PRE-TREATMENT OF OIL PALM BIOMASS FOR ALKALINE PEROXIDE PULPING

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Oil palm biomass in the form of an empty fruit bunch (EFB) was examined for defining the extent of pre-treatment required by the biomass before an alkaline peroxide pulping process. Minerals such as silica and the derivatives of transition metals were identified as problematic to the pulping process. Specifically for silica removal, initially, hammering and pressing appeared as two powerful processes while, for transition metals, chelation with diethylenediaminepentaacetic acid (DTPA) was performed. The results obtained show that a complete treatment removed calcium, copper, manganese and sodium by 50, 100, 95 and 93%, respectively, while a total of 86% of silica bodies were also identified as removable. From these figures, the removal of 54% of the silica bodies was determined by the mechanical treatment, while 10% was attributable to the effect of DTPA. Since silica is inert towards DTPA, it is plausible that silica was closely associated to other minerals. The removal of the minerals by chelation with DTPA, therefore, reduced the attachment of the silica bodies to the biomass matrix, resulting in the liberation of silica. The procedure studied allowed a milder pulping process, eliminating the need for screw pressing, in the case of alkaline peroxide pulping. The use of DTPA during pulping can be also eliminated.

Keywords: EFB, DTPA, chelation, desilication, silica, minerals, APP

INTRODUCTION

At a global scale, Malaysia's palm oil industry is the second largest after Indonesia. Besides palm oil as the country's commodity, about 30 million tons of wet fresh fruit bunch (FFB) or some 5.2 million tons of dried empty fruit bunch (EFB) are available annually.[1] This raw material has captured the interest of researchers such as Singh *et al*., Wanrosli *et al*., Ahmad *et al*. and Muhamad, for the production of mulch,[2] chemical pulp,[3] panel product,[4] and glazing materials,[5] respectively, all of them aiming at converting the agro-waste to value-added products.

To this end, researchers also discovered that some of the EFB constituents hampered the quality of the final product, while others pose problems during raw material processing. Silica, as a mineral component, for instance, is recognized as causing the wear of cutting tools. According to specialty literature, 0.3% of the abrasive materials is sufficient to hamper the efficiency of the process,[6] requiring a periodic replacement of the cutting tool. For pulp production by caustic soda treatment, silica dissolution causes problems of chemical recovery,[7,8] caused by the thickening of the black liquor. Equipment scaling is another commonly difficult problem of soda pulping, induced by silica deposition. For paper products, silica could cause the abrasion of such gadgetry as knives, dies, punch, type-writer,[9] printer head – as a result of micro-scratches on sensitive surfaces.

For alkaline peroxide pulping (APP), mineral constituents such as manganese, copper and iron are the transition metals giving adverse effects on pulp and paper production. Colour reversion, for instance, is attributable to the presence of metals such as copper, iron and manganese.[10,11] Besides hampering paper brightness, manganese was commonly reported to cause uncontrolled peroxide consumption.[11] This is particularly disadvantageous for systems employing peroxide, as the main active chemical ways should be designed to remove these hindrance factors from the pulping system.

Chelation, an essential approach for stopping metal reactivity, could be performed in various ways. The chelating agent is usually incorporated in the pulping liquor or applied directly on the final paper product, as shown by Mirshokraie and Abdulkhani[12] for obtaining the desired effect. In this study, however, the treatment of EFB with DTPA was performed as a pre-treatment process, for reducing the interference of chelated metals with the alkaline peroxide process, as reported by Hyovenen and co-workers.[13] Furthermore, by performing the treatment as a separate process, the effects of DTPA chelation on EFB could be delineated. The process was aimed at removing mainly manganese, copper and iron, which considerably hinder the efficiency of pulping. Chelation, however, may also retain a low level of the chelated mineral in the biomass structure of the lignocellulosics. This paper discusses the effects of both mechanical treatment for silica removal and of DTPA chelation on the mineral contents of EFB.

EXPERIMENTAL

EFB preparation

EFB, supplied by Sabutek (M) Sdn Bhd as vascular bundles, were washed and dried away from direct sunlight. The dried strands were then cut to 2 cm – having removed undesirable parts, like hard flakes and heavily coloured strands – then homogenized and stored in an air-tight container. For every withdrawal, the stored EFB was rehomogenized to ensure a random distribution of EFB and to reduce bias.

