ECO-FRIENDLY PULPING OF BANANA PSEUDO-STEM WASTES WITH POTASSIUM-BASED PROCESSES

EVREN ERSOY KALYONCU

Department of Material and Material Processing Technologies,
Arsin Vocational School, Karadeniz Technical University, Arsin/Trabzon, Turkey
✉ *Corresponding author: eersoy@ktu.edu.tr*

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This study aimed to investigate the usability of banana pseudo-stem wastes, remaining from banana cultivation, with eco-friendly K-based pulping processes. Three different K-based pulping processes, KOH, KOH-K_2SO_3, KOH-NH_4OH, and soda process as control were studied. The temperature and the total alkali ratio were kept constant, while the cooking time was varied (60 min and 120 min) for each K-based pulping method. It was found that 60 min at 165 °C with 20% alkaline charge (calculated as Na_2O) are the optimum conditions for all K-based pulping processes of banana pseudo-stems. K-based pulps produced under the same pulping conditions were compared with the control soda pulp. The pulp samples were characterized in terms of their mechanical, physical, morphological and optical properties. Also, their Fourier-transform infrared spectroscopy analysis was performed. Among the eco-friendly K-based pulping processes investigated here, the KOH process can be considered as a promising alternative for pulping banana pseudo-stem waste, due to the excellent papermaking properties achieved.

Keywords: KOH pulping, KOH-NH_4OH pulping, KOH-K_2SO_3 pulping, banana pseudo-stems, papermaking properties, delignification

INTRODUCTION

Considering the increasing utilization and consumption of paper, the limited forest resources and various environmental and ecological concerns, different alternative sources of raw materials for pulp and paper production are investigated. In recent years, natural fibers from non-wood annual plants and agricultural crop residues have gained importance as an alternative raw material for the pulp and paper industry. Their natural abundance, availability, sustainability, low cost and good mechanical properties are among the most important advantages of natural fibers.[1]

One of the natural fibers that can be considered to be used as an alternative raw material for paper-making is banana pseudo-stem waste. From an acre of land, on average 1000 to 1500 pseudo stems can be obtained, and 1-2 kg of banana fiber can be produced with 10-13 of these stems.[2] Because of the special cultivation technique of bananas, a considerable amount of underused by-products remain every year in plantation areas.[3] Banana stem wastes obtained from the pseudo-stems of the banana plant are the main by-product of banana cultivation and are usually discarded as agricultural waste after harvesting.[1,4] These pseudo-stem wastes, which are left on the ground after banana harvesting, occupy large land cultivation areas and become a source of pollution, causing the release of toxic gases, such as CO_2, over time.[2] On the other hand, these wastes can be a very suitable alternative lignocellulosic raw material, with many advantageous characteristics for pulp and paper-making, due to their very high percentage of cellulose and comparatively good mechanical properties.[1,5-7] Many studies have been reported on pulp production with banana pseudo-stem wastes.[1,6,8-11] Increasing environmental concerns, large quantities of harvest wastes and low production costs also make it reasonable to use banana pseudo-stems for paper-making.[12]

The development of environmentally friendly K-based processes for pulping can be an alternative to the widely used conventional chemical processes. Thus, the problem of discharging black liquor can be eliminated or greatly reduced by using nutrient-enriched black liquor as fertilizer. Black liquor is one of the main by-products of the pulp and paper industry, which

is considered as pollutant.[13] Environmental problems have led to the development of cleaner technologies in all industries, including the pulp and paper industry.[14]

This study aimed to investigate the usability of agricultural residues, namely, banana pseudo-stems, as a raw material in eco-friendly K-based pulping processes.

EXPERIMENTAL

Materials

Banana pseudo-stems were collected from a banana plantation area in Mersin, Turkey. The pseudo-stem samples were washed with tap water to remove dirt and then allowed to dry for about a week in the open air. The samples were chopped to small pieces (approximately 2-3 cm in length) and oven dry measurement was performed before the pulping experiments.

