Study on the Application of *Zizania latifolia* Straw in Papermaking

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Zizania latifolia is a vegetable that is native to China. *Z. latifolia* has a long history and a huge yield. Usually, the biological mass of leaves and sheaths of *Z. latifolia* account for 50% to 70% of the total mass of the plants, so there is a lot of residual *Z. latifolia* straw after cultivation. This causes pollution to the local environment and rivers. At the same time, non-wood fiber materials have always been one of the raw materials used in the paper industry. The purpose of this study was to turn the large-scale abandoned *Z. latifolia* straw into a valuable resource and bring a new treatment idea of *Z. latifolia* straw papermaking. By comparing the *Z. latifolia* paper with conventional old corrugated container paper, this study introduced a new idea for solving the treatment of *Z. latifolia* straw abandoned in Jinyun, China.

DOI: 10.15376/biores.17.3.5106-5115

Keywords: Zizania latifolia straw; Pulping; Papermaking

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INTRODUCTION

Zizania latifolia is the second largest aquatic vegetable in China. *Z. latifolia* is a unique vegetable with remarkable economic benefits (Deng and Chen 2017). Jinyun County is a large producer of *Z. latifolia* in China, and *Z. latifolia* has a long planting history. In recent years, the development momentum of Jinyun's *Z. latifolia* industry has strengthened. By 2020, Jinyun county had a planting area of 65,800 mu, yielding 127,000 tons of production. This accounted for 8% of China's *Z. latifolia* production, an output value of 450 million yuan. This had an impact on the entire production chain output value of 1.5 billion yuan, with more than 35,000 employees. Many farmers also have left Jinyun to plant *Z. latifolia* throughout China (Zhu 2021).

In 2018, the whole industrial chain of Jinyun's *Z. latifolia* was identified as the demonstration agricultural whole industrial chain of the Zhejiang province. In 2019, *Z. latifolia* from Jinyun was recognized as an agricultural product with geographical indication. In 2020, Jinyun was awarded as one of the top 100 counties with national characteristic industries (Jinyun *Z. latifolia*), making Jinyun worthy of the name "Hometown of *Zizania latifolia* in China" (Xia and Shen 2017).

According to statistics, about every 666.7 square meters of *Z. latifolia* will produce one ton of straw, and the annual output of *Z. latifolia* is as high as 130,000 tons (Deng and Chen 2017). Due to the lack of utilization channels, a large amount of *Z. latifolia* straw is discarded by farmers during harvest in the spring and autumn (Fu 2009). The residual *Z. latifolia* straw becomes garbage for landfill treatment or in paddy fields. This affects the appearance of the village and causes the waste of straw resources and serious environmental pollution, such as the eutrophication of water, bad odors, and so on (Wang 2018). The resource utilization of *Z. latifolia* straw has become a bottleneck problem that restricts the sustainable development of the *Z. latifolia* industry in Jinyun.

Paper is one of the most important inventions in the history of civilization and an indispensable commodity for people all over the world (Rojas and Hubbe 2005). However, the resources of papermaking raw materials are becoming increasingly scarce. At the same time, there is no better solution to the environmental pollution of *Z. latifolia* straw. Therefore, the research idea of this paper is to study the kraft pulping with *Z. latifolia* straw instead of traditional old corrugated container (OCC) material. When *Z. latifolia* is applied in the field of papermaking, it realizes the waste utilization of waste broad-leaf goose grass, and has more environmental affinity than conventional kraft corrugating medium and linerboard, which is in line with the idea advocated by China.

EXPERIMENTAL

Materials

The abandoned *Z. latifolia* straw was obtained from Jinyun County, Zhejiang Province, China. Before the experiment, we left the straw in a dry place for two weeks. In the experiment, one kind of pulp treatment method was used for the pulping. The raw materials were pulped by the kraft process and the caustic soda anthraquinone process. The parameters of the production process conditions are shown in Fig. 1.