Mechanical treatment of EFB

EFB was packed in a plastic bag to produce a single-EFB-layer mat, then hammered systematically with a fast, elastic effect known as staccato impact – as illustrated in Figure 1.

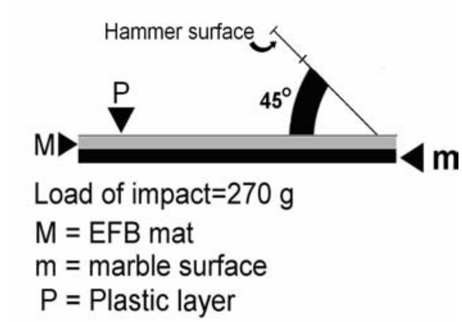

Figure 1: Illustration of the mechanical impact named staccato hammering impact due to the elasticity or short-time contact between the hammer impact surface and the EFB mat

Chelation of minerals in EFB

EFB was premixed with warm distilled water (70 °C) before the addition of 1% (mass on mass percentage) diethylenetriaminepentaacetic acid, DTPA, or of lower level DTPA, to attain a liquor-to-EFB ratio of 10:1. This colour change of EFB prepared at ambient pressure is denoted as '0.2% – ambient', a comparison being also made with the results of EFB treatment under a 14 psi pressure, as demonstrated in Figure 9. Alternatively, after premixing with warm distilled water (70 °C), the biomass was pressed at 2200 psi for about 5 min, which was the time to achieve a dewatering rate of 3 drops per min. Upon release of pressure, the pressed EFB was allowed to re-expand in DTPA. Under such conditions, for instance, the results presented in Figure 9 are presented as '0.2% – 2200 psi'. From the perspective of alkaline peroxide pulping, this pressure effect eliminates the need for the shear effect of screw pressing, which requires more complex pulping machinery and presents high chances of fiber shortening.

Whether in an ambient or a pressurized system, EFB was allowed to react with DTPA for 45 min at 70±2 °C. Later on, the treated strands were washed thoroughly to neutrality before drying at 50±2 °C. These were ground and fractionated to different particle sizes in a Retsch sieve shaker, and then packed in an air-tight container for analyses.

Control runs

To evidence the effects of DTPA and of the fluid and mechanical treatments (hammering or pressing), EFB was separated into portions. One portion was treated with DTPA, while the other was simultaneously soaked in distilled water and stored at 70 °C for the same duration, thus permitting the delineation of the DTPA effects from the hydraulic ones.

Analysis

Ash determination was performed by the TAPPI test method T211. The EFB ash obtained from a larger quantity of EFB was dissolved in acid, in accordance with the TAPPI test method T244, and the filtrate was collected and analyzed as to its metal content by Atomic Absorption Spectroscopy (AAS). Some of the ash prepared by the TAPPI test methods T211 and T244 was further examined with a Leo Supra 55VP scanning electron microscope interfaced with an energy dispersive X-ray analysis (SEM/EDAX). To examine the morphology of the intact ash, an adhesive tape was used for picking up the freshly prepared cool ash. Atomic mass percentage was obtained by dividing the mass of each element from the 'mass percentage' by their atomic mass, yielding the mole value of the individual element. The total of these mole values was then determined, followed by dividing the individual mole by this total value, multiplied by one hundred, to represent the "atomic mass percentage".

For determining the amounts of silica, a light microscope with image analyzer was used to view the surface of the 2 cm EFB strands before chelation. Scanning electron microscopic analysis of the treated EFB surface was carried out to investigate the chelation effect, and the silica counts were obtained at the same magnification by spotting on 15 different areas. From the counts of silica in these areas, the efficiency of desilication was determined, based on the difference between the percentage of silica lodged on the EFB surface, both before and after the treatment (Equation 1).

Desilication efficiency =

$$(\text{Initial \% Si}) - (\text{Post-treatment \% Si}) = ([A_i/B]100)_{\text{Initial}} - ([A_t/B]100)_{\text{Post-treatment}} \quad (1)$$

Symbol A in equation (1) is the number of silica bodies, while B denotes the total number of pits, *i.e.* the number of empty pits plus the number of lodged silica. As subscript "i" stands for "initial" and "t" for "post-treatment", A_i denotes the number of silica bodies before the treatment, while A_t denotes the number of silica bodies on the chelated EFB strands.

