and plotted for assessment using the formulae: $\sigma = F/A_C$ (N/mm^2, MPa) and $\varepsilon = \Delta L/L_I$ (%). Maximum stress was determined as the peak of the stress strain curve. Elastic modulus ($E = \sigma/\varepsilon$) was determined as the slope of a linear fit trendline in the common linear elastic region for all samples (0.05–0.10% strain). Toughness was calculated by differentiating a polynomial fit trendline and solving for the area under the curve.

2.6. Statistics

Statistical analysis was performed on the following data sets: contact angle, grammage, fiber diameter, swell ratio, weight loss, elastic modulus, toughness, and max stress. The interquartile range was determined for each data set and the data was assessed for statistical outliers. Gaussian distribution was assessed *via* the Shapiro-Wilk normality test. Normally distributed data sets were compared using the Welch's t-test to determine significance. Non-normal data sets were compared using the non-parametric Kolmogorov-Smirnov t-test to determine significance. A p-value < 0.05 was selected for all statistical analyses.

3. Results and discussion

3.1. Pulp characterization

3.1.1. Collection and visual observation

Upon visual observation, the UB pulp was slightly difficult to release from the mold and produced an uneven paper texture with a darker color. The OB pulp had less difficulty releasing from the mold and formed an even paper texture with a lighter color.

Optical contrast microscopy was performed to examine the morphology and variability of the beaten, and hydrated, hemp fibers. The paper industry uses water retention measurements to determine the fibrillation on the pulp fibers, as there is a known correlation between water retention and the degree of fibrillation. (Sundstrom et al., 1993) Qualitatively, the UB fibers showed less fibrillation of the majority of the fibers (Fig. 1**A**) while the OB fibers increased fibrillation, or breakdown of the main fiber with more space occupied by smaller, suspended components of the fibrous network (Fig. 1**B**). Due to higher amounts of fibrillation from longer beating times, the OB pulp had a significantly smaller ($p < 0.0001$) average fiber diameter compared to the UB pulp. The OB pulp had an average fiber diameter of 15 ± 7 μm, compared to the UB hemp pulp which had an average fiber diameter of 21 ± 8 μm (Fig. 1**C**).

3.2. Paper characterization

3.2.1. Scanning electron microscopy (SEM)

SEM was used to observe the morphology of the paper. Qualitatively, the UB paper had a less homogeneous composition with a rougher texture of interwoven larger fibers, shown in the SEM representative image (Fig. 2**A**). The ridged topography of the paper was due to the retention of a dense fibrous network, represented by thicker fibers compared to the OB samples (Fig. 2**B**). The OB paper images showed an overall smoother texture with a more homogeneous composition, with smaller fibers encased in an amorphous fibrous network. The fibrillation is due to the longer beating times, and more entanglements between smaller suspended fibers. The shorter beating time provided less of an opportunity to breakdown the fibrous network compared to longer beating time. The differences in the pulp properties and the formed paper are the result of varying the beating process.

3.2.2. Grammage

Paper density is related not only to packing of the pulp, but also the retention of highly crystalline, dense structures found in hemp stalk fibers. Crystalline materials, such as self-organized biopolymer fibers, are denser compared to amorphous materials. As crystalline structures are broken down, such as mechanical beating, fiber components become more soluble and amorphous, reducing the material density. Data was collected, and paper density was calculated. The UB paper had an average density of 140.4 ± 13.8 g^*m^{-2} and the OB paper had a significantly lower ($p < 0.0001$) average density of 115.9 ± 6.9 g^*m^{-2} (Fig. 3**A**). The data indicates that the longer beating time of the OB pulp resulted in a greater mechanical breakdown of the fibers which decreased the paper density due to a loss of crystallinity.

