

## Refining, Dewatering, and Paper Properties of Soda-anthraquinone (Soda/AQ) Pulp from Rice Straw

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The dynamic drainage, zeta potential, cationic demand, fiber morphology, ash content, and silica content of rice straw soda-anthraquinone (soda/AQ) pulps were measured to study the effects of a mechanical treatment on the drainage performance. The physical properties of handsheets prepared from each beaten sample were also analyzed. It was indicated that pulp fibers played an important role in increasing the beating degree in comparison with non-fibrous cells during refining. The dynamic drainage curve could be divided into three different stages in terms of the drainage rate, and the difference between the pulps screened-out non-fibrous cells ( $P_{\text{nof}}$ ), and unrecovered non-fibrous cells ( $P_i$ ) decreased with refining. Due to the absence of a large quantity of non-fibrous cells, as the beating proceeded, the straw pulp presented an ever-increasing tendency in terms of kink index and curl index. Also, cationic demands of pulps increased linearly and the zeta potential of the fibers decreased gradually with beating. Rice straw was found to be favorable for papermaking, helping to compensate for an acute shortage of wood in China.

*Keywords:* Rice straw pulp; Drainability; Beating; Surface charge; Fiber morphology

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### INTRODUCTION

Rice straw, a crop residue, is one of the most abundant renewable biomass resources. In terms of production share, it is the third most important crop in China, next to wheat straw and corn stover, and it accounted for approximately 14% of total straw production (including wheat straw, corn stover, sugar cane, cotton stalk, hemp, *etc.*) in 2008 (Zhou *et al.* 2011; Li *et al.* 2012). Part of it is used for livestock, compost, barnyard manure, *etc.*, but the vast majority of it is burned in the field, which is a waste of an important resource and causes increased air pollution (Zhang *et al.* 2017). It is hoped that the conversion of rice straw into biorefinery products will become commercialized to make full use of the plant, but examples, such as the successful application of a digester mainly from rice straw, remain sparse. Over the last 20 years, it is impressive how much the mass production of pulp from rice straw has grown, and this has had a huge impact on the development of the Chinese paper industry due to its compensation for an acute shortage of wood.

It is well known for rice straw to have low lignin content, approximately 52 g/kg  $\pm$  16 g/kg rice straw (Van Soest 2006). And it is a fibrous material suitable for papermaking, besides the characteristics of its easy pulping, because of its high percentages of cellulose and hemicellulose, in the range of 32% to 47% and 19% to 27% (Binod *et al.* 2010), respectively. Rice straw has been widely processed with soda-anthraquinone (soda/AQ) technology for small industrial productions with the following advantages: (a) lower investment; (b) increasing high value of straw residue; (c) high throughput with short cooking time (Rodriguez *et al.* 2010; Daljeet *et al.* 2017) into pulp

and paper. However, there are many problems with this process, such as the low extraction efficiency of black liquor (less than 80%), silicon disturbance, and the resulting poor thermal efficiency and recovery cycle efficiency in the alkali recovery system (Daljeet *et al.* 2016), due to large amounts of ash (up to 22%), silica content (9% to 14%) (Abdel-Mohdy *et al.* 2009), and non-fibrous cells such as parenchyma, vessels, epidermis, sclereid, *etc.* that are present in rice straw. As a result, these problems are greatly restricting the development of the clean pulping of rice straw.

As for the negative impact from the silicon disturbance, it can be alleviated and even eliminated through desilication of straw black liquor with flue gas (Ma *et al.* 1991), the adsorption of silica on straw pulp during alkali-oxygen pulping (Chen *et al.* 1996), or with the help of silicon retention aids such as aluminum oxide, *etc.* (Tutus and Eroglu 2003) in soda pulping. The poor drainability of straw pulp now looks fatal to the development of the straw pulping industry, because a large number of non-fibrous cells existing in straw pulp are considered to be the main cause of the slow drainage. How non-fibrous cells affect the pulp drainability is very poorly understood. Better recognition of the drainage property will be helpful for clean production and good use of straw pulp.

Beating or refining, one of the most important processes in paper manufacture, is commonly applied to increase pulp quality by modifying the fiber's structural properties, including hydration, fiber swelling, internal/external fibrillations, fines formation, fiber shortening, *etc.* (Oksanen *et al.* 1997; Fasdim and Duran 2003; Lecourt *et al.* 2010; Gharekhani *et al.* 2015). Normally, those changes happening to fibers are characterized by the beating degree value, °SR (Mutjé *et al.* 2005; González *et al.* 2013). In contrast, treatment of the pulp is found to change the electrokinetic properties of the fibers treated (Nishi *et al.* 2007), and change fiber swelling and inter-fiber bonding strength (Nishi *et al.* 2004a). All of these characterizations tend to play vital roles, not only in the dewatering rate of the stock, but also in the quality of the end products.