Samples were also prepared for colour analysis using a Minolta CM3500B Spectrophotocolorimeter, based on the concept adopted by Ghazali and co-workers.[14] Due to the relatively higher sensitivity of a spectrophotocolourimeter towards small colour changes (*cf.* brightness meter for measuring the brightness of handsheet), the CIE (*Commission Internationale de I'Eclairage)* lightness (L*) was used to measure the changes in the occurrence of the DTPA-treated EFB. Another governing factor recommending this device was its flexibility in accommodating the varying sample forms, may they be powder, liquid or solid blocks. This made possible the analysis of the ground and fractionated particles of the treated EFB, without refining and preparing the handsheets, which demands a larger sample volume. Analyses were therefore performed on ground EFB, fractionated according to different sieve openings – of 0.50, 0.25, 0.18 and 0.15 mm. Stress is here laid on the ground EFB collected from sieves with opening-sizes of 0.25 mm and 0.18 mm, denoted as 'medium' and 'small', respectively, for the reasons discussed in the preceding section.

RESULTS AND DISCUSSION

Atomic absorption spectroscopy (AAS) evidenced the abundance of sodium, followed by manganese and calcium, with very scarce amounts of copper for EFB at origin (Table 1). Pre-processing, or the step 1 process, which involved mechanical treatment with washing, removed sodium, manganese, calcium and copper by 44, 22, 11 and 100%, respectively, was probably determined by the presence of organic pieces adhering to the plastic casing (Fig. 2).

The subsequent chelation process further removed 32% calcium, 93% manganese and 87% sodium, representing quite expected percentages of riddance. The incomplete removal of calcium was due to the low affinity of DTPA to calcium, while poor acid solubility and calcium accessibility might also contribute to the resilience of the element. Similar incomplete removal of calcium caused by the chelation effect of DTPA on other biomass was also reported by Dyer and Ragauskas.[15]

Table 1
Mineral Components in EFB and treated EFB

Signal	Quantity			
	Elements in reference EFB	Elements in EFB after Step 1	Elements in EFB after Step 1 and Step 2	Percentage of Total Removal, %
AAS:				
Calcium	2.8±0.1 μg/g	2.5±0.1 μg/g	1.4±0.1 μg/g	50
Copper	0.8±0.1μg/g	Not detected	Not detected	100
Manganese	7.4±0.2 μg/g	5.8±0.3 μg/g	0.4±0.0 μg/g	95
Sodium	11.0±0.2 μg/g	6.2±0.8 μg/g	0.8±0.3 μg/g	93
EDAX:				
Silica	21.4% atomic	-	-	
Oxygen	42.3% atomic	-	-	
SEM:				
Silica[1]	83±17%	38±16%	12±3%[2]	

[1] Counts of silica bodies per total pit; [2] EFB pressed at 2200 psi before impregnation with DTPA
Step 1 – Staccato hammering impact with washing; Step 2 – Chelation process