In the paper industry, high cellulose and low lignin contents are desired properties. Banana fruit plant belongs to the genus *Musa*, family *Musaceae*,[1,4,15] and in a previous study by Omotoso and Ogunsile,[16] it was determined that *Musa* species were rich in cellulose and low in lignin content, compared to hardwoods.[17] The chemical composition (77.5% holocellulose, 51.0% α-cellulose, 5.3% ash and 0.98% silica) and solubility (9.2% etanol, 33.3% NaOH (1%) 17.3% hot water and 13% cold water) of banana pseudo-stem wastes were determined and reported in a previous study of Ersoy Kalyoncu and Ondaral.[18] Fiber dimensions were measured as morphological characteristics. The fiber length was found as 2.7 mm, fiber diameter – 22.84 µm, fiber lumen width – 16.98 µm, and fiber cell wall thickness – 2.93 µm.[18]

Pulping

Three different K-based pulping processes, KOH, KOH-K_2SO_3, KOH-NH_4OH, and a control soda process were studied. Cooking trials were performed in a 15 L electrically heated, stainless steel rotating digester, equipped with digital instruments for measurement and control of pressure and temperature. The banana stalk fiber charge (on oven dry basis) was 200 g per batch. The ratio of stalk fiber to cooking liquor was fixed at 1/6 (d.w.). Total active alkali (calculated as Na_2O, based on oven dry weight of banana stalk fiber) ratio and cooking temperature were selected as 20% and 165 °C for each pulping process. The cooking time, as a variable condition, was selected as 60 min and 120 min for each K-based pulping process, but it was kept constant at 60 min for soda pulping.

Pulping conditions are presented in Table 1. After cooking, the black liquor was separated from the pulps and the pulps were thoroughly washed in a 200 mesh washing screen with tap water. Then, the washed pulps were fiberized in a wet disintegrator and screened on a laboratory screen having 0.15 mm slots to determine the screened pulp yield, reject ratio and total yield. Kappa number and viscosity of screened pulp samples were determined according to TAPPI T 236 om-13 (2013) and SCAN-CM 15:88 standards (1998), respectively. DP values were calculated by applying the Immergut[19] formula: $DP^{0.905} = 0.805\ [\eta]$. The screened pulp was dewatered and stored in polyethylene bags at 4 °C until further processing.

The separated black liquors, produced under optimum conditions from each K-based pulping process, were also analysed to shed light on their usability as fertilizer. Potassium (K) contents of the solutions were determined by an inductively coupled plasma optical emission spectroscopy instrument (ICP-OES; Perkin Elmer, Optima 7000 DV), while carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents were determined with an elemental analyzer (Leco TruSpec Micro).

Table 1
Pulping conditions of soda, KOH, KOH-K_2SO_3 and KOH-NH_4OH pulping processes of banana pseudo-stems

Pulping process	Cooking time (min)	Time to max. temperature (min)	Temperature (°C)	Liquid to solid ratio (mL/g)	KOH (%)	K_2SO_3 (%)	NH_3 (%)	NaOH (%)
KOH*	60	60	165	6	35	-	-	-
	120	60	165	6	35	-	-	-
KOH-K_2SO_3*	60	60	165	6	28	10	-	-
	120	60	165	6	28	10	-	-
KOH-NH_4OH*	60	60	165	6	28	-	10	
	120	60	165	6	28	-	10	-
Soda*	60	60	165	6	-	-	-	25

*Total active alkali as Na_2O: 20%

Preparation of paper sheets and their characterization

For each pulp sample, handsheets of about 60 g/m^2 were prepared on a Rapid Köthen Sheet Making Machine according to Tappi T 205 sp-12. Before preparing handsheets, all pulp samples were beaten in a laboratory PFI mill in accordance with Tappi T 248 sp-15 for 850 revolutions. Freeness was measured using a Schopper Riegler tester.