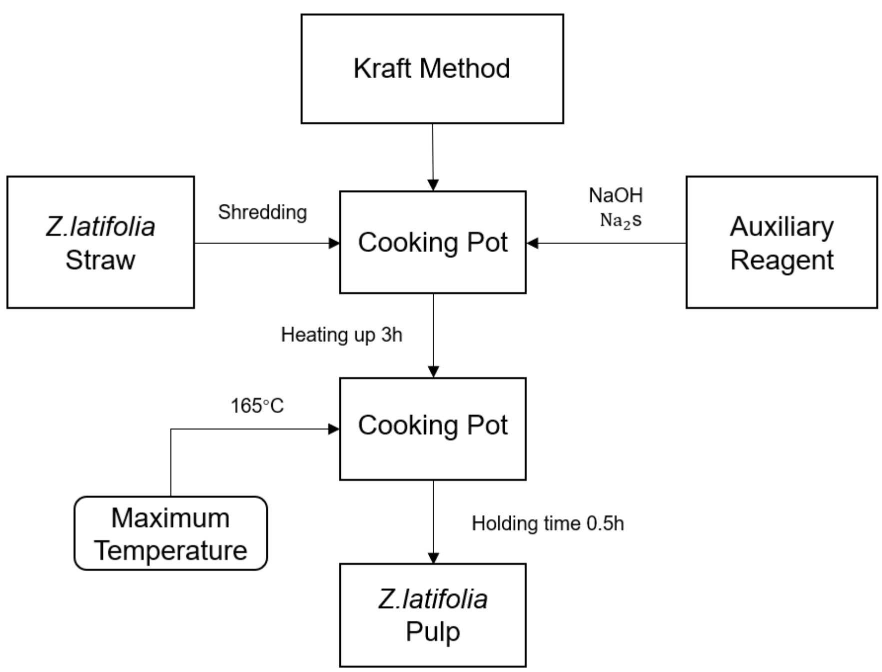

Fig. 1. Flow chart of the production process

Pulping Analysis

The pulping yield of *Z. latifolia* straw is 60.0%, which is similar to that of kraft pulp for virgin corrugating medium and linerboard base paper. Therefore, it can be preliminarily judged that *Z. latifolia* straw papermaking is feasible for its future industrialization. At the same time, further physical property detection and composition analysis is needed.

Table 1. Pulping Parameters

Raw Material	Beating Degree (°SR)	Water Content of Slurry (%)	Absolute Dry Pulp Yield (%)	Moisture Content of Raw Material (%)	Pulping Yield (%)
Z. latifolia Pulp	38	81.35	18.65	48.8	59.98
Corrugated Pulp	34	78.95	21.05	92.0	95.0

Visual Comparison of *Z. latifolia* Paper and Old Corrugated Container Paper

As shown in Fig. 2, one can obtain white paper and OCC paper according to the standard of (GB/T24324-2009). The surface of the *Z. latifolia* paper was smoother and had a noticeably smaller particle size than the OCC. However, there were still a small number of black spots, which may be due to the fact that the straw material came from rural areas and contained soil or other ingredients that were not removed.

