EFFECTS OF MULTIPLE CHEMICAL IMPREGNATION

ON APP OF EFB

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A simple pulping method, defined as alkaline peroxide pulping (APP), which integrates both pulping and brightening actions into a single process, was attempted on abundant industrial waste – the oil palm empty fruit bunch (EFB). Originating from alkaline peroxide mechanical pulping (APMP), the major processes making up an APP system involve impregnation of alkaline peroxide (AP) into the biomass prior to refining, to finally yield APP pulp. By applying alkaline peroxide at a 2:2.5% (wt/wt) alkali-to-peroxide ratio, one-stage impregnation gave an EFB pulp brightness of 55% ISO. The subsequent impregnation stages offered 68 and 70% ISO for two- and three-stage impregnation, respectively. In fact, the said optical property and other mechanical properties of the sheets prepared via two-stage and three-stage 2:2.5% (wt/wt) alkali-to-peroxide impregnations also showed better results, as compared to those of the one-stage treatment with 4:4.5% (wt/wt) alkaline peroxide. The results of the two-stage impregnation of AP, prepared at a high concentration of 4:5% (wt/wt) alkali-to-peroxide ratio, also showed improvement in the sheets' mechanical properties, as compared to those of the one-stage process. This demonstrates the advantage of maximizing the AP chemical power by mechanical forces that could enhance its accessibility to EFB structures, rather than increasing the AP dose for attaining the same effect. Maximisation of AP is particularly important for reaching the expected sheet properties, while ensuring the eco-friendliness of an APP system.

Keywords: alkaline peroxide, pulping, APP, APMP, EFB, impregnation, paper properties

INTRODUCTION

The oil palm empty fruit bunch (EFB), an abundant biomass waste, available throughout the year, was subjected to an attempted conversion into a value-added material. Known by its scientific name[1] of *Elaise guineensis*, this initially ornamental plant of West African first came to Indonesia in 1848 and to Malaysia in 1911, as cash crop. Today, Malaysia and Indonesia are world leading producers of palm oil and cellulosic biomass, known as EFB.

In the effort of utilizing the biomass for preventing its accumulation, EFB was tested for the production of panel products,[2] ash glaze,[3] animal feed,[4] and briquette as biofuel feed.[4] Out of all these, the pulp production offers the most significant cash return, due to both high yield and attractive existing market price per ton of material.

To further enhance the attractiveness of the cash return, a low cost and high yield process would help do the trick. An example

of such a process is predictable for Alkaline Peroxide Mechanical Pulping (APMP), which was first introduced[5] by Andritz Sprout-Bauer in 1989, as an improvement of the Chemi-Thermo-Mechanical Pulping (CTMP) process. In an early stage, the process was used in wood pulping. Maple,[6,7] birch[6,7] aspen[5] and poplar[8] biomass were recording successful APMP pulp production. Later, non-wood species, such as jute,[9] kenaf,[10] straw[10] and baggase,[11] further extended the list of successes, evidencing the flexibility of the process in pulp property development.

Enticed by the successful attempts recorded in literature, the concept of APMP was applied on EFB with processes that mimicked the working principle of APMP. For making use of rather different gadgetry, the system designed for EFB pulping is abbreviated as APP, to denote alkaline peroxide pulping. This paper reports the

possibly acquired high-end properties of the APP pulp from EFB, coupled with an environmental control of the process.

EXPERIMENTAL
Raw material preparation

The vascular bundles of EFB – the raw material selected for the study – were obtained as bales. These were loosened, washed thoroughly and air-dried before grinding to 500-micron particles. Dewaxing was done by soaking the biomass particles in distilled water at 70 ºC for 30 min, for removing 50% of the extractive components. At the end of the dewaxing process, the biomass particles were demoisturized by pressing at 15 psi.

Alkaline peroxide impregnation

The alkaline peroxide (AP) was prepared by premixing hydrogen peroxide and sodium hydroxide of Merck Schuchart, Germany. By weight percentages, the selected alkali-to-peroxide ratios were of 2:2.5, 4:5 and 10:11%. The reaction was allowed to proceed for 40 min at 70 ºC, after which the biomass was again pressed at 15 psi and the liquor was collected for analysis. To achieve multiple impregnations, the process was repeated by applying fresh chemicals on the biomass.

