World Applied Sciences Journal 8 (2): 185-192, 2010
ISSN 1818-4952

Influence of Alkaline Peroxide Treatment Duration on the Pulpability of Oil Palm Empty Fruit Bunch

M.Y. Rosnah, A. Ghazali, W.D. Wan Rosli and Y.M. Dermawan

Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Abstract: The oil palm empty fruit bunch (EFB), the by-product of the palm oil milling activity, was converted to pulp via the concept of alkaline peroxide pulping process. Prior to the simulated pulping process, the EFB biomass was cleaned and dewaxed to suit pulping and paper making needs. EFB was treated with the pre-optimised alkaline peroxide of 2.5% hydrogen peroxide and 2% of sodium hydroxide. Reaction between the pre-mixed chemicals and the biomass was allowed at varying time with a fixed temperature of 70°C and consistency of 10-to-1 liquor-to-EFB mass ratio. When the biomass was refined and made into hand sheet, the relationship between paper properties and treatment time was revealed. Such paper properties as folding endurance, burst and tensile indices were generally enhanced with treatment time, with optimality exhibited by the EFB undergoing 40 min reaction with alkaline peroxide (AP). The 40 min optimality was also depicted on brightness versus time profile, which correlated with the vigorous consumption of peroxide in the first 40 min inferred from monitoring residual peroxide behaviour with time. Coupled with properties enhancement, results suggested that in the first 40 min, penetration of the AP into EFB was adequately pronounced to influence swelling, softening and brightening of the biomass for an optimum pulpability of EFB.

Key words: EFB · APP · APMP · Mechanical properties · Brightness

INTRODUCTION

The palm oil milling sector in Malaysia generates millions of metric tonne of oil palm wastes annually. These include the empty fruit bunch (EFB) generated at the oil mill, the oil palm fronds (OPF) available throughout the year and the oil palm trunks (OPT) which are generated at felling. Within the cluster of biomass in this country, the oil palm wastes constitute 94% of the lignocellulosic materials [1] with 36 million tonnes (odmt) of EFB [2] milled for its vascular bundles also known as the dried long fibre.

Valuable fibres obtained from EFB are presently used for developing value-added products such as wood composite product, medium density fibreboard (MDF) and fibreboard [3]. Owing to its lower lignin content relative to OPF and OPT, high cellulose content, moderate level of extractives and acceptable level of starch, EFB has been the most suitable raw material for pulping and paper making, as compared to the other two oil palm derivatives, OPT and OPF. Besides reducing environmental impacts from waste accumulation, EFB utilization for pulp production can also help Malaysia to be independent of imported fibre [3]. One attractive way of materializing the idea is by adapting the concept of alkaline peroxide mechanical pulping (APMP) on the raw material.

APMP is a process that combines bleaching and pulping in one process with alkaline peroxide as the main driving agent. This process was introduced by Andritz Sprout-Bauer, United States of America in 1989, which has since been recognized as the most efficient chemi-mechanical pulping technique for hardwood. The pulping process had gained worldwide research and industrial interests due to its outstanding features like environmental friendliness analogous to mechanical pulping but offering pulp quality comparable to chemical pulp [3]. In addition, APMP is a flexible pulping process in that it is adaptable to a variety of biomass including such non-wood materials as bagasse, kenaf, jute and straw. Furthermore, APMP is proven cost-effective due to elimination of a separate bleach plant and it is this that helps reduce the overall capital investment [4], adding sustainable value to the process and the entailing product.

Despite its excellent features, APMP is still not operationally adopted in the Malaysian pulp and paper

Corresponding Author: A. Ghazali, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Tel: + 604-6532239; Fax; +604-6573678

industry due to the need to thoroughly study the process and the ensuing costs. For this reason, more researches and investigations are underway in order to understand the process comprehensively. As one in the list, the primary aim of this study is to examine the effect of treatment time on the properties of alkaline peroxide pulp from EFB, which is hereby presented.

MATERIALS AND METHODS

Preparation of Raw Material and Chemicals: The EFB vascular bundles obtained in the form of mats were loosened, washed thoroughly and segmented to 2 cm. The segmented biomass was then dewaxed by soaking in distilled water at 70°C for 30 min in order to produce approximately 50% extractive-free biomass.

Hydrogen peroxide and sodium hydroxide manufactured by the Merck Schuchart, Germany were premixed to obtain 2% of hydrogen peroxide and 2.5% of sodium hydroxide by weight percentage.