Straw pulp with inferior drainability is an indisputable fact, and this property tends to get worse with mechanical stirring or deflaking of the pulp (Shao *et al.* 2016), unlike wood pulp, which is impervious to such non-destructive agitations. This quality also results in the increase of the beating degree of straw pulp in the industrial flow process because of inevitable actions from the pump and mixer blades. Through the authors' previous research (Shao *et al.* 2016), it has been shown that the presence of non-fibrous cells raises the initial beating degree of rice straw pulp by *ca.* 10 °SR, but the increase in deflaking seems tied to fibers other than non-fibrous cells. This means that the description of the drainability of straw pulp is far beyond what one imagined. To be sure that the beating degree of straw pulp would be higher than that of wood pulp they were subjected to the same refining levels. (Hou *et al.* 2011). Although the beating characteristics of wood pulp are already widely known, the details of how fibers and non-fibrous cells play respective roles in the beating of straw pulp are still unfamiliar. Limited understanding of straw pulp drainability has been a hindrance to its commercial use.

Rice straw, as received, may not be acceptable for papermaking because of a higher proportional presence of non-fibrous cells and silica, which are considered to be two major obstacles to drainability. Based on the pulp obtained from soda-AQ pulping of rice straw, this study focused on the impact of a mechanical treatment on the drainage performance, such as the dynamic drainage, zeta potential, cationic demand, fiber morphology, ash content, and silica content of the pulps with or without non-fibrous cells. In addition, the handsheets of the pulp subjected to beating were evaluated for their

strength properties. This research aims to provide valuable information for the rational use of straw pulp.

## EXPERIMENTAL

### Materials

The rice straw used for this study came from Wuding County (Yunnan Province, China). The air-dried sample was manually cut and sieved to obtain a length of 30 mm to 50 mm, free of impurities, such as leaves, spikes, and dust.

### Methods

#### *Pulping*

The prepared straw was cooked in a 15-L electrically heated autoclave *via* the soda-AQ (anthraquinone) method under the following conditions (Alejandro *et al.* 2010): NaOH charge of 14% (on oven-dried (OD straw)), AQ dosage of 0.1% (on OD straw), liquor to straw ratio of 1:4 (on OD straw), time to maximum temperature of 30 min, cooking time at the maximum temperature of 50 min, and maximum temperature of 148 °C.

#### *Screening and determination of the pulp properties*

After pulping, the resulting pulp was uniformly grouped into two parts and then passed through a screen (AB Lorentzen & Wettre Inc., Stockholm, Sweden) with a 0.2 mm slot. One part was collected at the nozzle with a 120-mesh nylon bag to screen out the non-fibrous cells (referred as to  $P_{\text{nof}}$ ), and the other part went through a 350-mesh nylon bag that did not remove non-fibrous cells (referred as to  $P_f$ ). Meanwhile, each screening liquor was percolated through a 500-mesh bag, and the fraction retained in the bag was named  $F_{120}$ , for smaller than 120-mesh sizes, and  $F_{350}$ , for smaller than 350-mesh sizes. The screened pulp yield, fines yield, kappa number, brightness, and viscosity of the pulps and fines untreated mechanically were examined under about pH=7.0 condition.

#### *Refining of the pulps and its drainage property test*

The screened pulps were individually beaten to several given levels in a PFI mill at 10% consistency according to the TAPPI T248 sp-00 (2011) standard. The drainage resistance ( $^{\circ}\text{SR}$ ) of the pulps was measured as per ISO 5267-1 (2000) using a Müttek<sup>TM</sup> dynamic freeness retention tester (DFR-05, BTG International Co. Ltd., Germany). The dynamic drainage curve concerning the drainage time against filtrate weight was also provided by the same instrument.

#### *Fiber qualities measurements*

The fiber qualities of the pulp including mean length- weighted length ( $L_w$ ), curl index (CI), kink index (K), and fines (F) were characterized *via* an OpTest laboratory fiber quality analyzer (FQA, OpTest Equipment Inc., Hawkesbury, Canada). The analysis of the same sample was repeated twice or more within allowable error.

#### *Ash and silica contents of the samples*

The pulp slurries obtained from the drainage resistance test were evaporated in a boiling water bath until the solids content was close to 50%. Next, the samples were

transferred into pre-weighed bottles and oven-dried at 105 °C to obtain the constant weight for calculation of the ash content. The ash of the pulps and fines was examined in agreement with the TAPPI T211 om-02 (2002) standard, and the silica content of the pulps was examined in agreement with the TAPPI T244 cm-11 (2011) standard. The silica content was counted as the percentage in ash.

#### *Measurement of pulp zeta potential*

The zeta potentials of pulp samples were determined using a Mütek™ System Zeta Potential (SZP-10, BTG International Co. Ltd., Germany). Two repeated tests were performed to obtain an average value for each sample.