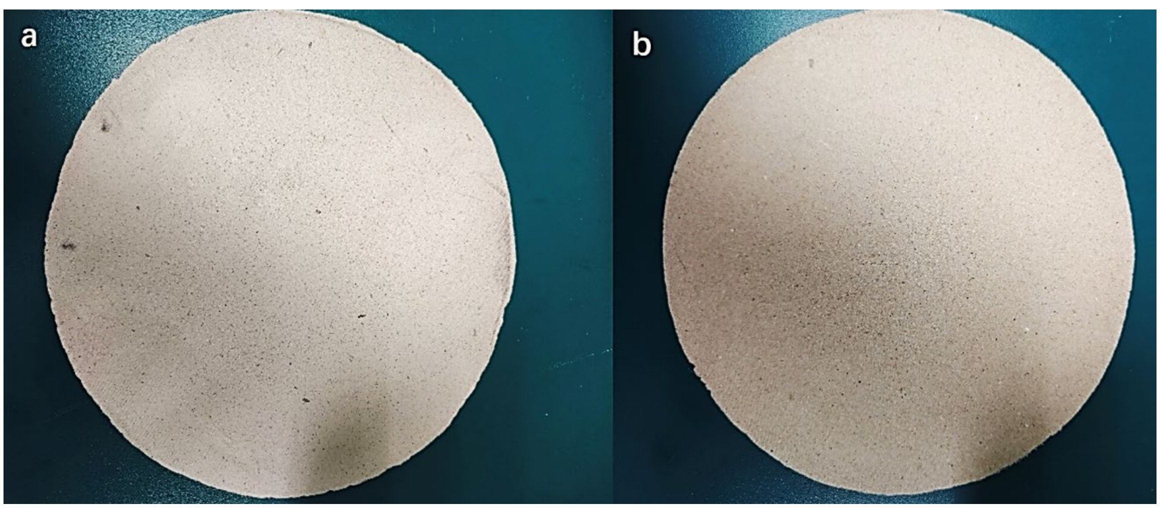

Fig. 2. a) *Z. latifolia* paper and b) old corrugated container (OCC) paper handsheets

Testing Method for the Physical Properties of Pulp

The *Z. latifolia* straw and OCC handsheets were made, fixed and quantified, and the tearing strength, tensile strength, and bursting strength were tested. The tear strength of the paper was determined according to (GB/T455-2002). The tensile strength of the paper was measured according to (GB/T12914-2008). The burst strength of the paper was measured according to (GB/T454-2020). Figure 3 presents the physical properties of the *Z. latifolia* and OCC handsheets. The tear strength, tensile strength, and burst strength of the two kinds of paper were compared. As seen in Fig. 3, the tear index of the *Z. latifolia* paper was 6.96 Nm·m^2/g, which was slightly lower than that of the OCC (7.32 Nm·m^2/g). This may have been related to the calcium carbonate ($CaCO_3$) content in the OCC paper (Manandhar *et* *al.* 2022). However, the tensile index and burst index values of the *Z. latifolia* paper were 10.84 Nm·m^2/g and 1.01 Nm·m^2/g, respectively, which were much higher than the respective 4.44 Nm·m^2/g and 0.565 Nm·m^2/g values of the OCC. This also showed that *Z. latifolia* had better paper performance than the OCC, so there may be a certain advantage for its use in the paper industry.

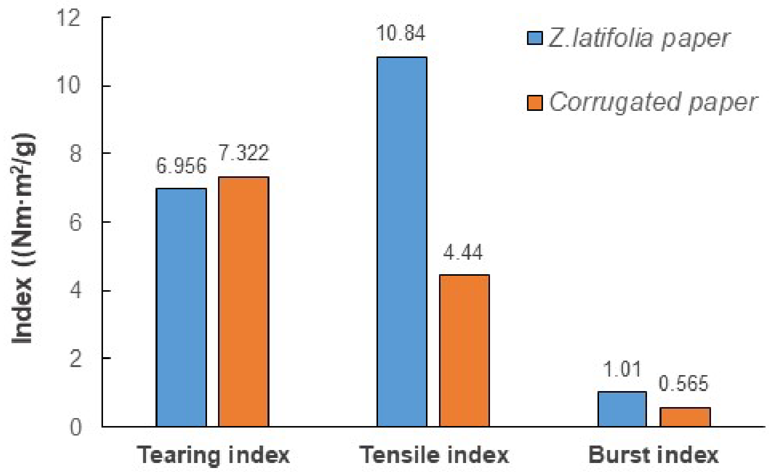

Fig. 3. Physical properties of the *Z. latifolia* and old corrugated container paper handsheets

Fiber Quality Analyzer (FQA)

An FQA measures the fiber length, width, fine fiber content, fiber crimp, and fiber kink, among other indexes. These values can be used to identify fiber raw materials, control refining conditions, predict pulp coating, and identify pulping the process, among other things. The pulp fiber was sampled and analyzed according to the GB/T 10336 (1989) standard.

Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscope photos are grayscale images, which are divided into secondary electron images and backscattered electron images. Scanning electron images are mainly used for surface micro-morphology observation or surface element distribution observation. The morphologies of the different treated straw surfaces were examined with a scanning electron microscope (SU1510; Hitachi, Tokyo, Japan) operating at an accelerating voltage of 15 kV. Before observation, the samples were coated with gold using a vacuum sputter-coater (MSP-2S/MSP-Mini; IXRF Systems, Austin, TX, USA).

Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The infrared spectra of 0, 10, 25, and 40 min of the *Z. latifolia* straw, *Z. latifolia* pulp, OCC, straw dissolved matter, and straw raw materials were studied *via* FT-IR spectroscopy. The FT-IR was recorded on a spectrophotometer (8400s; Shimadzu, Kyoto, Japan). The number of scans was 32 and the resolution was 4 cm^{-1}. In the transmittance mode, the spectrum of 500 to 4000 cm^{-1} was obtained.

X-Ray Diffraction (XRD) Analysis

X-ray diffraction is the most powerful method to study crystal structure (such as the type and position distribution of atoms or ions and their groups, cell shape, cell size, *etc.*). This experiment analyzed the crystallinity of the *Z. latifolia* straw, *Z. latifolia* pulp, and OCC through XRD analysis.

The XRD test parameters were Cu target, a tube pressure/tube flow of 40 kV/20 mA, a scanning speed of 4°/min, a scanning step length of 0.04°, and 2θ = 5° to 45°. The crystallinity was calculated and analyzed using Jade 6.0 software (Materials Data Inc., Livermore, CA, USA) (Chen *et al.* 2021).

RESULTS AND DISCUSSION

FQA Analysis

As shown in Figs. 4 and 5, the length distribution of the OCC pulp and the *Z. latifolia* fiber was approximately the same, but the width distribution of the *Z. latifolia* fiber was smaller. This provides a basis for *Z. latifolia* fiber to replace OCC pulp as raw material for papermaking.

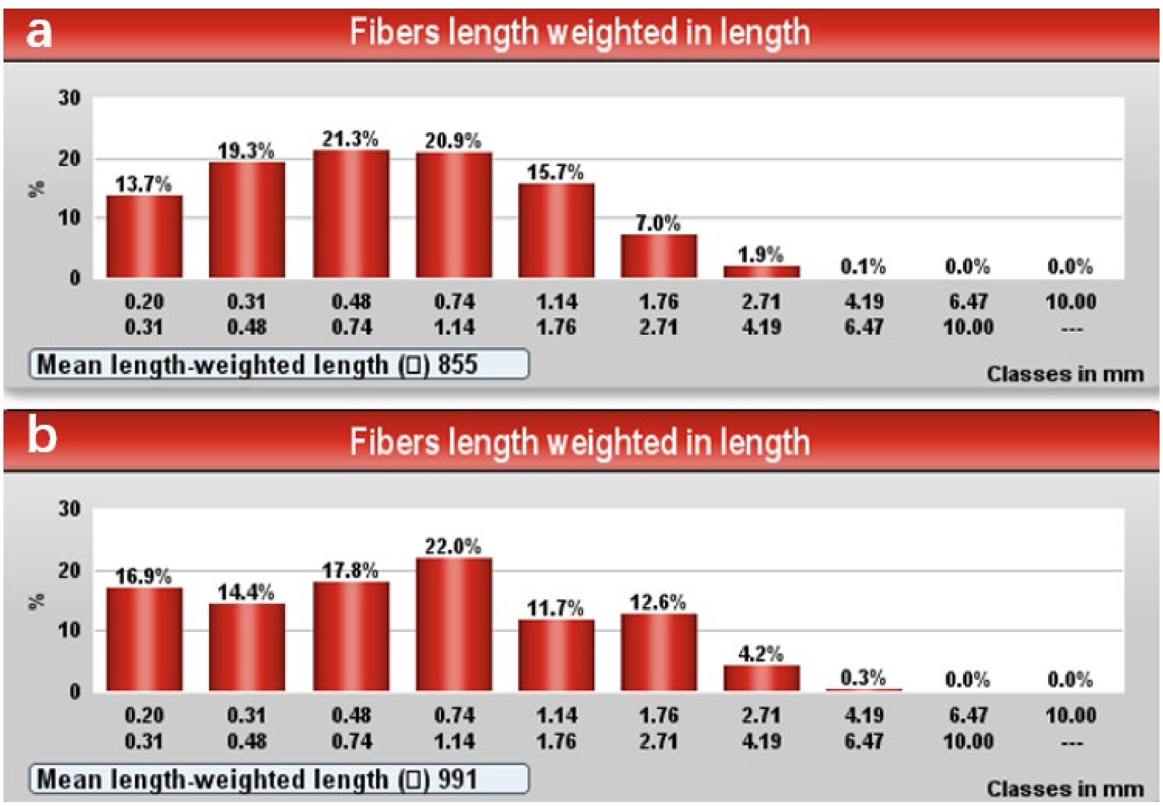

Fig. 4. FQA diagram of the fiber length a) *Z. latifolia*; b) old corrugated container (OCC)