Impregnation of Alkaline Peroxide (AP) into Oil Palm Empty Fruit Bunch (OPEFB): After soaking process, the dewaxed biomass was pressed at 15 psi for 80% demoisturisation. After pressing, the alkaline peroxide was added to obtain the final immersion of EFB in alkaline peroxide of 10% consistency. Prior to refining, the mixture was transferred to the water bath to allow reaction to occur at 70°C at varying times ranging from 10 to 120 min with 0 min reaction acting as control.

Refining and Making of Hand Sheet: Refining process was performed using Sprout Bauer Refiner while the making of hand sheet was performed in accordance to TAPPI Test Methods 1997 [5].

Chemical Analysis of Oil Palm Empty Fruit Bunch (OPEFB) Pulp: Analyses performed on alkaline peroxide treated pulp were in accordance to TAPPI Test Method 1997. Prior to chemical analyses, moisture content was determined by adopting TAPPI Test Method 12. Other TAPPI Test Methods employed include TAPPI 222 for the determination of acid-insoluble lignin and TAPPI 211 for the determination of ash content. Apart from that, holocellulose was determined in accordance to the method established by Wise and co-workers, published in 1946 [6].

Mechanical and Optical Testing: The mechanical and optical properties of hand sheets were also determined in accordance to TAPPI Test Methods 1997. These were folding endurance (TAPPI 511), tensile index (TAPPI 494) and burst index (TAPPI 403) [5].

Residual Peroxide: Residual peroxide was determined by spectrophotometric method based on the successful attempt of Chai and co-workers published in 2004 [7]. As reported, a color agent of 2.4 M molybdate was prepared by dissolving 0.10 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 250 ml of 0.5 M H_2SO_4. Calibration was done by preparing a set of standard solutions and this was achieved by adding varying amounts of hydrogen peroxide solution (3%) into 5 ml molybdate solution. To confirm the positions of the desired signals, the spectrum for each solution was acquired by using Shimadzu UV-Visible 1601PC Spectrophotometer.

Scanning Electron Microscope (SEM) Analysis: Morphology of the AP treated EFB was examined using Leo Supra, 50 VP, Carl Ziess scanning electron microscope. SEM micrographs were taken as hand sheet's top view as well as cross-section of the fibre network. The latter was performed by embedding the sheet in polyester resin, which was then cut using diamond cutter. The samples were mounted on a stub using double sided electrically conducting carbon adhesive tapes. The samples were then gold-coated to a thickness of 20 μm using a Polaron Equipment Limited model E500 of voltage set at 1.2 kV (10mA) and vacuum of 20 Pa for 10 min to allow conduction with incident electron beam.

RESULTS AND DISCUSSION

Fibre network observed under scanning electron microscope revealed the importance of AP treatment time in ensuring fibrillation and excellent inter-fiber bonding. Figures 1a and 1b show poorly bonded pulp in a hand sheet attributable to an insufficient penetration of alkaline peroxide (AP) into the biomass, which consequently limited the extent of reaction between EFB and AP. Owing to the inadequate reaction, the fibres were still stiff and resisted consodilation, leading to an overall poor inter-fibre bonding (Fig. 1a and 1b). The resultant paper, therefore, was bulky and porous.

On the contrary, sheets produced with EFB treated for 40 min in AP showed good network of bonded fibre (Fig. 1c and 1d). It was shown that 40 min alkaline peroxide treatment provided adequate chemical penetration into fibre, causing enough fibre softening and this, in turn, resulted in well fibrillated pulp mass and hence, excellent improvement in the inter-fibre bonding as apparent from Fig. 1c and 1d.