#### *Measurement of charge density*

The charge densities of both  $P_{\text{nof}}$  and  $P_f$  were measured with a colloidal titration method with standard cationic polyelectrolyte and polydiallyldimethyl ammonium chloride (Poly-DADMAC, molecular weight 150 g/mol to 200,000 g/mol), which are widely used as cationic reactants. The end point where the streaming potential was 0 mV was determined by means of a Mütek™ Particle Charge Detector (PCD-05, BTG International Co. Ltd., Germany). The reported value was an average of three measurements.

#### *Scanning electron microscopy (SEM) of the samples*

Prior to the morphology measurements, the dried fibers from different beating levels were coated with a Sputter Coater (COXEM Co. Ltd., Daejeon, Korea) followed by observation *via* scanning electron microscopy (Quanta200, FEI, Eindhoven, Netherlands) with an accelerating voltage of 5 kV.

#### *Characterization of papersheets*

The different refined pulp samples were prepared to obtain 60 g/m<sup>2</sup> handsheets by using a ZQJ1-B-II (Xianyang Tongda light industrial equipment co., LTD, Xianyang, China) sheet former, and subsequent placement in a humidity-controlled room for 24 h. The sheets were determined following the standard methods for physical properties, including tensile strength ISO1924-2 (2008), folding endurance ISO 5626 (1993), tear index ISO 1974 (2012), and burst index ISO 2758 (2001). Each pulp sample was tested six times to obtain an average value.

## RESULTS AND DISCUSSION

### Properties of the Pulps and Non-fibrous Elements

The fundamental characteristics of the pulps with screened-out non-fibrous cells and not screened-out non-fibrous cells, and non-fibrous elements, are listed in Table 1. Strictly speaking, the screened-out non-fibrous elements could be thought of as consisting of the majority of parenchyma cells, some other non-fibrous cells, and fines fractured from fibers. It was clear that the non-fibrous part had an assignable impact on the properties of the pulp. This is because the non-fibrous part accounted for *ca.* ¼ of the total yield, close to 60% (*i.e.*, 17.8% for  $F_{120}$  and 12.8% for  $F_{350}$ , respectively). The 5 percentage points difference in yield were attributed to intact parenchymas and a small quantity of shorter fibers in the range from 120 µm to 43 µm in diameter (Fig. 1). The proportion of parenchyma cells remaining in  $P_{\text{nof}}$  was regarded as normal, because the

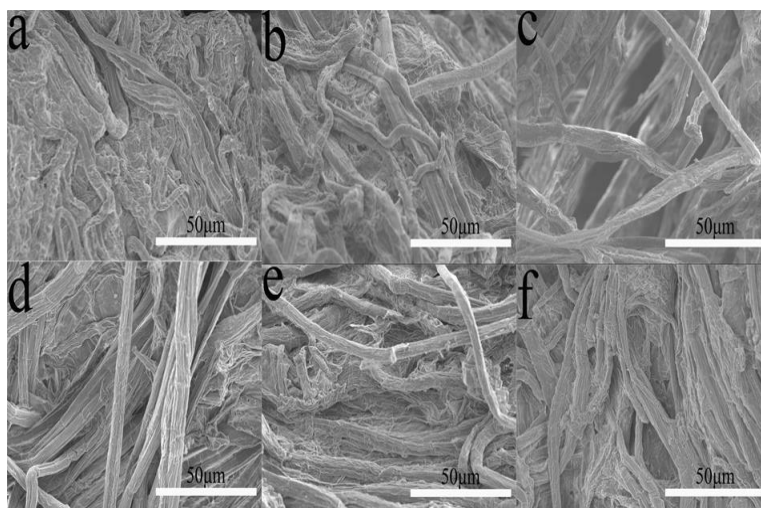
screening out of non-fibrous with a 120-mesh nylon bag is not expected to be perfect.

It is reported that there is a similar chemical composition between fibers and non-fibrous cells in original straw (Lin *et al.* 1987), despite the significant differences in their cell morphology (Lin *et al.* 1993). After soda-AQ pulping,  $P_{\text{nof}}$  with fibers was notably different from  $F_{120}$  and  $F_{350}$  in Kappa number, viscosity, *etc.* The residual lignin in the latter was twice the former, but  $F_{120}$ 's degree of cellulose polymerization was only approximately 65% of the fibers', and even down to near 50% for  $F_{350}$ . In other words, the smaller the dimension of the fines, the lower the viscosity. Additionally, the poorest drainage occurred in  $F_{120}$ , in which the beating degree reached 62 °SR, which was twice that of  $F_{350}$ . The reason for these profound differences arising from parenchymas and fibers will be discussed in the authors' subsequent paper. In this study, the existence of non-fibrous cells in straw pulp must not be overlooked.