3.2.3. Water retention

A water retention experiment was used to determine the swell ratio and the percent weight loss of paper from ambient conditions to lyophilization. [5] The average swell ratio for UB paper was 171.4 ± 14.4%, with a percent weight loss of 4.5 ± 0.4%. The average swell ratio for OB paper was 179.4 ± 1.1%, with a percent weight loss of 4.8 ± 0.1%. Each material group indicated that the wet weights were more than double the original dry weight of the paper samples. The swell ratio of the OB paper was not significantly different from UB paper ($p > 0.400$) (Fig. 3**B**). Accordingly, the percent weight loss of OB paper

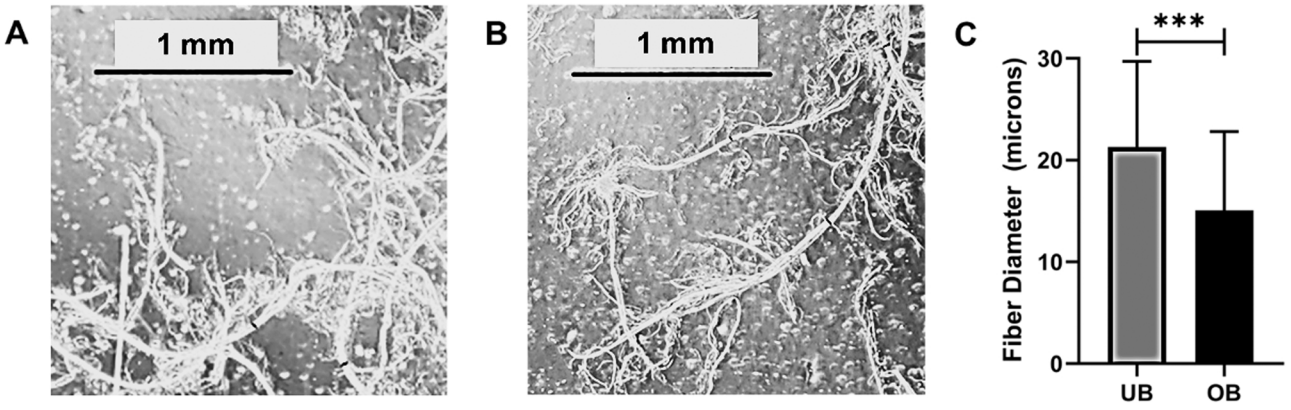

Fig. 1. (A) Contrast microscopy qualitative analysis of under beaten (UB) and **(B)** over beaten (OB) hydrated hemp fibers. All representative images were taken at 40x magnification. **(C)** Average pulp fiber diameter under contrast microscopy. UB fibers had significantly larger fibers compared to OB fibers ($p < 0.0001$).

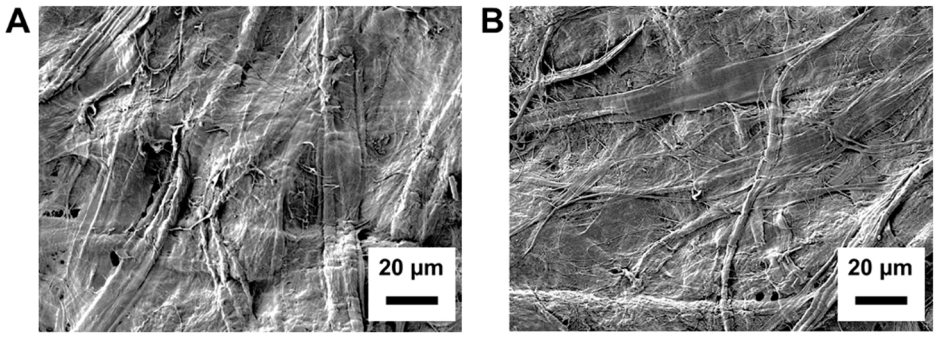

Fig. 2. Representative scanning electron microscopy images of **(A)** under beaten (UB) and **(B)** over beaten (OB) dehydrated hemp paper (500x magnification).