The handsheets were conditioned at 23 °C ± 1 °C and kept in a 50% ± 2% relative humidity conditioned room overnight before testing. The tensile strength, burst strength and tear strength of the sheets were determined according to Tappi standards T494 om-13, T403 om-15 and T414 om-12 test methods, respectively. ISO brightness and yellowness of the paper sheets were measured in accordance with ISO/DIS standard 2470 (2016) and ASTM standard E313 (2005), respectively. The color values giving L^*, a^*, b^* values were measured with a UV-spectrophometer (Konica-Minolta CM-2600d, Osaka, Japan), using a UV filter, according to Tappi T527-om 19. Ten different test paper sheets were used for each measurement.

In addition, the FTIR-ATR spectra (Fourier-Transform Infared Spectroscopy-Attenuated Total Relectance Shimadzu IR Prestige-21, with a Pike Miracle ATR attachment) of the test papers were measured to obtain some qualitative information about the functional groups and chemical characteristics of the pulps. Each spectrum was obtained within the range of 600-4000 cm^{-1} with 16 cm^{-1} resolution and 16 repetitions.

Pulp fiber dimensions

In order to determine the pulp fiber sizes, samples were macerated by the Franklin[20] method. According to this method, samples were treated with a prepared mixture of equal volume (1:1) of 98% acetic acid and 30% hydrogen peroxide for 48 hours, at 60 °C in a closed flask. After maceration, permanent micro-slides were prepared and digital photos were taken at 56x magnification for fiber length and 90x magnification with a Projectina light microscope, for fiber and lumen width measurements. Digital photos were analyzed with the DIGIMER^{TM} image analysis program and fiber dimensions were determined. For each fiber dimensions, 100 fibers were measured randomly on each slide.

Average fiber dimensions were calculated from these obtained data and then the felting ratio,[21,22] elasticity ratio[23] and Runkel classification[24] derived indexes were calculated with the formulas given below:

$$\text{Slenderness ratio} = \text{(Length of fiber/Diameter of fiber)} \quad (1)$$

$$\text{Flexibility ratio} = \text{(Lumen width of fiber/Diameter of fiber)} \times 100 \quad (2)$$

$$\text{Runkel ratio} = 2 \times \text{(Wall thickness/Lumen width)} \quad (3)$$

RESULTS AND DISCUSSION

Pulp properties

K-based pulping processes (KOH, KOH-K_2SO_3 and KOH-NH_4OH) for the production of paper pulp from banana pseudo-stems have been compared, with varying cooking time. The results are listed in Table 2.

As can be seen in Table 2, the increase in cooking time has little effect on delignification for all the cooking processes. While the kappa number of KOH-K_2SO_3 pulp decreased by 5.34 units with increasing cooking time, the kappa number of KOH-NH_4OH pulp did not change and the kappa number of KOH pulp increased by 5.27 units. Despite the increased cooking time, the lack of expected reduction in the kappa numbers of KOH and KOH-NH_4OH pulps was thought to be due to the formation of hexenuronic acid (HexA) contents during pulping. HexA consumes permanganate, together with lignin, in the kappa number measurement of pulps.[25,26] Kappa number reflects not only the lignin content, but also the carbohydrate structures sensitive to permanganete oxidation, especially xylan-linked hexenuronic acid groups.[27] The most abundant hemicellulose in nature is xylan, with a higher occurrence rate in agricultural and agro-industrial residues.[28,29] In banana pseudo-stems, xylan can reach up to 25% of the dry mass.[29,30] Glucuronoxylans are major forms of hemicelluloses present in wood and agricultural fiber.[31] In an alkaline pulping process, 4-O-methyl-α-D-glucuronic acid groups, which is an important constituent of xylans, react with alkali and form hexeneuronic acids through beta elimination of the methoxyl linked to the xylan structure.[32-36] Despite the increasing cooking time, the increase was seen in the kappa number of KOH pulp. The lack of a significant change in the kappa number of KOH-NH_4OH pulp is related to this situation. The content of HexA increases with increasing cooking time until the maximum is reached and then decreases.[37]

The pulp yields of the K-based pulps obtained from banana pseudo-stems are also shown in Figure 1, in comparison with the kappa number values. The yield values decreased, depending on the kappa numbers of the pulps. Terminating the cooks at high kappa numbers resulted in high yield pulps,[38,39] as in the KOH-NH_4OH process. In addition, the viscosity value and polymerization degrees (DP) of all K-based pulps varied with increasing cooking time. The degree of polymerization decreased for KOH and KOH-

K_2SO_3 pulps, but increased for NH_4OH pulp with increasing cooking time.