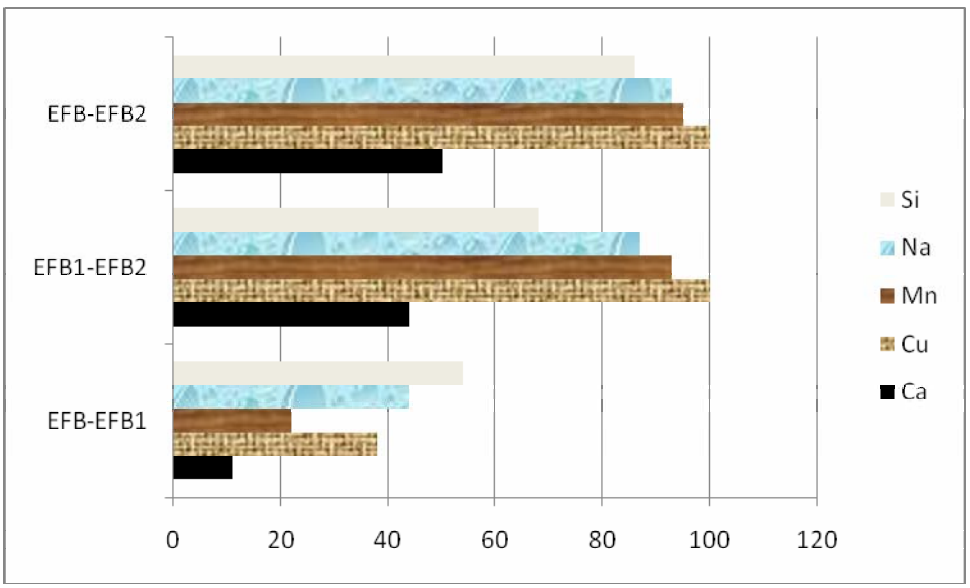

Figure 2: Percentage reduction of elements after the treatment
EFB-EFB1 – Difference between the percentages of minerals in EFB and in the mechanically-treated EFB (reference EFB and EFB after the first treatment); EFB1-EFB2 – Difference between the percentages of minerals in the mechanically-treated and chelated EFB (EFB treated in the first and second treatment and EFB after the first treatment); EFB-EFB2 – Difference between percentages of minerals in EFB and chelated EFB (EFB in its original form, without any treatment, and EFB that had undergone the first and second treatment)

Silica

Figure 3 shows the surface of the EFB vascular bundle before treatment. On the surface, silica bodies were present. The SEM/EDAX atomic percentage signal shows a ratio of Si-to-O of 1-to-2, suggesting that the structure is in the form of SiO_2 (Table 1) and thus supporting the findings of Abasolo *et al.*, Rochow and Goto for silica in other botanic species like bamboo,[6] wheat straw[16] and rice,[17] respectively. The surface resulting after chelation (Fig. 4) was almost void of silica. In terms of percentage of silica bodies, an about 8% desilication appears when applying pressure from the fluid (hydraulic pressure), which may be possibly explained by the control runs performed in repeated trials, only with water containing no DTPA, while keeping all other parameters unchanged. After blank correction, it was observed that an about 10% desilication was attributable to the effect of DTPA.

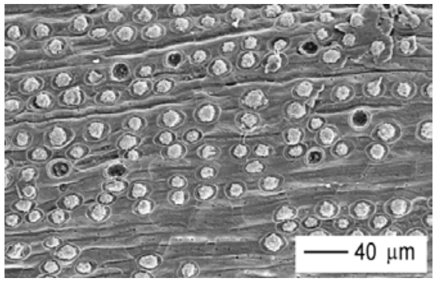

Figure 3: Initial surface of the intact EFB vascular bundle

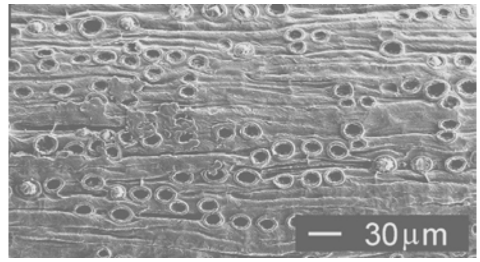

Figure 4: EFB surface after treatment with DTPA

Silica removal was considered the result of the changes produced in the bonding nature of the minerals surrounding the silica bodies. Due to the chelation of the surrounding elements with DTPA, for instance, the initial bonds or the coordination of elements to silica bodies were probably exchanged by coordination to DTPA.

As a consequence of the bond exchange, and thus, of the reduced attachment of the silica-bodies to the EFB strand, the application of 2200 psi pressure during impregnation removed more silica (Fig. 4). This resulted in a 68% desilication, relative to the mechanically treated EFB, giving a total of 86% desilication, relative to the reference EFB.

Once known the role of botanic silica in metal detoxification, it was also suggested that minerals surrounded silica bodies in a simplified manner (Fig. 5). In addition, the close association between silica bodies and other minerals is also assumed as quite logical, by the attractive nature of its negative charge – as described by Goto and co-workers.[17] Microscopically, this may also explain the adjacent layer of minerals encountered in the analysis of the ash of untreated EFB (Fig. 6).