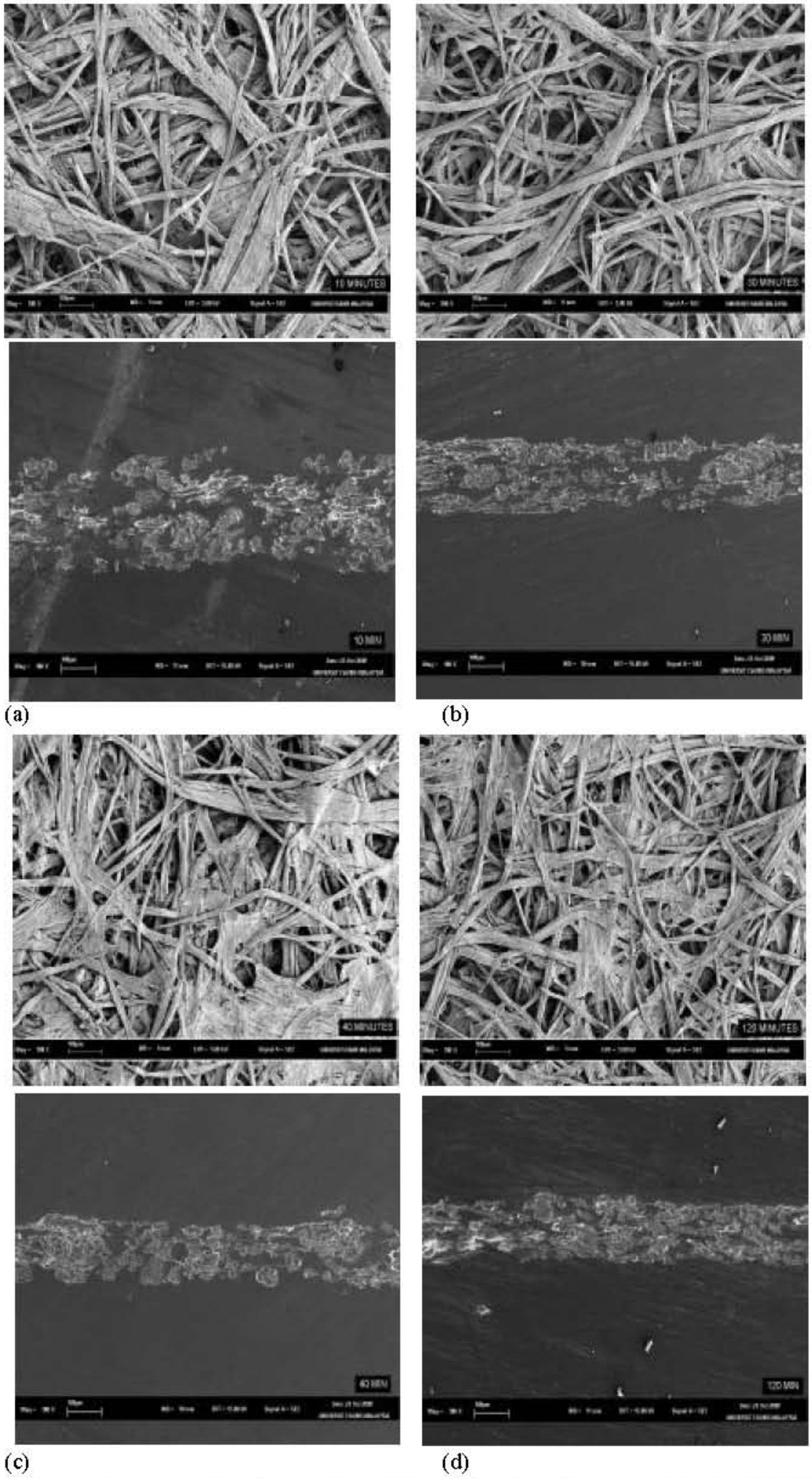

Fig. 1: Scanning electron micrograph of the top surface of fibre network and cross-sectional of EFB fibres network at X100 magnification for a) 10 min b) 30 min c) 40 min and (d) 120 min

Table 1: Chemical composition of AP treated EFB pulp at various treatment time

	Treatment time			
Pulp analysis	0 min	10 min	40 min	60 min
Moisture content (%)	30.30 (1.38)*	34.53 (0.98)	12.40 (1.56)	27.15 (1.67)
Acid insoluble lignin (%)	18.20 (0.31)	16.80 (0.44)	14.80 (0.32)	15.1 (0.45)
Holocellulose (%)	75.30 (0.33)	67.27 (0.45)	59.43 (0.44)	58.49 (0.38)
Ash content (%)	5.51 (1.85)	4.33 (1.67)	2.33 (2.10)	1.67 (1.93)

(* Values in parenthesis are standard deviations)