Refining and making of handsheets

Refining was conducted with a Sprout Bauer Refiner, to allow fibrillation. The fibres obtained were made[12] into handsheets, according to TAPPI Test Methods 1997.

Mechanical and optical testing

The mechanical testings conducted in the study involved folding endurance (TAPPI 511), burst index (TAPPI 403), tensile index (TAPPI 494), tear resistance index (TAPPI 414) and zero span strength (TAPPI 231), while optical testings included brightness and opacity of handsheets (TAPPI 452). These were all compiled in TAPPI Test Methods 1997.

Spent liquor analyses

The COD, TDS and turbidity of the pulping spent liquor batches were analysed by the methods of the American Environmental Protection Agency (EPA). Residual peroxide was determined on a Shimadzu UV-Visible 1601PC Spectrophotometer, based on the method of Chai,[13] for accuracy, simplicity and rapidity.

RESULTS AND DISCUSSION
Spent liquor analyses

The spent liquors resulted from alkaline peroxide pulping (APP) of EFB contained leaching materials, such as residual extractives, inorganics, residual alkaline peroxide, as well as other organic compounds, like lignin and modified lignin, produced by the reaction of chromophoric groups from the lignin structure with alkaline peroxide.[14-15]

The role of alkaline peroxide in fading the colour of lignin is more dominant than removing of lignin from the EFB structure, which resulted in spent liquor with lower COD, turbidity and TDS – compared to other pulping processes.

As shown in Figure 1, the spent liquor from the first stage showed the highest COD and TDS, which were attributable to leaching of materials, such as lignin, extractives and other organics, and to inorganics, such as silica, which were more loosely bound to EFB after a second impregnation pressure of 15 psi. Meanwhile, the highest turbidity in the second stage of impregnation might have contributed by the release of silica, being possibly dislodged by mechanical actions,[16,17] as well as other minerals liberated from the EFB strands.

The residual peroxide plotted in Figure 1 (d) reflects both the way in which AP impregnation occurred, and also the effect of the multiple impregnation stages. Residual peroxide was the highest in the liquor collected from the first stage impregnation, and the lowest after the third impregnation stage.

Stiffness of the EFB strands in the first stage AP impregnation might explain the poor consumption of peroxide in the first impregnation. The presence of residual extractives and silica in the craters might have also hindered the penetration of the AP chemical into the fibre wall, thus hindering the brightening effects.

Subsequent impregnations, however, allowed more access of AP to the fibre strands, favouring more handy reactions between AP and the active sites of EFB and, consequently, lower values of residual peroxide. Softening of the EFB strands could have liberated more silica bodies from their crater – as a synergistic effect of mechanical pressing, which had generated numerous macro- and micro-ruptures. Softening, on the other hand, arose from the liberation of lignin, which was initially the adhesive contributing to the contracting forces of the fibre.[18-19] Lignin removal itself was affected by the space between lignin molecules, relative to the pore size of the fibre wall.[18] Thus, by removing lignin, the new available

space allowed more occupation of the active alkaline peroxide species which, in turn, triggered increased lignin removal from EFB. Besides lignin removal, the alkali in AP could also have access to the fibre wall, thus deliberately softening the biomass strands.

The loss of unwanted materials was in line with the declining values of yield with the number of AP impregnation stages (Fig. 1).
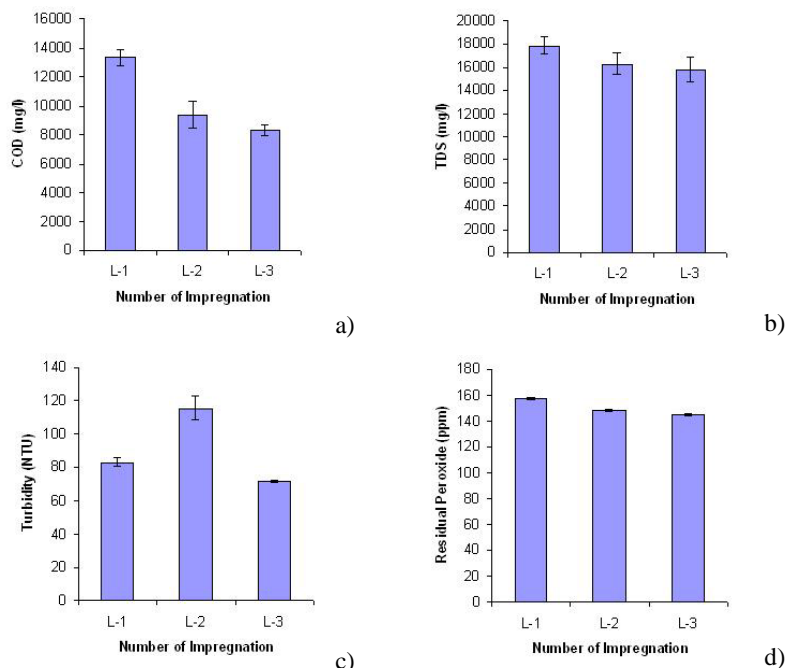