**Table 1.** Results from Soda-AQ Pulping of Rice Straw

Products	Kappa Number	Viscosity (mL·g <sup>-1</sup> )	Brightness (%ISO)	Yield* (%)	Ash* (%)	Silica in Ash* (%)	Beating Degree (°SR)
$P_{\text{nof}}$	12.3	1157	36.3	43.0	8.9	82.8	26.0
$P_f$	12.8	1072	35.4	55.1	8.7	82.4	29.3
$F_{120}$	25.3	759	20.9	17.8	11.9	84.9	62.0
$F_{350}$	26.0	597	10.8	12.8	14.1	86.3	29.0

Note:\* the data expressed as weight percent, o.d. basis



**Fig. 1.** SEM images of the straw pulp at 1000x magnifications; (a, b, and c) Beating degree of  $P_{\text{nof}}$  at virgin stock, 55 °SR, and 75 °SR, respectively; (d, e, and f) Beating degree of  $P_f$  at virgin stock, 55 °SR, and 75 °SR, respectively

### Effect of Beating on the Drainage Properties of the Pulps

Pulp drainability is of environmental and economic importance as an evaluation index in pulping and papermaking because it is highly related to the extraction of black liquor, washing of the pulp and paper formation (Shao *et al.* 2016). In light of this, it was necessary to evaluate the drainage performance of the straw pulp. An important parameter, the Schopper-Riegler degrees (°SR), was used in this study. By means of beating of the straw pulp with PFI, as shown in Fig. 2, the beating degree of the straw

pulp, without exception, increased as the revolutions increased. But, unlike the slow increase of the beating degree of wood pulp (Hou *et al.* 2011), a trend of the sharp increase initially and the noticeable slowdown thereafter can be found in the curves. This was also a distinguishing feature that almost all straw pulps have. There was concern over the influence of non-fibrous cells' impact on the pulp drainability during beating. Figure 2 shows that the values from  $P_f$  were always higher than those from  $P_{nof}$  at the same PFI revolutions. However, the value of the difference between them varied throughout the experiment. The original pulp  $P_f$  in Table 1 displayed that its beating degree was 3.3 °SR higher than the initial  $P_{nof}$ . This gap increased quickly, within less than 100 revolutions from the beginning, to ca. 10 °SR, and the maximum difference (about 9.5 °SR) between them occurred at 1200 revolutions. Subsequently, the difference was smaller even only a 3°SR or less when the beating degree was over 65 °SR.

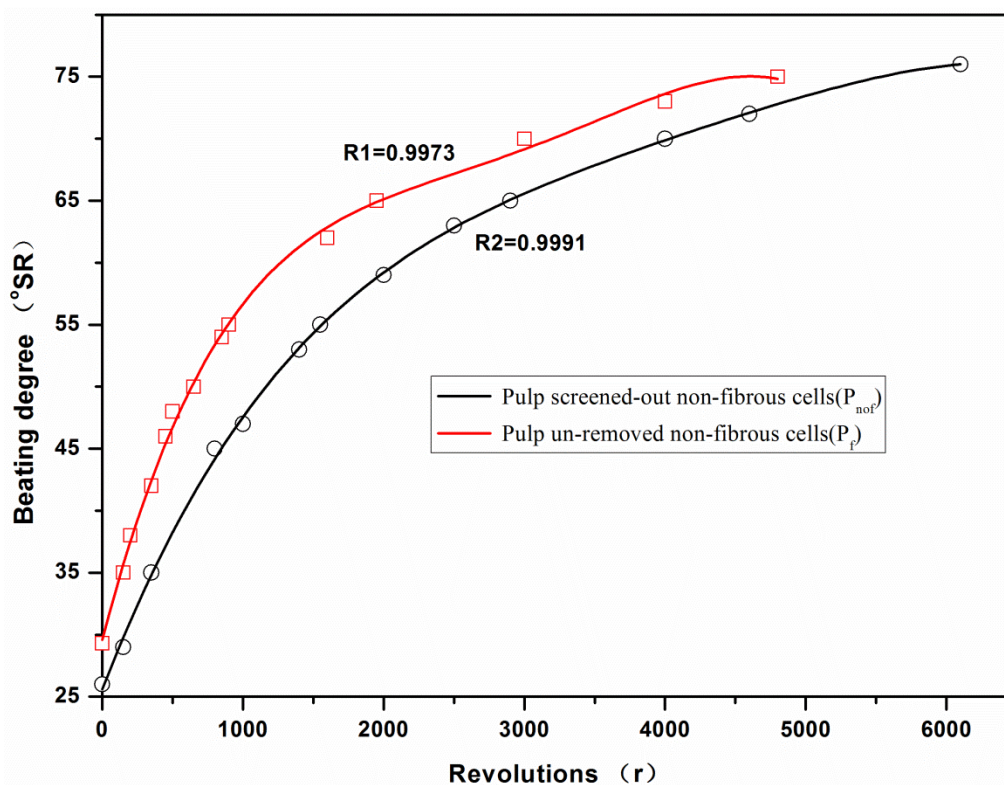
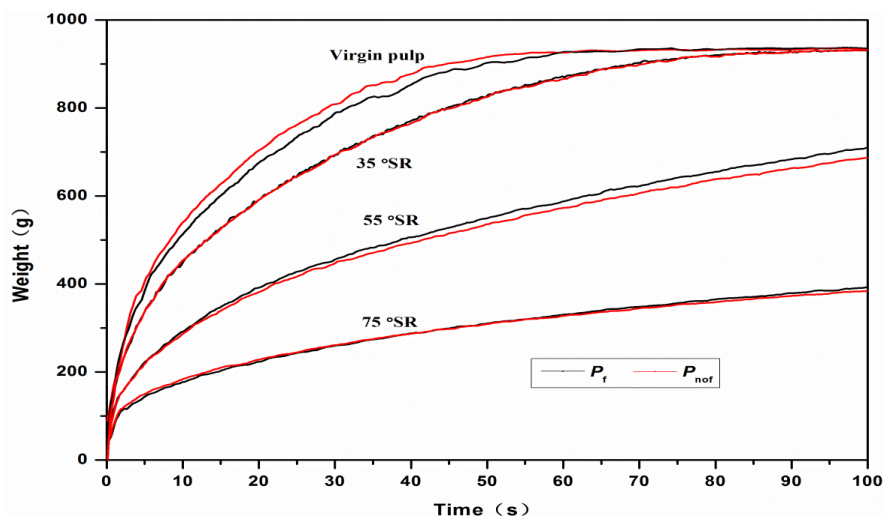