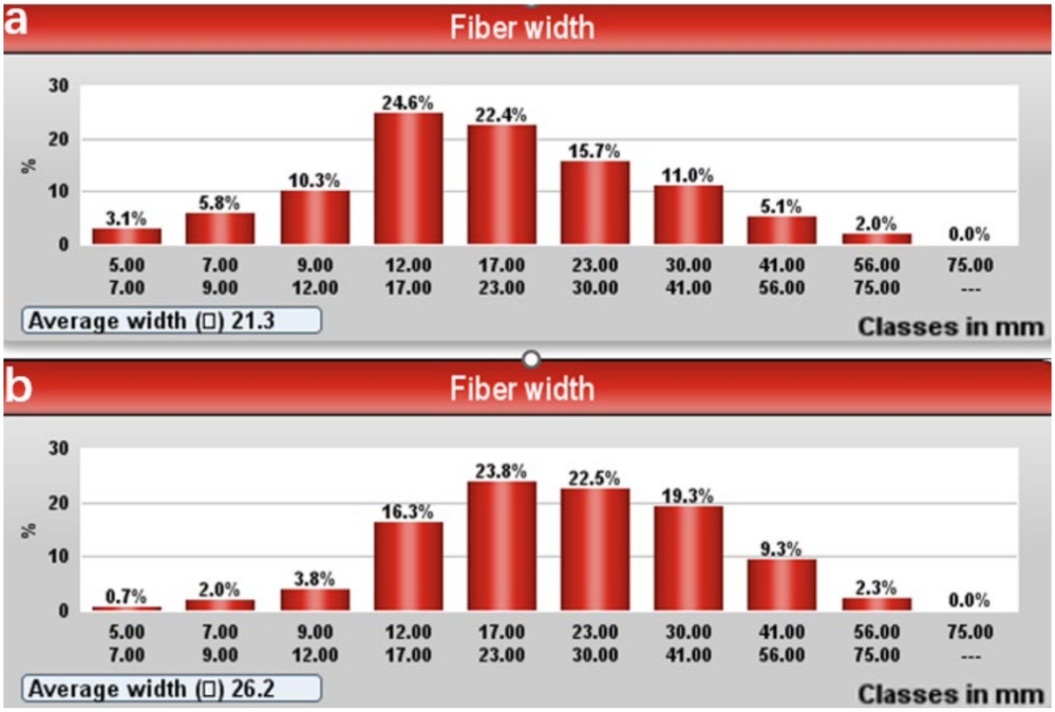

Fig. 5. FQA diagram of the fiber width a) *Z. latifolia*; b) old corrugated container (OCC)

SEM Analysis

As shown in Fig. 6, there were randomly distributed micron particles around the fiber structure.