Figure 1: Liquors from impregnation of EFB with 2:2.5% (wt/wt) alkaline peroxide analysed for (a) COD, (b) TDS, (c) turbidity and (d) residual peroxide; L-1 – spent liquor from one-stage impregnation; L-2 – spent liquor from two-stage impregnation; L-3 – spent liquor from three-stage impregnation
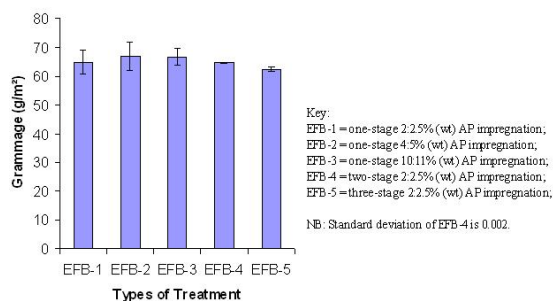

Figure 2: Grammage of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

Mechanical properties

For a handsheet grammage of 63 ± 2 g/m^2 (Fig. 2), folding endurance, which is the reflection of fibre and handsheet elasticity,[20] was seen as appreciably affected by the chemical level and impregnation stage. Consistent with the high stiffness, difficult to fibrillate and thus, with low access of alkaline peroxide (AP) into EFB strands, the handsheet prepared from EFB impregnated with a 2:2.5% (wt) alkali-to-peroxide ratio had, as expected, lacked of folding endurance (cf. EFB-2, which was impregnated with 4:5% (wt) AP).

When the AP level was increased to a 4:5% (wt) alkali-to-peroxide ratio, the fibre became softer and more fibrillation was expected to be generated upon refining. On the contrary, above a 10:11% (wt) alkali-to-peroxide ratio, the folding endurance of the handsheet decreased, which could be prompted by a higher generation of fines instead of fibrils, due to severe causticity, which triggered heating of AP in the EFB

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particles, thus accelerating cutting of fibres. The main cause of heating of the refining plate was its friction with residual chemicals and biomass during refining.

At a 2:2.5% (wt) alkali-to-peroxide ratio, the handsheet prepared from two-stage AP impregnation showed the highest folding endurance, indicating a better sheet elasticity. The sheet produced from two-stage AP impregnation evidently offered high zero span strength, as well as high burst and tensile indices. Three-stage AP impregnation, on the other hand, could develop a better sheet resistance to tearing (Fig. 3d). Sufficient fibre length, better network, or the synergistic effect of fibre bonding and fibre length mostly influenced the high tear strength. From this point of view, three-stage impregnation offered relatively better tearing resistance in comparison to two- and one-stage impregnation (despite the increased AP level).

Optical properties

Figure 4 illustrates the optical properties of the handsheet, exhibiting a strong relationship with the physical properties.

Handsheets prepared from one-stage 2:2.5% (wt) alkali-to-peroxide seemed high in opacity (95% for TAPPI Opacity and 93% for Print Opacity). Additional impregnation stages, as well as the increase in AP concentration apparently hampered Print and TAPPI Opacity by 14 and 7 points, respectively, with reference to EFB-1 and EFB-5. This may only be applicable to the 2:2.5% (wt) AP, and an extended study is needed to ascertain if the effects are also applicable to other higher AP strengths.