Fig. 2. Effects of beating revolutions on °SR of rice straw soda-AQ pulps

The easy beating of straw pulp may have been attributable to the delaminated primary wall (P and  $S_1$ ) debris, and the ruptured non-fibrous cells may have been responsible for the fast increasing resistance in pulp filtration (Shao *et al.* 2016). It must be admitted that the characterization of the beating degree variation from pulp with non-fibrous cells or not was more complicated than originally thought. Here, the sample moderately beaten to 55 °SR, the sample heavily beaten to 75 °SR, and the virgin pulp were tested for their dynamic drainage curves to investigate the impact of non-fibrous cell involvement. From Fig. 3 there emerged three stages in the dynamic drainage process, *i.e.*, early fast filtration, intermediate dramatic deceleration filtration, and late slow constant filtration. The fast drainage of the pulps at the beginning should have resulted from the water and fines quick passing through the filter net to the fiber mat,

which lasted only approximately 5 s. Subsequently, the decelerated drainage with increased thickness of the pulp mat developed lasted approximately 60 s. After that, a compact network structure of the mat, composed of fiber and fines material, had been generated, which made the drainage begin to increase at a certain rate dependent on the given beating degree.

In particular, beating could affect the trends of the dynamic drainage curves of the two pulps, and even resulted in a reversal in the rate between them when the beating degree rose up to 55 °SR. After that, the higher the beating degrees, the more consistent the change of the two curves became, though very small differences occurred between them for some periods. Such complicated drainage variation from  $P_{\text{nof}}$  and  $P_f$  could have been attributed to the state of the non-fibrous cells. It is well known that parenchymas make up the main elements of non-fibrous cells. They are pliable but easily ruptured due to their thin cell wall. Most of the parenchymas in the virgin  $P_f$  had not been destroyed, and thus would remain in the pulp mat to a high degree. In comparison with the virgin  $P_f$ , it was no surprise that the drainability of  $P_{\text{nof}}$  screened-out non-fibrous cells was better. Because both pulps were subjected to beating, the fibers in both  $P_{\text{nof}}$  and  $P_f$  endured the same mechanical action, so the subtle change in the dynamic drainage curves between the two pulps should have more to do with the presence of non-fibrous cells.



**Fig. 3.** The dynamic drainage curves of pulps under different beating levels

At the same beating degree, the drainage performance of  $P_{\text{nof}}$  was better than that of  $P_f$  up until 55 °SR. Due to the higher beating degree of  $P_f$  at the same beating revolution (see Fig. 2), it was required to beat  $P_{\text{nof}}$  with more revolutions to reach the same beating degree as  $P_f$ . As shown in Fig. 2, the straw pulps could be beaten to 55 °SR easily with less than 1500 revolutions. For the beating of wood pulp, a similar treatment of a low amount of revolutions should be viewed as light beating, not seeming serious enough to cause damage. Due to this fact, the rise in the beating degree of  $P_{\text{nof}}$  was mostly caused by the rupture of the primary cell wall and the delamination of the secondary wall from the fibers, and from the limited fibrillation of exterior fibrous wall (Haavisto *et al.* 2008). Beating the two pulps to 35 °SR brought about the reduction of the gap between their dynamic drainage curves and even the reversal at 55 °SR. This change may have been explained by the fragmentation of the parenchymas and low-revolution beating of the fibers in  $P_f$ . For the former, the large extent of the fragmentation

implied the increase of the fragments' freedom. In addition to the freedom of the fibers withstanding a beating of a lesser extent than  $P_{\text{nof}}$ , it was understandable that the drainage performance of  $P_f$  gradually grew closer and even superposed to that of  $P_{\text{nof}}$ . As for the reversal from  $P_f$ , it should still be closely related to a further miniaturization of the ruptured parenchymas, so that the gap that occurred after the reversal could be maximized at 55 °SR. This explanation could be well supported by the inverse relationship between the beating degrees and the sizes of their fines ( $F_{350}$  and  $F_{120}$ ), as shown in Table 1.