On the other hand, the cellulose reactivity and the hemicelluloses content were too little affected in KOH and KOH-K_2SO_3 pulps. The technical properties of pulp and paper depend on cellulose characteristics, namely the degree of polymerisation (DP).[40,41] The degree of depolymerization is related to the pulp viscosity and process efficiency. Carbohydrates with a low degree of polymerization can either dissolve directly in the cooking liquor or degrade through peeling reactions. This leads to process yield losses, without having a visible effect on pulp viscosity.[42] Viscosity, commonly used to check the extent of cellulose degradation caused by the pulping processes,[43,44] also plays a major role in the evaluation of pulp quality.[42] It was observed that the viscosity values of the pulps decreased (193 units in KOH pulp and 142 units in KOH-K_2SO_3 pulp), depending on the increasing cooking time, except for KOH-NH_4OH pulp. Despite the increasing cooking time, the increasing viscosity values and polymerization degree of KOH-NH_4OH pulp were thought to be caused by partial precipitation of some dissolved xylans to the fiber surfaces. The cooking results with low residual effective alkali give higher yields, due to preserved hemicelluloses and partial precipitation of dissolved xylans on the fiber.[45,46] The cooking liquor of the KOH-NH_4OH pulping process was a mixture of strong alkali and weak alkali. The strong alkali KOH is completely ionized, while the weak alkali NH_4OH is partially ionized, so the kinetics of the process has to be different from that of conventional alkaline pulpings.[47]

The element contents of the black liquor samples from the K-based pulping processes are given in Table 3. The produced black liquors can be used as an environmentally friendly disposal alternative of a potassium rich fertilizer for soil.[47] According to the results, 60 minutes has been chosen as the most suitable cooking time for all K-based processes. For comparison with K-based pulping processes, the soda pulping process was also performed as control under the same pulping conditions.

Table 2
Pulp properties for different pulping processes

Pulping processes	Cooking time (min)	Reject (%)	Yield (%)	Kappa number	Viscosity (cm^3/g)	Degree of polymerization (DP)
KOH*	60	0.94	48.12	14.44	1284.64	1982.19
	120	0.98	43.71	19.71	1091.45	1655.53
KOH-K_2SO_3*	60	2.52	49.12	27.95	1701.21	2703.53
	120	1.46	46.16	22.61	1558.99	2454.90
KOH-NH_4OH*	60	2.98	53.17	44.75	1480.96	2319.49
	120	3.32	50.38	44.84	1570.17	2474.37

*Constant total active alkali as Na_2O: 20% (based on oven-dried raw material)
*Constant cooking temperature: 165 °C

Table 3
Elemental composition of black liquor samples from K-based pulping processes

Black liquor sample	pH	Elements content (g/L)	(wt%)			
		K	C	H	N	S
KOH	10.49	27.97	21.98	3.63	0.57	-
KOH-K_2SO_3	10.15	38.21	19.77	3.68	0.65	0.86
KOH-NH_4OH	9.64	30.79	21.64	3.70	0.87	-