Key:
EFB-1 = one-stage 2:2.5% (wt) AP impregnation;
EFB-2 = one-stage 4:5% (wt) AP impregnation;
EFB-3 = one-stage 10:11% (wt) AP impregnation;
EFB-4 = two-stage 2:2.5% (wt) AP impregnation;
EFB-5 = three-stage 2:2.5% (wt) AP impregnation.

NB:
Average folding endurance for EFB-1 and EFB-3 were 2 and 18 with standard deviation of 1.95 and 2.56 respectively. These are too small to indicate on the graph.
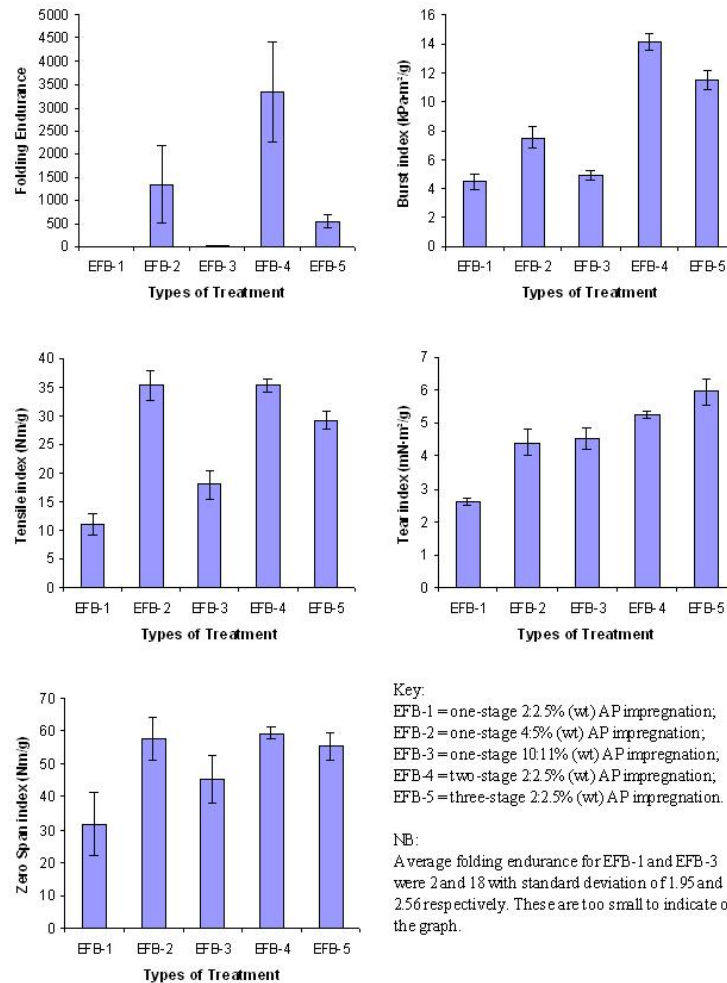
Figure 3: Mechanical properties of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)
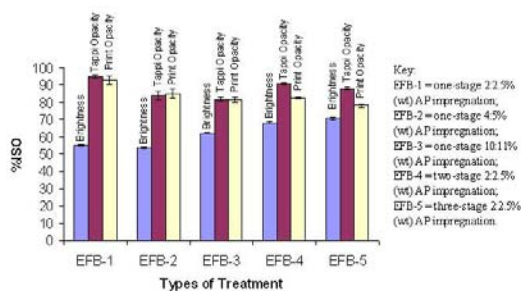
Figure 4: Optical properties of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

Figure 5: Light scattering coefficient of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

The highest brightness, of 70% ISO (Fig. 4), was possibly acquired by a three-stage 2:2.5% (wt) alkali-to-peroxide impregnation process, while the lowest brightness, of 53% ISO, was offered by one-stage 4:5% (wt) alkali-to-peroxide impregnation. The data suggest that an increase in the chemical level may not be a measure for enhancing brightness. A more efficient means of enhancing brightness was to maximize the lower level AP chemical power, by triggering access of the chemical to the more hidden interior of the biomass. Alkaline peroxide of 2:2.5% (wt) alkali-to-peroxide was apparently sufficient to trigger a pronounced brightening effect, by applying a pressure of 15 psi onto the softened EFB in the second and third impregnation stages. This was apparently an effective measure, evident for brightness enhancement from 55% ISO in one-stage AP impregnation to 68% ISO in two-stage impregnation and to 70% ISO in subsequent pressurised AP impregnation.