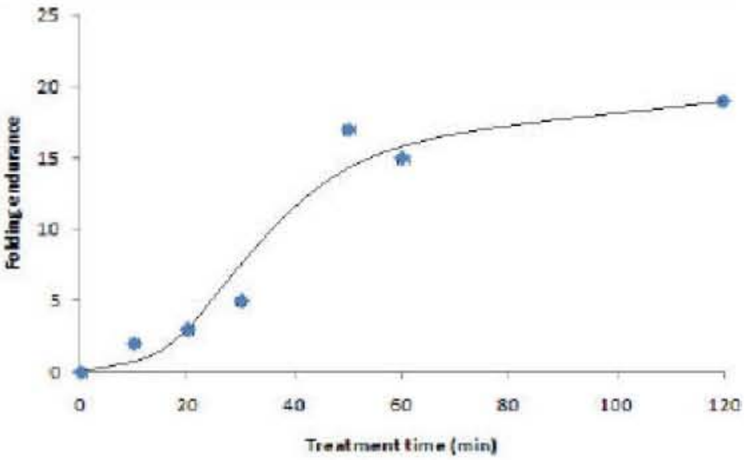

Fig. 2: Relationship between folding endurance and alkaline peroxide treatment time. (NB: Standard deviation of each of the plotted average value lies between 0 to 2.6.)

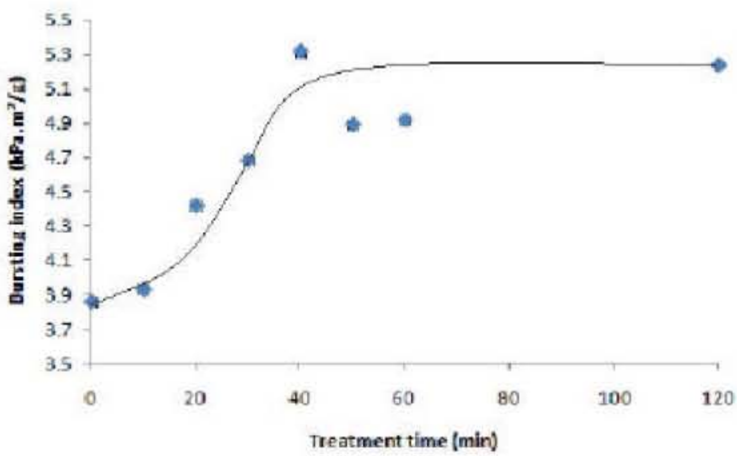

Fig. 3: Relationship between burst index and alkaline peroxide treatment time. (NB: Standard deviation of each of the plotted average value lies between 0.03 to 0.25)

Along with the AP treatment process for softening of EFB biomass, the subsequent mechanical abrasion arising from refining had effectively loosened the fibre wall, causing fibrillation. To a certain extent, fibrillae were liberated and these formed additional bonding points, filling the gaps between fibres [8]. As we previously encountered, in the presence of these fine elements with cross sectional dimension of 400x100 μm, an excellent improvement in the inter fibre bonding [9] and thus, strength properties such as burst and tensile, could well be promoted.

Table 1 shows the chemical composition of AP treated EFB pulp at various treatment time. It can be seen that AP treatment performed for 40 min offered the lowest pencentage of acid insoluble lignin in comparison to other samples. This implies that, 40 min treatment

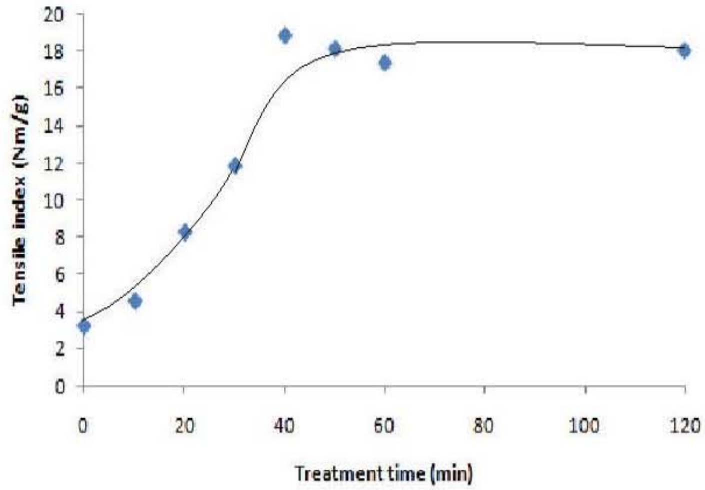

Fig. 4: Relationship between tensile index and alkaline peroxide treatment time. (NB: Standard deviation of each of the plotted average value lies between 0.21 to 1.84.)