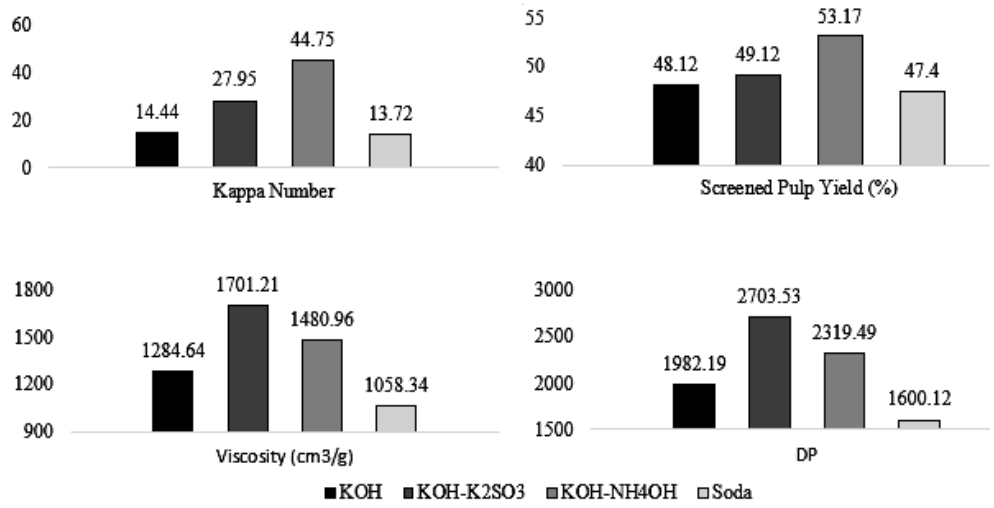

Figure 1: Comparative pulp properties of K-based pulps and control soda pulp
(total active alkali as Na_2O (%): 20, 60 min, 165 °C)

Comparative pulp properties of KOH, KOH-K_2SO_3, KOH-NH_4OH and soda pulps

In Figure 1, the pulp properties of all the K-based pulps and the control soda pulp are given comparatively. According to Figure 1, among the K-based cookings, the best delignification was obtained in the KOH pulping process, similarly to control soda pulping. The pulp yields of all the K-based pulps were better than that of the control soda pulp. Satisfactory kappa number and higher pulp yield values were obtained with the KOH process. As can be seen in Figure 1, unlike other pulp types, KOH-NH_4OH pulp has high kappa number and high pulp yield. The pulp yield also depends on kappa number. High screen yields are obtained with cookings completed at higher kappa number.[39,48-50] The viscosities of K-based pulps are higher than that of the control soda pulp. The best viscosity and degree of polymerization (DP) values were achieved for KOH-K_2SO_3 pulps. DeHaas and Lang,[51] as well as Park and Phillips,[52] determined that pulping with ammonia was much more selective, but the lignin content was significantly high.[53,54] As can be seen in Figure 1, it can be deduced that, compared to the K-based processes, the soda process is not selective, producing low yield, viscosity and polymerization degree values of pulp. Among all pulp types, satisfactory kappa number and pulp yield, higher viscosity and higher DP values can be obtained by the KOH-K_2SO_3 pulping process.

Mechanical and morphological properties of pulps

Figure 2 shows the changes in the Schopper Riegler values of the pulps as a function of PFI laboratory beating at 850 revolutions. The inital Schopper Riegler values of the pulps were between 16-18 °SR.

As can be seen in Figure 2, the KOH-K_2SO_3 and the control soda pulps, with the same °SR before the beating, showed similar changes under the effect of beating. The results showed that beaten KOH-NH_4OH pulp gave the highest °SR value, hence the lowest freeness degree. Thus, the protective pulping property of the KOH-NH_4OH process provides pulp with rich hemicelluloses content.

The mechanical properties of the test paper sheets from each kind of beaten and unbeaten pulp were summarized in Table 4. All the strength properties, except for the tear index, increased during beating. As can be seen from Table 4, the tensile strength, breaking length and burst index of the test papers from K-based pulps were better than those corresponding to the control soda pulp. The result can be partly attributed to the increased inter-fiber bonding with fibrillation, leading to higher tensile and burst strength properties, which are important for paper quality.[39,55] Beating is mostly related to the fiber-fiber bonding ability, owing to the formation of sufficient hydrogen bondings, which are much more extendable in hydroxyl groups.[56]

The highest tensile index and burst index values were obtained for the test papers from beaten KOH-K_2SO_3 and KOH-NH_4OH pulping processes, respectively.