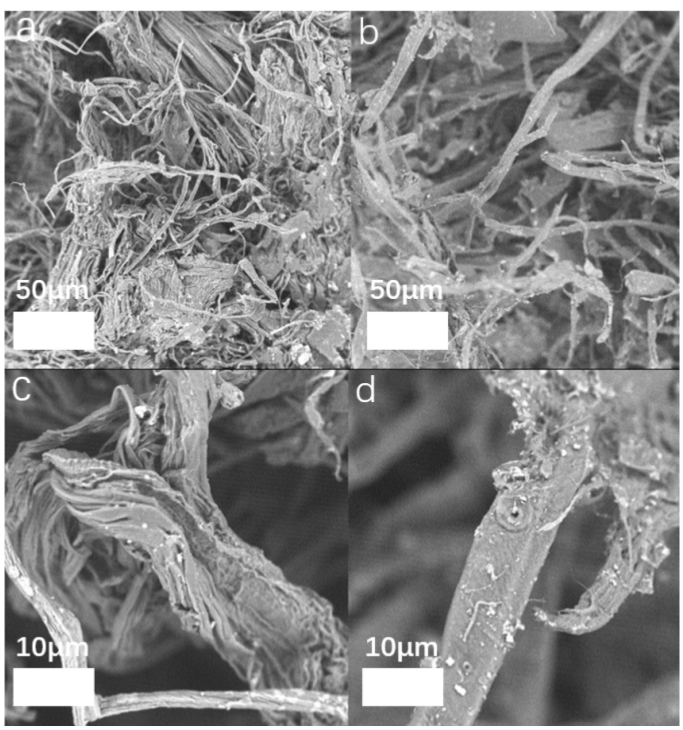

Fig. 6. SEM images of the a) *Z. latifolia* pulp at 500× magnification, b) OCC at 500× magnification, c) *Z. latifolia* pulp at 2,500× magnification, and d) OCC at 2,500× magnification

This may have been due to the presence of clay minerals in the *Z. latifolia* and OCC, which was confirmed by the XRD analysis (Figs. 6c and 6d). At the same time, the diameter of the fiber was found in an enlarged image at 2,500× magnification (10 µm) (Fig. 6c). After cooking, the fibers assembled horizontally to intertwine and form fiber bundles, which was better than OCC (Fig. 6a). There were more fibers in the *Z. latifolia* pulp (Fig. 6a) than the OCC (Fig. 6b) at the same 500× magnification. This may mean that more *Z. latifolia* straw fiber can be used.

FT-IR Spectra

The FT-IR spectra of the *Z. latifolia* straw, *Z. latifolia* paper, and OCC were distributed according to the literature, as seen in Fig. 7. The absorption peak of at 2916 cm^{-1} represented the antisymmetric tensile vibration of the $–CH_3–$ and $–CH_2–$ lignin groups, after cooking, the intensity of the peak decreased, which indicated that the lignin degraded (Ohra-aho and Linnekoski 2015). The peak value at 1650 cm^{-1} represented lignin conjugated carbonyl (CO=). This also showed a decrease in the peak intensity after enzymatic hydrolysis, which indicated the ring opening or substitution of aromatic rings. The peaks at 1222 cm^{-1} represented lignin degradation products, such as phenol, ethers, and alcohols. The increase in the peak intensity for these bands indicated an increased amount of lignin degradation products (Omoike and Chorover 2006). In addition, the absorption peak at 1140 cm^{-1} was characteristic of the eugenyl unit. However, obvious peak was observed at 1168 cm^{-1}, which indicated that there were no p-hydroxyphenyl units present in the lignin. The results show that the alkaline lignin sample may be eugenol-guaiacol lignin (Zhang *et al.* 2020). The peak value at 1037 cm^{-1} indicated the C–H vibration of the guaiacol unit. The decrease of the peak intensity indicated that the guaiacol structure was destroyed, which further indicated the lignin degradation (Pandey and Pitman 2003).