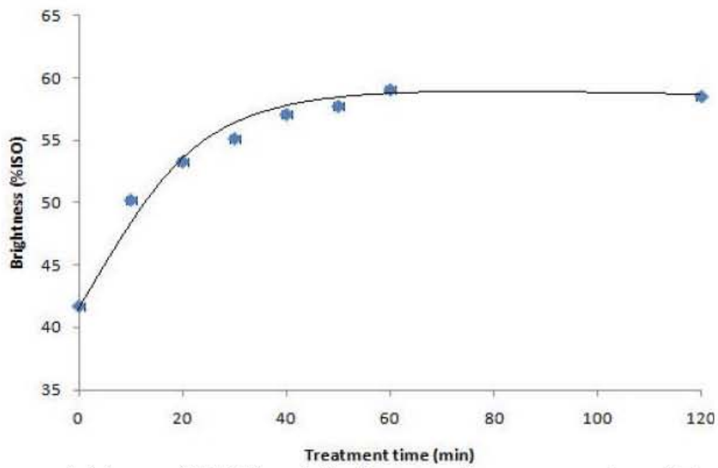

Fig. 5: Relationship between brightness (% ISO) and alkaline peroxide treatment time. (NB: Standard deviation of each of the plotted average value lies between 0.11 to 0.51)

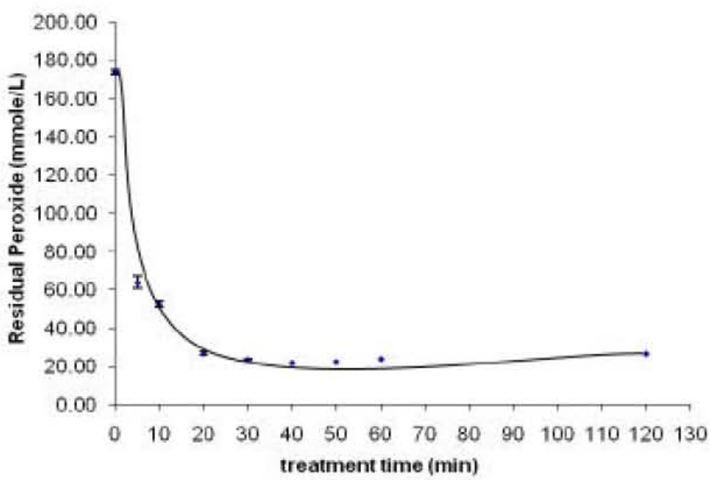

Fig. 6: Relationship between residual peroxide in the spent liquor and alkaline peroxide treatment time. (NB: Standard deviation of each of the plotted average value lies between 0.3 to 0.5).

with AP removed approximately 20% lignin and improved hydrogen bonding between cellulose (Table 1). This, effectively, improved such paper properties as tensile strength and burst, giving a strong correlation between Figs. 3 and 4.

Besides that, the pre-treatment also improved brightness of paper (Fig. 5). This can be ascribed to the lower lignin content of the pulp as lignin is the main factor for coloration of paper.

Holocellulose was highest in EFB that was set as control, suggesting loss of cellulosic component in the form of cellulose and/or hemicellulose as a result of AP treatment. Lowest holocellulose value was given by EFB treated for 60 min in AP, indicating maximum loss of the said components.

Hemicellulose, however, might not have been significantly lost throughout AP treatment duration and this is portrayed in the improving strength properties of the hand sheet, with treatment time. From its non-cystalline hydrophilic nature and the ability to adsorb into fibre surfaces during pulping and refining, hemicelluloses is believed to have contributed to swelling of the pulp and conformability of wet fibres during sheet formation as explained in literature [10]. Subsequently, upon dewatering, the hydrogen bonds between celluloses would be reformed by desorption of water. The hemicellulose-assisted swelling ability of the cellulose molecules consisted in the pulp mass has potentially enhanced such paper strength properties as folding endurance, burst and tensile [11] as evident from Figs. 2, 3 and 4.

Apart from that, Table 1 also shows the percentage of ash that decreased with the increase of AP treatment time. The ash content, which is an inorganic residue obtained after combustion at 575°C [12], is undesireable for pulping especially if it is rich in copper, iron, manganese and nickel. These elements are active consumer of alkali and and could accelerate decomposition of hydrogen peroxide [12, 13]. For 40 min treatment in AP, approximately 60% of ash was removable from the paper making raw material and this also corresponds to the point of maximum rapid release of minerals. At prolonged reaction time, release of minerals have been sluggish.