A further beating of the pulps toward higher beating degrees would strengthen the miniaturization of the parenchymas to weaken their flow resistance, while the fibrous change, such as deformation, exterior fibrillation, interior flexibility promotion, and even a certain curtailment, dominated the rise of pulp beating degrees. Because the effect of parenchymas on the dynamic drainage performance was weakened greatly, the result was that the dynamic drainage curve of  $P_f$  would be flipped and aligned with that of  $P_{\text{nof}}$ , with the beating degree near high values like 75 °SR, in Fig. 3. In short, the existence of the intact parenchymas brought maximum drainage resistance to the virgin straw pulp. Beating of the pulp broke up the easily-fractured parenchymas prior to the fibers, and finally their miniaturization at high beating degrees weakened and even eliminated their impact on the drainage performance of the pulp. Thus, how to deal with the correlation between beating extent and parenchymas is very valuable for good use of straw pulp.

### Effect of Beating on the Fiber Qualities of the Pulps

As stated above, the effect of beating on the drainage performance originated from the morphological variation of the fibers and non-fibrous cells in the obtained pulps. Table 2 lists fiber weight length, kink index, curl index, and fine proportion, which were regularly changed with beating of the pulps. From this table, the decrease in the fiber length and the increase in the fine proportion corresponded to the intensity of beating, but the decrements of 5.29% and 3.02% in fiber length for  $P_{\text{nof}}$  and  $P_f$  up to 75 °SR, respectively, were unexpectedly small. This indicated that the cutting of the fibers was very limited during beating, and the rise of the beating degree should have been dominated by the deformation of the fibers and non-fibrous cells as well, as aforementioned.

The virgin  $P_f$  showed fines approximately 5 points higher than its  $P_{\text{nof}}$  due to the involvement of a large number of non-fibrous cells present. It was normal that the beating would bring an increase in fines in the pulps. Interestingly,  $P_{\text{nof}}$  subjected to a slight beating of 35 °SR experienced a large increase of the fines, and it even approached the values from  $P_f$  after being beaten to 65 °SR. But this did not mean that the miniaturization of the beaten  $P_{\text{nof}}$  was comparable to  $P_f$  at the same beating degree. After all, most of the non-fibrous cells were not removed in the latter. In view of the pulp filtered out part of fines for determination of the morphology, fines in  $P_f$  should have been removed more so than those in  $P_{\text{nof}}$ , due to the easily-fractured non-fibrous cells. Even so, it must be admitted that beating of  $P_{\text{nof}}$  to the same beating degree as  $P_f$  did take more revolutions; therefore the more fines derived from  $P_{\text{nof}}$  was easy to understand compared to  $P_f$ .



**Table 2.** Effects of Beating on the Fiber Qualities of these Two Pulps

Drainage Resistance °SR	$P_{nof}$				$P_f$			
	Lw (mm)	K	CI (%)	F (%)	Lw (mm)	K	CI (%)	F (%)
Virgin Pulp	0.681	1.81	0.085	34.9	0.662	1.95	0.091	39.5
35	0.682	1.98	0.090	37.4	0.658	1.94	0.090	40.2
45	0.673	2.03	0.092	38.6	0.653	1.90	0.087	42.3
55	0.665	2.33	0.124	40.0	0.650	1.85	0.085	42.5
65	0.656	2.43	0.130	42.0	0.646	1.83	0.084	42.6
75	0.645	2.51	0.135	42.8	0.642	1.79	0.082	43.8

Note: Virgin pulp refers to non-beaten pulp with initial beating degree

It must be pointed out that  $P_f$  presented an ever-decreasing tendency in terms of kink index and curl index, opposite to the behavior of  $P_{nof}$  and contrary to the rule that beating would usually increase the two indices of commercial pulps, because the fibers became deformed and more flexible. However, for  $P_f$ , a large number of non-fibrous cells may have played a role during beating. In the authors' previous study about deflaking of rice straw pulp (Shao *et al.* 2016), this result was explained as the fragmented parenchymas offsetting the fibrous kink and curl. Here, because the damaging effect of beating on the pulp was far superior to deflaking, the fragmentation of parenchymas toward their miniaturization would improve the mobile environment of the fibers in  $P_f$  during beating, directly offsetting deformation, such as the kink and curl of fibers. A slight decrease of the two indices could have been associated with the limited cutting of the fibers. Unlike  $P_f$ , the deformation without the cushion effect from the parenchymas actually took place in  $P_{nof}$  fibers during beating, as a result, the kink index and curl index of the fibers increased with continuing beating.