From this perspective, it is also apparent that, both before and after the treatment, the ash of intact EFB showed a microscopically different compactness, probably due to the afore-mentioned changes in the bonding ability of the minerals to silica bodies. This loosened attachment and higher scattering of the surrounding minerals were reflected in the reduced ash density, as evident from Figure 7. The phenomenon was possibly determined by the release of the chelated minerals from the EFB strand into the DTPA liquor, indicated as a disappearance by Atomic Absorption Spectroscopy (AAS) analysis (Table 1 and Fig. 1).

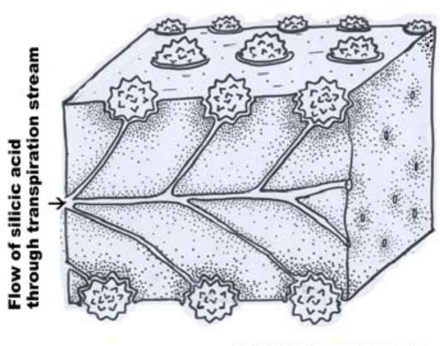

Figure 5: Silica surrounded by minerals (indicated by dots) consisting of different elements

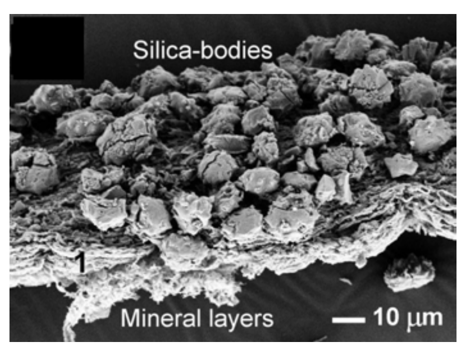

Figure 6: Micrograph of intact ash showing silica lying on the top of the mineral layer

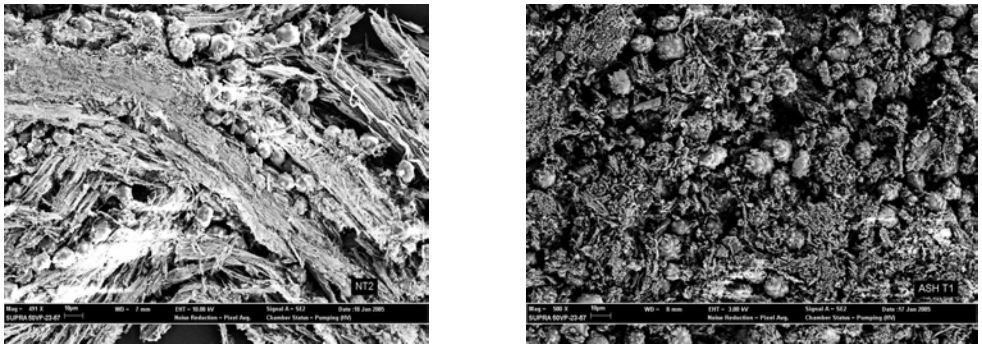

Figure 7: Ash of EFB without treatment (left) and after chelation with DTPA (right)

The reduction of the metals present in the EFB strand has also resulted in favourable brightening, similar to that reported by Pan and Leary.[18] The L* trends corresponding to the found reduction of metals are evidenced in Figure 8. Apparently, DTPA enhanced the lightness of EFB fines by 6 units, which resulted from the decrease in the degree of redness and from the increase in the degree of yellowness, as noted earlier in a work of Ghazali and co-researchers[14]. The reason for selecting fines is shown in Figure 10. The analysis of the ash of different EFB particle sizes shows the predominance of minerals in fines. As the organometal complexes present in plants are also responsible for plants colouration, removing metals from the plant biomass is expected to enhance the lightness of the plant material (as demonstrated in Fig. 8), while the further enhancement of lightness as a result of metal removal was plotted in Figure 9.

A more consistent pressure effect was better delineated at a DTPA level as low as 0.2%. As evident from Figure 9, CIE lightness showed a consistent 2-point increase in lightness, despite the varying sizes of the ground EFB. This implied an enhanced chelation effect by the application of a 2200 psi pressure during impregnation.

As earlier reports[12,14] proposed a close association between minerals and cellulose, improvement in biomass lightness is designed to have a direct aesthetic impact on the pulp produced from pretreated EFB biomass. This is particularly important, making products commercially acceptable.