Mechanical Properties: Folding endurance also increased with the time of treatment of EFB with AP. This profile also defines optimum time needed for the alkaline peroxide to penetrate into fibres to soften the biomass, assist swelling and lubricate the subsequent refining process. As folding endurance reflects the flexibility of paper, 40 min in AP was apparently sufficient in promoting paper flexibility as depicted in Fig. 2.

Burst test which is governed by fibre length and fibre bonding (Fig. 3) shows further correlation for optimality of 40 min treatment in AP. This corresponds to 35.11% improvement in comparison to AP treatment at 10 min. Besides low fibre length, moisture content could also lower burst strength of paper [14]. Specifically for this study, however, moisture effect could be ruled out as the same standard condition of 19°C of temperature and 50±0.02 of relative humidity was consistently applied throughout the period of analysis.

The overall improvement in strength of the paper prompted by the optimal time of treatment in AP is reflected in Fig. 4. High tensile strength (index) means that the web could resist from breaking and this is particularly important in the manufacturing process [14].

Optical Properties: High brightness is one of the important features that could add value to the pulp produced. Thus, as a way of enhancing pulp quality, the change in pulp brightness was monitored in the same way as the mechanical strength of paper. Theoretically, when alkali and hydrogen peroxide were pre-mixed, the perhydroxyl anions (OOH^-) were generated (reaction 1).

$$H_2O_2 + HO^- \rightarrow HOO^- + H_2O \quad (1)$$

Signs of brightening effect appear when the OOH^- has changed the nature of the initial chromophore groups consisted in the biomass and this occured after the 10th min of reaction between alkaline peroxide and EFB as shown in Fig. 5.

As reflected by the slope of the graph shown in Fig. 5, brightening increased rapidly in the first 30 min, indicating effective action of HOO^- (reaction 2). This strongly nucleophilic species is capable of changing the chromophores (denoted C) structurally to become a non-chromophoric substance. Theoretically, Solange and co-workers proposed that the reaction is not reversible and could lead to permanent removal of chromophoric groups in lignin molecule [15].

$$H_2O_2 + HOO^- \rightarrow HO^- + O_2^- + H_2O \quad (2)$$

Furthermore, the combination action of two separately forming chromophore-hydrogen peroxide from reaction 3 and chromophore-hydroxide from reaction 4, results in the formation of a large intermediate indicated in reaction (5), This intermediate then dissociated to a light organic product shown in reaction (6) [16].

$H_2O_2 + Ç \leftrightarrow H_2O_2Ç$ (3)

$OH^- + Ç \leftrightarrow OH^-Ç$ (4)

$H_2O_2Ç + AOOH\text{-}OH^-Ç \rightarrow AOOH\text{-}OH^-Ç$ (5)

$AOOH\text{-}OH^-Ç \leftrightarrow AOOH + OH^-Ç$ (6)

(Ç = Chromophore; AOOH= light organic product)

In addition, radical species such as hydroxyl radicals ($HO^\cdot$) from alkaline peroxide decomposition shown in reaction (2) were also responsible for delignification and solubilization of hemicelluloses, which in turn, enhance the brightness of paper [3]. For the applied conditions (consistency, level of alkaline peroxide and, form and type of biomass), 40 min, which is apparently the start of a plateaux (Fig. 5) appeared to be the duration of reaction between EFB and AP offering maximum brightening effect to the biomass. This corresponds to approximately 40% improvement in brightness relative to the biomass at origin (t=0). A concurrent observation on the paper made from the pulp prepared under the same condition, which has been exposed to the sunlight for more than a year now also demonstrated unhampered brightness. This verifies the irreversibility of the brightening effect of hydrogen peroxide.

Residual Peroxide: The spent liquor obtained as the discharge of the impregnation process exhibits an exponential decrease of residual peroxide with time and peroxide reaction almost ceased beyond 40 min duration of treatment (Fig. 6). This implies that reaction between EFB and AP was vigorously consumed in the first 40 min. During this period, swelling and softening were also maximum and this resulted in the yield of well fibrillated pulp mass, which in turn also rendered a relatively enhanced mechanical properties such as burst, folding and tensile and also optical properties such as brightness.