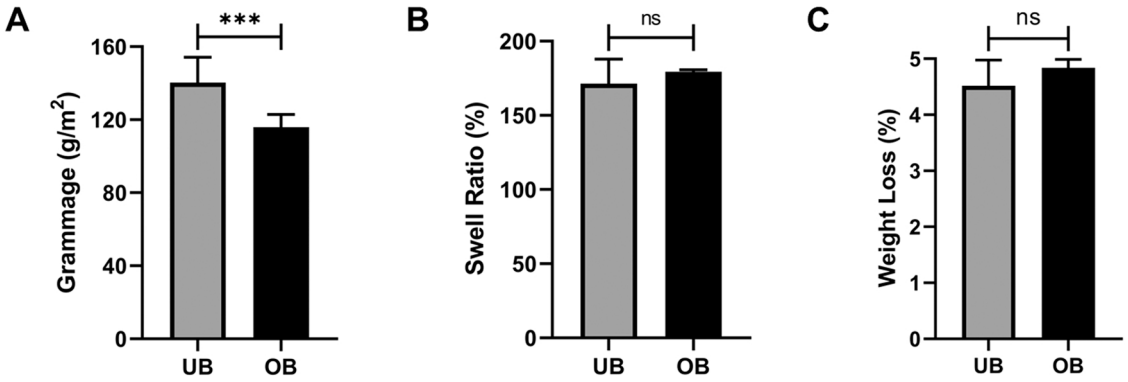

Fig. 3. **(A)** Grammage (*i.e.,* density) of over beaten (OB) and under beaten (UB) paper samples. The OB paper exhibited significantly lower densities compared to the UB paper ($p < 0.0001$). **(B)** Absolute swell ratio and **(C)** weight loss graphs for the OB and UB paper, where no significant differences were seen between paper groups.

was not significantly different from UB paper ($p > 0.260$) (Fig. 3**C**). Therefore, the properties of the cellulose fibers are not changed regarding the ability to swell with very little degradation, or significant weight loss. [20,21].

3.2.4. Contact angle

To determine the wettability of the paper, water contact angles were calculated. The average initial contact angle of OB paper was $72 \pm 39°$. (Fig. 4**A**)This paper was in the wetting phase as the contact angle was less than 90°. The UB paper had a contact angle of $105 \pm 37°$ (Fig. 4**B**). This paper was in the non-wetting phase as the contact angle was greater than 90°. While the variability of the values within each group was large due to the surface topography of the paper samples, there is a clear distinction between the two materials. The UB paper, which had a rougher surface and thicker fibers, had a higher contact angle in the non-wetting phase, or more hydrophobic. The OB paper, which was smoother and consisted of more amorphous material, had a lower contact angle in the wetting phase, and was more hydrophilic. These results are also indicative of a large degree of fiber fibrillation in the OB paper – large crystalline fibers are less hydrophilic than small molecules suspended in an amorphous solution. The structure of the fibers thus correlates with the wettability of the different paper materials.

3.2.5. Paper mechanical properties

The tensile properties, *i.e.*, the elastic modulus, ultimate tensile strength (UTS) and toughness, were calculated for the two different paper groups from stress-strain plots (Fig. 5**A**). Both types of paper failed quickly after a tensile load was applied, with a tear forming perpendicular to the direction of applied stress. The UB paper had an elastic modulus of 1.9 ± 0.2 GPa, which was significantly lower ($p < 0.05$) compared to the OB paper with a modulus of 2.1 ± 0.2 GPa (Fig. 5**B**). The UB paper had an average UTS of 44 ± 7 MPa, which was

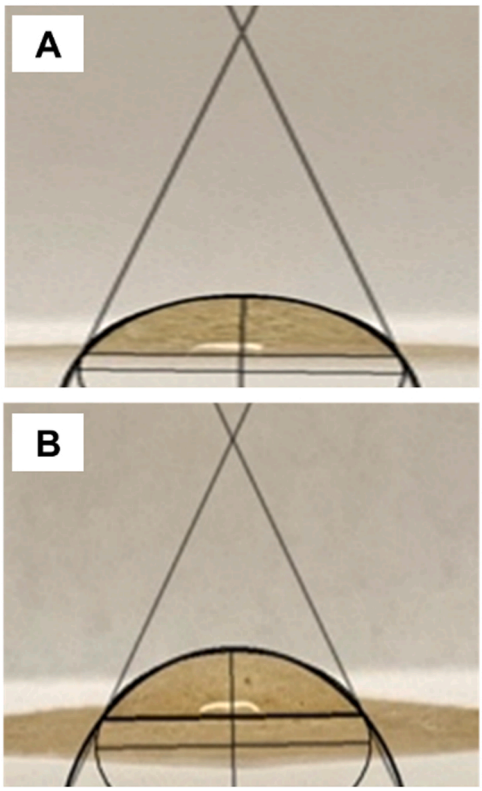

Fig. 4. Aqueous contact angles for **(A)** over beaten (OB) and **(B)** under beaten (UB) paper samples.