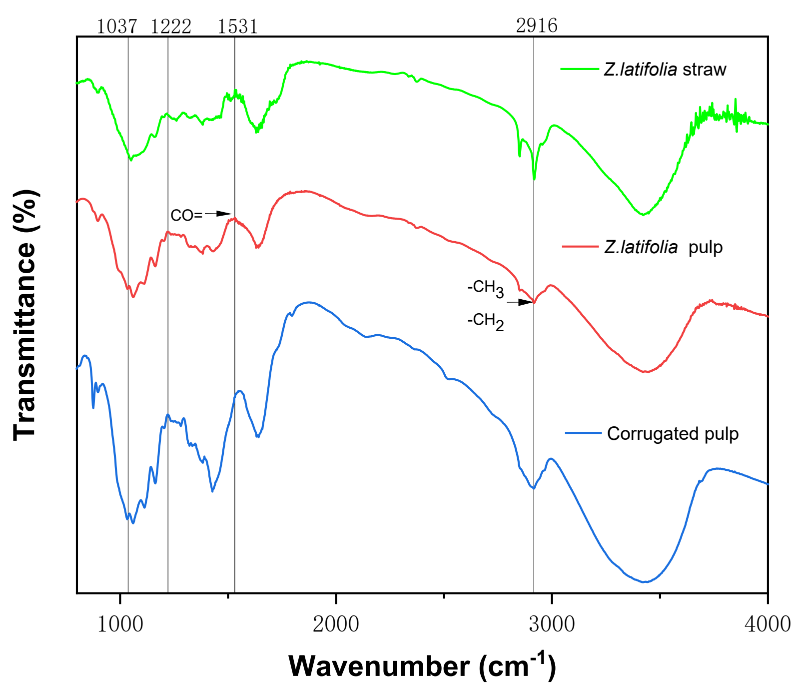

Fig. 7. The FT-IR spectra

XRD Characterization

The images of the straw raw materials, straw residues, and straw microcrystalline are shown in Fig. 8. The structure and surface functional groups of three samples were studied by XRD analysis. As shown in Fig. 8, all the samples had two wide diffraction peaks that centered on the diffraction angles of 15.3°and 22.5°. Cellulose is one of the most important polysaccharides in the plant cell wall, and it is widely used in paper industry (Ju *et al.* 2015; Aminah and Kose 2019). The weak diffraction peaks of 12.4°and 25.0° in the OCC sample indicate the existence of kaolinite ($Al_2Si_2O(5OH)_4$). Similarly, the diffraction peak of 29.4° indicated the existence of $CaCO_3$ (Pesenti *et al.* 2008; Kłosek-Wawrzyn *et al.* 2013). In contrast, there were none of these diffraction peaks in the *Z. latifolia* samples, which indicated that the composition was cleaner and mainly composed of cellulose, which is more suitable for use in the paper industry.

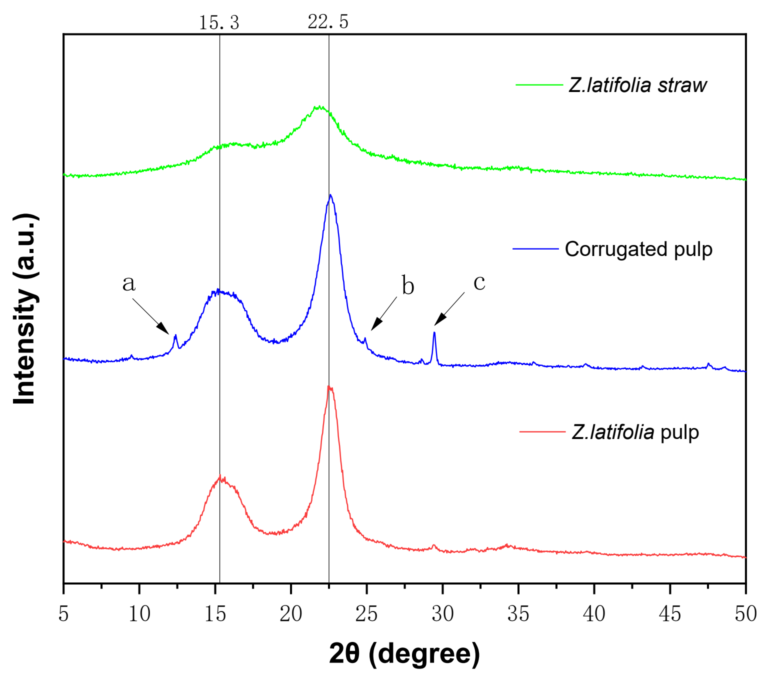

Fig. 8. XRD peak intensity diagram a) 12.4°; b) 25.0°; c) 29.4°

CONCLUSIONS

1. *Z. latifolia* straw was pulped by the kraft process. The physical parameters of the pulp, such as the beating degree, moisture content, and pulping yield were measured. The *Z. latifolia* pulp and old corrugated container (OCC) pulp were made into paper handsheets. The physical properties of the handsheets, including the tear strength, tensile strength, and burst strength were evaluated. The pulp slurry was characterized by XRD analysis, FT-IR spectroscopy, scanning electron microscopy, and an FQA. The *Z. latifolia* paper was not noticeably different than the paper made from OCC.
2. Utilizing waste *Z. latifolia* straw to manufacture paper is feasible. This study validates the preliminary assumption that more experimental data and field verification are needed for industrialization and final implementation.

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Article submitted: May 20, 2022; Peer review completed: June 26, 2022; Revisions accepted: July 5, 2022; Published: July 14, 2022.
DOI: 10.15376/biores.17.3.5106-5115