The results for the light scattering coefficient also consistently favoured the 2:2.5% (wt/wt) alkali-to-peroxide ratio, provided that AP impregnation was done under the established pressure. The factor behind this is also the effectiveness of chemical penetration into the biomass, which would in turn soften the inner structure, facilitate fibrillation and inter-fibre bonding. The application of pressure as a mechanical way for promoting accessibility of AP into EFB also helped maximization of AP power. Residual alkalinity from AP, for instance, could induce alkaline darkening, typical for the isolated action of the hydroxyl ion on a chromophoric group in the biomass.[21] Similarly, residual alkalinity could also trigger darkening of biomass through re-deposition of leaching materials onto the
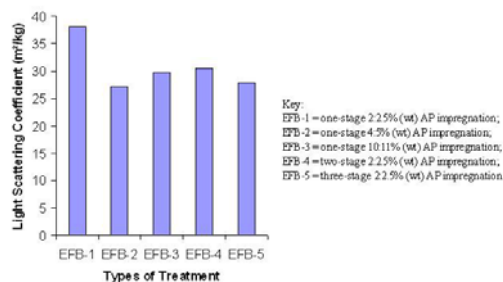
EFB surface,[22] which could in turn result in biomass stiffness and poor fibrillation during refining. As to the darkening phenomenon, raising the ratio of alkali might have therefore increased the chances of alkaline darkening, as evident for the lower LSC obtained from AP impregnation at an alkali-to-peroxide ratio higher than 2:2.5%.

The Kappa number corresponding to these handsheets was of 101.4 for one-stage impregnation of 10:11 alkali-to-peroxide, while subsequent impregnations of the same AP level could reduce the Kappa number to 82.3, and further down to 75.3, for three-stage AP impregnation. This may in a way support the possibility of achieving an 80% ISO brightness, if subsequent pressurized impregnation of the same AP level was applied on the biomass. The contradictory trend of brightness could be explained by the light scattering coefficient (LSC) values. At the same level of chemicals, two-stage impregnation offered 30.7 units for LSC, while subsequent impregnation resulted in 26.7 LSC units. The reducing value of LSC implies reducing smoothness of the handsheet, arising from the gaps between fibres, which could be due to the non-uniformity of the fibre sizes.

As to delignification, it could be also observed that, with the release of leaching materials, more available spaces could be created between the pore size and the lignin molecules. This opened up more chances for hemicelluloses (hydrophilic hemicelluloses, especially,[5] and other substances in the fibre) to react with the chemicals. An evidence of recalcitrant residual lignin, therefore, suggests the dissimilar sizes between the lignin molecules and the available pores, which could be the factor limiting the AP access into the residual chromophoric groups. In relation to release of organics,

however, the COD and TDS contents in the spent liquor after the third impregnation stage could be thus mainly attributable to the hemicelluloses squeezed out of the biomass. This further demonstrates the sufficiency of the two-stage 2:2.5% (wt) alkali-to-peroxide impregnation (rather than a higher chemical dose) for brightness improvement, while sustaining the mechanical strength of the handsheet.

CONCLUSIONS

COD, turbidity, TDS and residual peroxide offered a simple way of checking the sufficiency of the alkaline peroxide level and impregnation stages in an alkaline peroxide pulping system, involving the extent of removal of unwanted substances, such as lignin, inorganics and extractives. The level of alkaline peroxide used and the number of impregnation stages could be adjusted to achieve the desired properties of the resulting pulp. Apparently, an additional impregnation stage for 2:2.5% (wt) alkali-to-peroxide could be more effective than an increment in the alkaline peroxide level, suggesting that the chemicals have to be maximized by enhancing their penetration into the EFB biomass. The mechanical forces involved during impregnation (15 psi pressure) allowed access of chemicals to a larger biomass area, and also triggered a better release of unwanted materials. Multiple-stage impregnation of 2:2.5% (wt) alkali-to-peroxide is therefore recommended for the production of high brightness pulp with overall good mechanical properties.

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