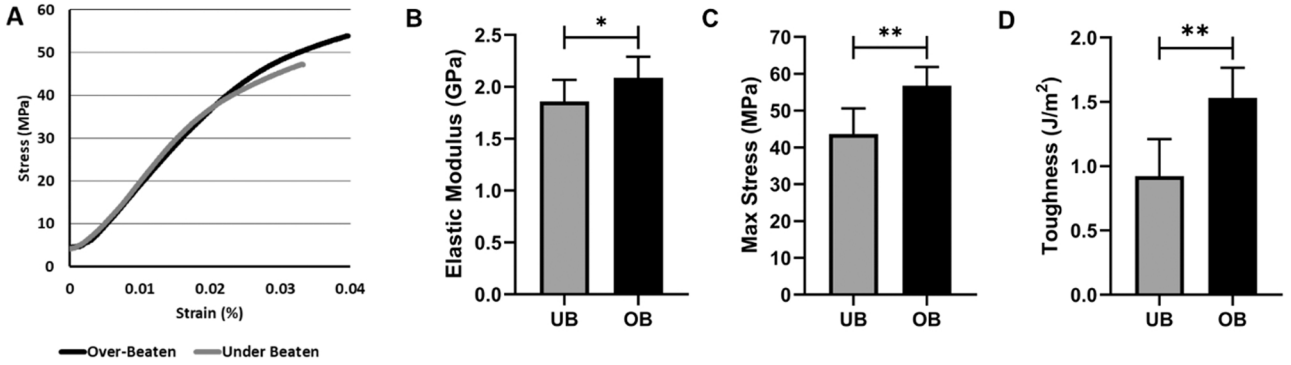

Fig. 5. **(A)** Representative stress-strain curves for under beaten (UB) and over beaten (OB) paper samples under uniaxial tensile loading at ambient conditions. **(B)** Young's elastic modulus, **(C)** ultimate tensile stress, and **(D)** tensile toughness graphs are shown for UB and OB paper samples (* $p < 0.05$, ** $p < 0.001$).

significantly weaker ($p < 0.001$) compared to the OB paper with a UTS of 48 ± 7 MPa (Fig. 5**C**). The UB paper had a toughness of 1 ± 0.5 MPa which was significantly lower ($p < 0.001$) compared to the OB paper had a toughness of 2 ± 1 MPa (Fig. 5**D**). The OB paper was stiffer, stronger, and tougher compared to the UB paper. The higher mechanical properties of the OB paper can be attributed to an increase in fibrillation, from a longer beating time, creating more amorphous regions which enables the formation of physical entanglements in solution, increasing network integration. As the fibrillation increased, more sites for bonding and entanglement between fibers were made available, which increased physical crosslinking between fibers within the paper. With more crosslinks, more energy was absorbed by the paper, leading to a higher toughness.

4. Conclusion

The hemp pulp and paper groups were analyzed using visual, chemical, physical, and mechanical tests. This study revealed that the characteristics of the hemp paper groups correlated with beating time. Ideal paper was produced from OB pulp, as it was stiffer, stronger, and tougher. The enhanced mechanical properties of the OB paper were the result of fibers with smaller diameters, from increased fibrillation, which resulted in a more amorphous, uniform paper product. The outcomes of this study will help with standardizing the hemp paper production process, obtaining more repeatable and desirable results for manufacturing, allowing for more widespread use of hemp while reducing the environmental impacts of the paper industry. Using hemp paper as replacements for common wood-based paper products like wax paper, parchment paper, filter paper, wrapping paper, and butcher paper is an intuitive way to improve the stainability of the paper industry.

CRediT authorship contribution statement

Lydia Axelrod: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization; **Patrick Charron:** Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization; **Irfan Tahir:** Investigation, Writing - review & editing; **Steven Kostell:** Conceptualization, Methodology, Investigation, Resources, Writing - review & editing, Supervision, Project Administration; **Rachael Floreani:** Conceptualization, Methodology, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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