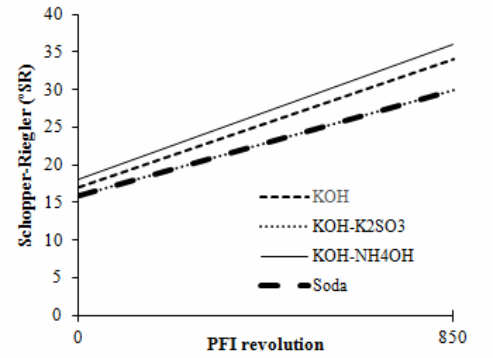

Figure 2: Effect of PFI beating on Schopper Riegler degree of pulps

Table 4
Strength properties of beaten and unbeaten pulps

Pulping process		KOH		KOH-K_2SO_3		KOH-NH_4OH		Soda	
		Mean value	Std. dev.	Mean value	Std. dev.	Mean value	Std. dev.	Mean value	Std. dev.
Tensile index (N.m/g)	Unbeaten	55.57	1.84	60.97	1.13	58.19	1.78	43.26	1.99
	Beaten	65.09	1.54	80.09	1.46	70.45	1.86	69.81	1.15
Breaking length (km)	Unbeaten	5.6	0.19	6.2	0.11	5.9	0.20	4.4	0.20
	Beaten	6.6	0.16	8.1	0.15	7.1	0.19	7.1	0.12
Burst index (kPa.m²/g)	Unbeaten	3.72	0.27	4.27	0.41	4.01	0.82	3.56	0.21
	Beaten	4.75	0.57	4.90	1.59	5.23	0.66	4.96	0.32
Tear index (mNm²/g)	Unbeaten	16.33	1.53	16.02	1.05	14.26	1.60	17.49	1.71
	Beaten	11.53	0.71	10.11	0.49	10.03	0.80	9.68	1.32

Table 5
Morphological properties of KOH, KOH-K_2SO_3, KOH-NH_4OH and soda pulp fibers

Pulping process	Fiber length (mm)	Fiber diameter (micron)	Fiber lumen width (µm)	Fiber wall thickness (µm)	Selenderness ratio	Flexibility ratio (%)	Modulus of rigidity (%)
KOH	2.61	18.87	8.90	4.99	138.31	47.16	26.41
KOH-K_2SO_3	2.54	21.01	9.80	5.61	120.89	46.64	26.68
KOH-NH_4OH	2.42	21.06	9.44	5.81	114.91	44.82	27.59
Soda	2.16	21.18	10.59	5.30	101.98	50.00	25.00

It was determined that the tear index values of K-based pulps were higher than that of the control soda pulp. The highest decrease in tear index occurring under the effect of beating was observed in the control soda pulp. The tear index property depends on the individual strength of the fibres and is mainly influenced by fiber length.[57,58] The highest tear index value, among the beaten pulps, was obtained for the test papers prepared from beaten KOH pulp. For correlations between fibre properties and paper properties, the fiber characteristics and morphological properties of the pulps are given in Table 5. Fiber length is one of the most important parameters among fiber properties, and has a significant effect on the tensile, burst and tear strength properties of the paper.[59] As seen from Table 5, the fiber lengths of the pulps are closer to each other, but the fibers of the K-based pulps are longer than those of the control soda pulp. The longest fiber length was obtained for KOH pulp; long fibers could have more chance to bond with other fibers than short

fibers. It was also determined that KOH pulp fibers had the lowest fiber diameter. Although the lowest fiber wall thickness was obtained for KOH pulp, the widest fiber wall thickness was obtained for the soda pulp.