From the perspective of pulping, the suggested pre-treatment is expected to offer several advantages. The first is that it eliminates the need for DTPA incorporation during pulping, which might increase alkaline peroxide efficiency, as the interference of the chelated metals can be removed.

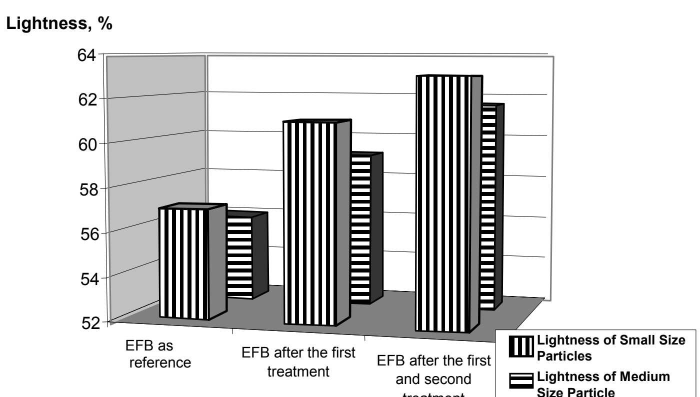

Figure 8: Lightness of EFB without treatment and after chelation with DTPA. Note that the error values for this set of data range from 0.0 to 0.4 and are, therefore, negligible. NB: Staccato hammering impact was the first treatment imposed on EFB, while the second treatment was chelation with DTPA

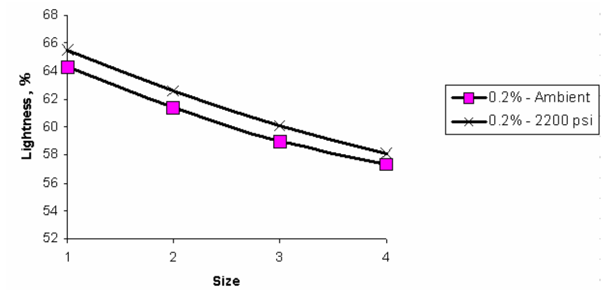

Figure 9: Lightness behaviour for the treatment performed at ambient and elevated pressure. Note that the error values for this set of data range from 0.2 to 0.8 and are, therefore, negligible.
0.2% – Ambient – 0.2% DTPA impregnated under atmospheric pressure; 0.2% – 2000 psi – 0.2% DTPA impregnated by the application of a 2200 psi pressure (the pressure experienced by EFB was of 15 psi); NB: "Size", representing the x-axis, refers to the EFB collected on the following sieve opening sizes: 1 – 0.5 mm, 2 – 0.25 mm, 3 – 0.18 mm, 4 – 0.15 mm

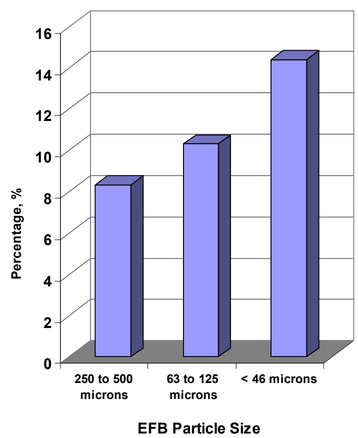

Figure 10: Ash contents by the variation of the EFB particle sizes. Fines are indicated by the bar for '<46 microns'. Note that the error values for this set of data range from 0.2 to 0.5 and are, therefore, negligible.

Despite the elimination of the screw press (typical of the original APMP system) from the APP system, the recommended series of pre-treatment, plus a multi-stage subsequent refining could fibrillate the EFB biomass up to producing a high quality pulp network.

CONCLUSIONS

Based on an independent treatment stage with DTPA and also with the preceding mechanical process, 86% silica was eliminated by a serial treatment, while calcium, manganese and sodium were removed by 50, 95 and 93%, respectively. As a result, the lightness of the raw material was enhanced by six points. Although lightness enhancement was not the targeted outcome, it appears as an extra advantage and a measure for controlling brightness impairment by the metals present in the EFB strand. This aesthetic value recommends the raw material for conversion into a value-added product.

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