### Behaviors of Ash and Silica Content in the Pulps during Beating

Rice straw pulp has been known to contain considerably more ash than other commercial pulps do, in which silica makes up its majority, such as ca. 80% or more, as shown in Table 3. Through tracking of the variation of ash content in the pulps with the beating, it can be seen that the values in both  $P_{nof}$  and  $P_f$  fell 22% and 17% from the original (virgin pulp) to 65 °SR, respectively. But a further beating of the pulps, up to 75 °SR, made the data unexpectedly ascended.

As previously described, the lost ash content was due to material filtered out along with the water during the determination of the beating degrees for the pulps. Comparing the similar silica proportion in ash to one another in Table 3, water-soluble matter was the minority, while the water-insoluble silica and/or hydrated silica and silicate were the majority of the ash. The water-soluble matter should have been released from the inside of the fibers that were deformed and fractured by beating. The water-insoluble silica and/or hydrated silica and silicate existed on and in the debris filtered out when dewatering. As for the abnormal result at 75 °SR, the increase of the ash and silica in the pulps may have been due to a noticeable slowdown in filtration of the pulp suspension, which would leave more debris remaining in the pulp mat. The rise of ash and its silica should arise from the debris because of its higher ash content (see also Table 1).

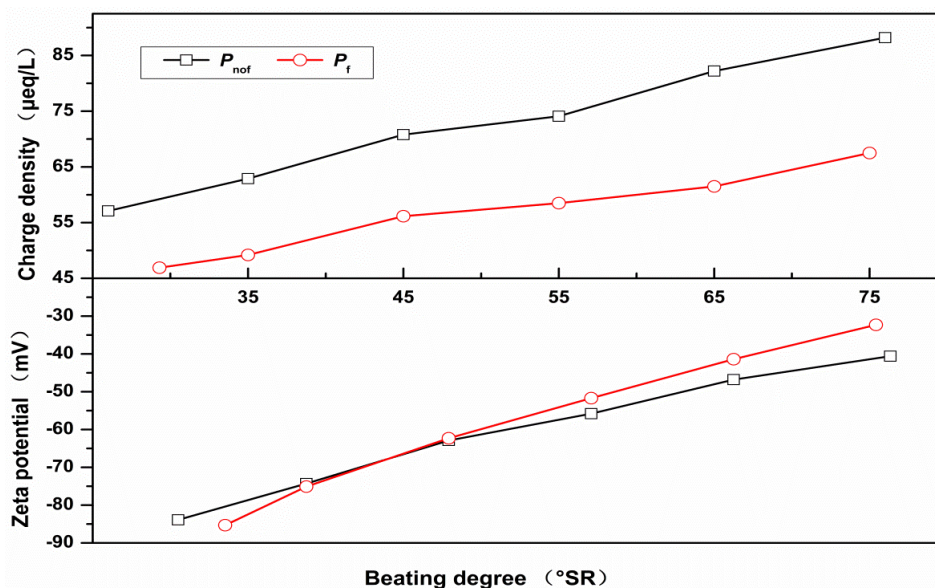
**Table 3.** The Effect of Drainage Resistance on Ash and Silica Contents

Drainage Resistance (°SR)	$P_{\text{nof}}$		$P_{\text{f}}$	
	Ash (%)	Silica in Ash (%)	Ash (%)	Silica in Ash (%)
Virgin Pulp	8.90	82.77	8.70	82.38
35	7.86	82.35	7.96	81.67
45	7.60	80.02	7.78	81.47
55	7.32	80.54	7.36	81.53
65	6.91	80.88	7.23	81.66
75	7.08	81.11	7.39	82.09

### Effect of Beating on Zeta Potential and Cationic Demand of the Pulps

The fibers were normally negatively charged due to the presence of ionisable acidic groups in the hemicellulose and lignin. The number of ionisable groups depended not only on the origin of the fibers and chemical treatments, but also greatly on the intensity of beating pulp (Nishi *et al.* 2004b). Figure 4 shows the changing trends of the zeta potential and charge density with an increased beating degree of the pulp. It was observed that the cationic demands approximately linearly increased as the degree of beating for the two pulps increased, being similar to other reported results (Nishi *et al.* 2004, 2007). Moreover, the charge densities of  $P_{\text{nof}}$  were higher at the same beating level in comparison with  $P_{\text{f}}$ . This was likely to be correlated with the non-fibrous cells charge itself. The results indicated that the amount of dissolved charge from  $F_{120}$  was more than twice as much as that of  $F_{350}$ , being  $360.5 \mu\text{eq/L}$  and  $162.6 \mu\text{eq/L}$ , respectively.