Fiber cell thickness is important in the pulp beating process. Among the pulps produced, the determined lowest cell wall thickness value was obtained for KOH pulp, while the highest value – for KOH-NH_4OH pulp. It is possible to produce highly dense, uniform and well-formed papers with thin-walled fibers. Papers produced from pulp with thick-walled fibers have low tensile and burst strength properties.[60,61] However, it will be a more objective approach to evaluate paper strength properties considering the properties derived from fiber dimensions.[22] A high value selenderness ratio provides better paper formation and well-bonded papers.[62] The selenderness ratio gives information especially about the tear index.[63] The highest selenderness ratio of fibers was obtained for KOH pulp and the highest tear index was also obtained for beaten KOH pulp (Tables 4 and 5). There is a positive relationship between the flexibility of the fibres and the tensile strength of the paper.[63-65] As seen in Tables 4 and 5, the lowest flexibility ratio and tensile strength values were obtained for KOH-NH_4OH pulp. Flexibility is also related to fiber wall thickness. The rigidity coefficient is the opposite of the elasticity coefficient. Papers produced from high rigidity coefficient fibers are expected to have low physical strength properties, because of weak fiber-fiber bonding.[64] However, the rigidity coefficient has a positive effect on the tear factor.[66] According to Tables 4 and 5, beaten soda pulp with the lowest fiber rigidity value, gave the lowest tear index (Table 4). Since the tear index values of K-based pulps were so close to each other (Table 4), the changes were thought to be caused by dissolved components in the pulp structure.

Optical properties of pulps

The optical properties of the pulps, before and after the beating, are shown in Table 6. As shown in Table 6, the brightness and L^* values of all the pulps were negatively affected by the beating. Although the brightness values of all K-based test paper sheet samples were lower than those of the control soda paper sheets, the closest brightness value to the control soda process was obtained for the KOH process. The L^* value of KOH and soda pulps, which had the same value before beating, differed under the effect of the beating. While the L^* value of the soda pulp remained the same, the L^* value of the KOH pulp decreased. The difference in the yellowness values of the pulps under the effect of the beating was seen in the KOH-NH_4OH pulp, with the highest yellowness value. The a-axis runs from red (+a) to green (-a) and the b-axis from yellow (+b) to blue (-).[67] Compared to the control soda pulp, the a^* (red) value of the K-based pulps slightly increased under the effect of beating. It was seen that KOH pulp has a lower value than the other pulps, among both beaten and unbeaten pulps. While the b^* value is higher in unbeaten soda pulp than in the other unbeaten K-based pulps, the opposite results were observed after beating.

Table 6
Optical properties of pulp samples

Pulping process			KOH		KOH-K_2SO_3		KOH-NH_4OH		Soda	
			Mean value	Std. dev.	Mean value	Std. dev.	Mean value	Std. dev.	Mean value	Std. dev.
Brightness (ISO) %		Unbeaten	25.27	0.44	19.75	0.43	16.25	0.28	27.69	0.20
		Beaten	23.88	0.90	18.58	0.73	14.35	0.61	24.87	0.88
Yellowness		Unbeaten	37.29	0.51	42.15	0.96	44.93	0.62	35.20	0.90
		Beaten	38.45	1.13	42.69	1.12	47.30	1.15	37.65	0.88
CIE values	L^*	Unbeaten	64.66	0.21	59.37	0.48	54.09	1.86	64.58	0.46
	a^*		4.47	0.07	5.74	0.15	5.84	0.13	5.47	0.13
	b*		13.27	0.11	13.99	0.25	13.86	0.20	14.87	0.29
	L^*	Beaten	62.98	0.72	57.87	0.74	52.44	0.72	64.51	1.08
	a^*		4.71	0.17	5.96	0.19	6.21	0.06	5.42	0.20
	b*		13.62	0.21	14.04	0.30	14.05	0.25	13.03	0.45

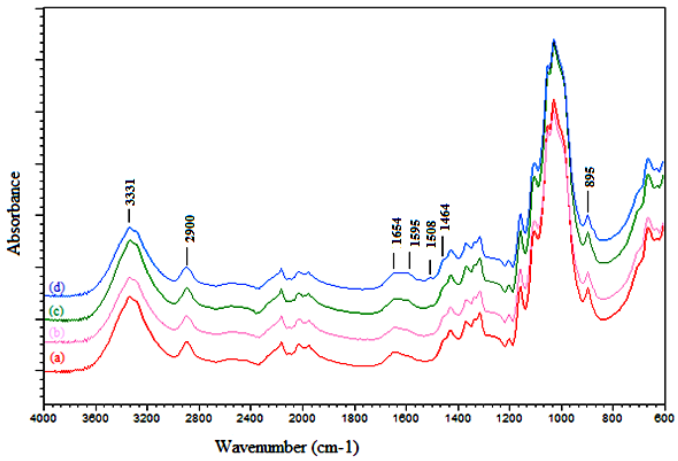

Figure 3: Infrared spectra of studied pulp fibers: (a) soda pulp fiber, (b) KOH pulp fiber, (c) KOH-K_2SO_3 pulp fiber, (d) KOH-NH_4OH pulp fiber