CONCLUSIONS

The optimality of 40 min for adequate reaction between EFB and alkaline peroxide was apparent from the results of this study. Consistency was depicted on the mechanical, optical properties as well as morphology of the resultant hand sheet. Results demonstrated the important influence of alkaline peroxide treatment time to effect both brightening of EFB and softening of the biomass. This, in turn, lubricated the subsequent refining process and thus, the overall pulpability of the biomass for optimal networking of fibres and fibrillae in the resultant paper.

ACKNOWLEDGMENTS

This project was funded by Ministry of Higher Education of Malaysia through FRGS grant [203/PTEKIND/671198] and partly funded by USM seed fund 304/PTEKIND/638033. The author of this paper is the holder of Universiti Sains Malaysia Fellowship awarded for her study duration (2007-2009).

REFERENCES

1. Baikan, B., 2006. Utilisation of Biomass for Renewable Energy: Present Scenario and Potential Workshop on Utilisation of Biomass for Renewable Energy 11-15 December 2006, Kathmandu, Nepal. Available at: http://www.apo-tokyo.org/biomassboiler/D1_downloads/presentations/Nepal_Program_DEC2006/Country_Papers/Malaysia/Malaysia_CP_0.ppt#295,16, Biomass in Malaysia.
2. Law, K.N., W.D. Wan Rosli and A. Ghazali, 2007. Morphological and Chemical Nature of Fiber Strands of Oil Palm Empty Fruit Bunch (OPEFB). BioResources, 2(3): 351-362.
3. Fang, J.M., R.C. Sun and J. Tomkinson, 2000. Isolation and Characterization of Hemicelluloses and Cellulose From Rye Straw by Alkaline Peroxide Extraction. Cellulose, 7: 87-107.
4. Ghazali, A., W.D. Wan Rosli and K.N. Law, 2006. Alkaline Peroxide Mechanical Pulping (APMP) of Oil Palm Lignocellulosics: Part 2.Empty Fruit Bunch (EFB) Responses to Pretreatments. Appita J., 59: 65-70.
5. TAPPI Test Method, 1996-1997. TAPPI Press, Technology Park Atlanta, 1: T200-T460.
6. Wise, L.E., M. Murphy and A.A. D'Addieco, 1946. Paper Trade J., 122: 35-43.
7. Chai, X.S., Q.X. Hou, Q. Luo and J.Y. Zhu, 2004. Rapid Determination of Hydrogen Peroxide in The Wood Pulp Bleaching Streams by A Dual-Wavelength Spectroscopic Method, *Analitica Chimica Acta*, 507: 285-288.
8. Casey, J.P., 1980. Pulp and Paper Chemistry and Chemical Technology. 3rd Edition, Vol. 2, John Wiley & Sons Inc.
9. Kamaluddin, N.H., A. Ghazali and W.D. Wan Rosli, 2008. Fine Elements Responsible for Strength Improvement of EFB APMP Pulp. In Proc. Seminar on Science and Technology 2008, Labuan, Sabah.
10. Roberts, J.C., 1996. The Chemistry of Paper. The Royal Society of Chemistry, United Kingdom.

11. Bhaduri, S.K., I.N. Ghosh and N.L.D. Sarkar, 1995. Ramie Hemicellulose as Beater Additive in Paper Making from Jute-stick Kraft Pulp. J. Industrial Crops and Products, 4: 79-84.
12. Ogunsile, B.O. and C.F. Uwajeh, 2009. Evaluation of the Pulp and Paper Potentials of a Nigerian Grown *Bambusa vulgaris*. World Applied Sci. J., 6(4): 536-541.
13. Casey, J.P., 1980. Pulp and Paper Chemistry and Chemical Technology. 3rd Edition, Vol. 1, John Wiley & Sons Inc.
14. Casey, J.P., 1981. Pulp and Paper Chemistry and Chemical Technology. 3rd Edition, Vol. 3, John Wiley & Sons Inc.
15. Solange, I.M., J.M.R. George and C.R. Ines, 2008. Hydrogen Peroxide Bleaching of Cellulose Pulps Obtained from Brewer's Spent Grain. Cellulose, 15: 641-649.
16. Liu, S., 2003. A Kinetic Study on Alkaline Peroxide Brightening of Mechanical Pulps. 89th Annual Meeting of the Pulp and Paper Technical Association of Canada, Montreal, Canada.