On the zeta potential of the pulps, there was a small difference, only *ca.* 1.4 mV, between the two virgin pulps, despite their clear different beating degrees. The pulps below 45 °SR had almost identical values, so it can be said that close to the intact cells, regardless of fibers or parenchymas, there was little difference in zeta potential at the same beating degree. Beating toward higher beating degrees, the increase of cell deformation and even destruction, for example, would open the gap in zeta potential between  $P_{\text{nof}}$  and  $P_{\text{f}}$ .

**Fig. 4.** Effects of beating on zeta potential and charge density of the pulps from rice straw

In contrast, the lost fines contained more silica than the pulp fibers. The silicone compound in the pulp may have existed in the form of silica and hydrated silica, which in the fines are usually negatively charged. The lost fines simultaneously brought the electronegative charge that was attributed to the silica. Charge magnitude of the fines even silicon compound dissolved into water and could have the potential to be much greater than the fibers. It was also worth noticing that the cationic demand of  $P_{\text{nof}}$  was higher than that of  $P_{\text{f}}$  during beating, and the gap widened towards a higher beating degree, against the change of their zeta potential.

### Characterization of Handsheets from the Beaten Straw Pulp

A summary of the strength properties of the handsheets prepared from  $P_{\text{nof}}$  and  $P_{\text{f}}$  at various beating levels is given in Table 4. In conclusion, moderate beating served the purpose of improving the physical properties of the papersheets, regardless of the presence of non-fibrous cells, compared with pulp sheet strength based on the unbeaten pulp. The deformation and fibrillation of the pulp fibers due to the beating were known for the promotion of the bonding strength of the pulp sheet, so the tensile, burst, and fold endurance strengths of the handsheets could be maximized with the increase of the beating degree to values of 55 °SR to 65 °SR. The strongest tear indices that occurred at 45 °SR may have been attributed to the good holding of the fiber length, which increased the bonding strength (Table 2). Moreover, even if the pulps were beaten to the high value of 75 °SR, the reduction in each strength property was within the acceptable range, which meant that rice straw pulp to paper products over a wide range of beating degrees, from lower to higher, would have no marked loss of their strength properties.

As for the effect of non-fibrous cells on the pulp strength, not all the properties from  $P_{\text{nof}}$  were superior to those from  $P_{\text{f}}$ . Values such as the burst indices of the  $P_{\text{f}}$  at 45 °SR or more were better than  $P_{\text{nof}}$ 's, or even better when beaten at high beating degrees. Judging from the increased curl and kink indices of  $P_{\text{f}}$  in Table 2, the involvement of non-fibrous cells in beating was helpful to the improvement of the burst strength (Wu and Chen 2003). A reasonable explanation for this could not be found by the current limited investigation. With the exception of the burst strength, there seemed not to exist any prominent difference in the other strength properties between  $P_{\text{nof}}$  and  $P_{\text{f}}$  during beating. The most concern should be with the pulp drainability, wet balance, and beating effect in the presence or absence of non-fibrous cells.

**Table 4.** Mechanical Properties of Papersheets

Drainage Resistance °SR	Folding Endurance		Burst Index (kPa·m <sup>2</sup> /g)		Tear Index (mN·m <sup>2</sup> /g)		Tensile Index (N·m/g)	
	$P_{\text{nof}}$	$P_{\text{f}}$	$P_{\text{nof}}$	$P_{\text{f}}$	$P_{\text{nof}}$	$P_{\text{f}}$	$P_{\text{nof}}$	$P_{\text{f}}$
Virgin Pulp	35	40	2.43	2.73	6.67	6.60	44.0	38.0
35	62	57	3.11	2.86	7.17	7.13	45.6	43.9
45	109	68	3.42	3.93	7.49	7.27	50.7	46.9
55	173	171	3.95	4.04	7.20	6.83	54.7	57.6
65	159	130	4.19	5.34	7.02	6.65	55.2	53.4
75	149	92	3.78	5.26	6.93	6.49	54.8	49.2

## CONCLUSIONS

1. A large quantity of non-fibrous cells had a distinct influence on the yield of the screened soda-AQ pulp from rice straw, which made it increase by approximately 12.1%, but the effect was subtle relative to other properties of the pulp (*e.g.*, kappa number, whiteness, viscosity, *etc.*) and the changing trend of the beating degree, which depended greatly on pulp fibers.
2. The dynamic drainage curve could be divided into three different stages in terms of the drainage rate, and the difference between the pulps screened-out non-fibrous cells and un-removed non-fibrous cells decreased with an increase in beating levels.
3. Pulp from which non-fibrous material had been removed ( $P_{\text{nof}}$ ) continuously increased in the kink index and curl index as the degree of beating increased, which improved the paper strength, except burst index, compared to pulp that contained the non-fibrous material ( $P_f$ ). The ash content in the pulp decreased with beating, but increased for further beating to 75 °SR, due to poor drainage.
4. Beating also caused the cationic demands of the pulp to increase linearly.

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