Fourier-transform infrared spectroscopy-attenuated total reflectance analysis

Figure 3 shows the FTIR-ATR spectra, indicating chemical changes recorded for each K-based pulp and the control soda pulp. A sharp absorption band observed at around 895 cm^{-1} is characteristic of β-glycosidic linkages between the glucose units in cellulose, and its intensity is linearly related to the percentage and crystallinity of cellulose.[68] A decrease was seen in the height of the peak at 895 cm^{-1} for KOH-NH_4OH pulp (Fig. 3d), and this was associated with the increase in amorphous regions. The absorbance peak at 1464 cm^{-1} can be assigned to asymmetric bending of CH_3 in methoxyl groups in lignin.[69] In this band, a weak peak was observed for soda (Fig. 3a) and KOH (Fig. 3b) pulps, and a slightly clearer peak for KOH-NH_4OH pulp (Fig. 3d). A weak absorption band at 1508 cm^{-1} for KOH-NH_4OH (Fig. 3d) pulp is related to the aromatic skeletal stretching vibrations in the aromatic structure (C=C) of lignin.[70-72] The disappearance of this peak, especially for soda (Fig. 3a) and KOH (Fig. 3b) pulps, indicates that lignin has been removed. A broad peak observed in the 1654 cm^{-1} and 1595 cm^{-1} area for KOH-NH_4OH pulp (Fig. 3d), corresponds to stretching vibrations of conjugated C=O of lignin[73,74] and stretching vibrations in the aromatic structure C=C of lignin.[70,75] The peak height at 1595 cm^{-1} was slightly lower for KOH-K_2SO_3 (Fig. 3c) pulp, when it was quite low for KOH (Fig. 3b) pulp and control soda (Fig. 3a) pulp. The prominent band around 3300 cm^{-1} for all the pulps was attributed to the stretching vibrations of the hydroxyl group in the presence of H-bonds.[75] The sharp intense peak at 2900 cm^{-1} corresponds to the -CH stretching vibrations of CH_2, CH_3 in polysaccharides[76] and is a common functional group characteristic of organic macromolecules found in natural fibers.[77-79] This peak shows lower intensity for KOH (Fig. 3b) and KOH-NH_4OH (Fig. 3d) pulps than for the others.

CONCLUSION

The pulping potential of banana pseudo-stem wastes was investigated with three different K-based pulping processes (KOH, KOH-K_2SO_3, KOH-NH_4OH), in comparison with the soda method, under the same total alkali ratio and the same pulping conditions. The lowest kappa number was achieved for KOH pulp, the highest viscosity and polymerization degree – for KOH-K_2SO_3 pulp and the highest screen yield – for KOH-NH_4OH pulps, when comparing the pulps obtained by K-based processes in terms of their properties. The highest tensile index and breaking length values were achieved for KOH-K_2SO_3 pulp, among all the pulps achieved, including the soda one. Although the desired kappa number value could not be obtained under the applied cooking conditions with the KOH-NH_4OH process, remarkable values were obtained in terms of mechanical properties. KOH-NH_4OH pulps can be considered as a promising alternative to conventional ones, especially when strengh is required. The KOH process provides pulps with similar kappa number, higher viscosity and higher screen yield values, but also similar tensile index, breaking length, burst index and higher tear index, compared to the soda process under the same cooking conditions. Overall, the findings of this

study reveal that KOH pulp has better results than the control soda pulp in reaction selectivity. The KOH process can be considered as a promising eco-friendly alternative for pulping banana pseudo-stem wastes.

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