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A GREEN AND SUSTAINABLE MATERIAL FROM

BIORESOURCES



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FROM THE EDITOR

Assalaamu'alaikum warahmatullahi wabarakatuh. Greetings.

INTROPica has reached its 8th year of Publication, with a total of 10 issues published to date. For the 11th issue, the Laboratory of Biopolymer and Derivatives (BADs) has been given an honour to publish this biannual INTROP magazine with the theme Nanocellulose: A Green and Sustainable Material from Bioresources. Nanotechnology is a modern technology and has been on the research limelight for the past decade. Nanocellulose is an example of nanomaterial which has versatile characteristics and is potentially applicable in various industries; namely polymer, material, medical, textile, coating, cosmetics, food and paper. Among the challenges to realize the utilization of nanocellulose for commercial purpose is due to the difficulty in processing nanocellulose at large scale, and afterwards to retain the nano-structure after its formation. Many research have been conducted to solve these and to scale-up process. In INTROP, we have involved in nanocellulose research since a couple of years ago, and the research conducted covers upstream and downstream processing, as well as the potential applications of nanocellulose. Being a tropical climate country, Malaysia is grateful as it is rich in bioresources of which many of them are lignocellulosic materials. These materials can be used as a starting material for the production of nanocellulose. With the advanced technologies available globally, it is hoped that nanocellulose commercialization will be realized in the near future.

In this issue, highlights are on the production of nanocellulose and utilization of local bioresources in nanocellulose production. Apart from that, there are several articles on other bioproducts such as biopolymer, pulp and paper and biofuel. INTROP activities and achievement throughout 2015 are also included. It is hoped that this magazine will be benefited to the readers. Enjoy reading!

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Manacellulase

A GREEN AND SUSTAINABLE MATERIAL FROM BIORESOURCES

Nanocellulose refers to cellulosic materials having at least one dimension in the nanometer range and it can be generally classified into nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). NFC is nano-structured long threadlike bundles of cellulose molecules stabilized laterally by hydrogen bonds between the hydroxyl groups and the oxygen atoms of adjacent molecules (Chang et al., 2012), while NCC can be referred to a rod-like highly crystalline short structured nanocellulose fiber with rectangular cross section (Habibi et al., 2009).

NFC vs NCC

NANOFIBRILLATED CELLULOSE (NFC)



NANOCRYSTALLINE CELLULOSE (NCC)



NFC has fibrillated structure, with diameter around 20 -100 nm, and several micrometers in length (Chang et al., 2012).	MORPHOLOGY	NCC are rigid rod-like crystals with diameter in the range of 10-20 nm and length of a few hundred nanometer (Peng et al., 2011).
NFC: Mechanical, physical, chemical, physiochemical or by combination of any of these treatments.	PRODUCTION	NCC: Strong acid hydrolysis treat- ment (Rueda, 2013)
Fiber web structures (paper, board), wood fiber composites, construction materials, membranes, filters, absorbents etc.	POTENTIAL APPLICATIONS	Pigments, fillers, strength-enhancing additives, coatings, functional surfaces, nanocomposites etc.



CELLULOSE PULP AS A SOURCE FOR NANOCELLULOSE FIBER

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Introduction

In pulp and paper industry, cellulose is a substance which remain after completing the pulping and bleaching processes. It is renowned as the most abundant polymer having an annual production over 7.5 x 1010 tons (French et al. 2004). The first isolation of cellulose was discovered by Anselme Payen in 1838 (Payen 1838). Many methods were used in order to extract the cellulose such as alkali/acid treatment and chlorine free extraction (Das et al. 2014, Simone et al., 2012, Nazir et al., 2013, Alemdar & Sain, 2008). At this stage, a huge portion of lignin and carbohydrates have been removed from cell walls. Cellulose pulp contains cellulose which is the main structural constituent of plants, linear polysaccharide of beta (1→4) linked D-glucose units and the frequent molecular weight varies over 1,000,000 g/mole. In practice, cellulose pulp can be derived from woody, non-woody and agro-waste fibers. The woody materials can arise from either softwood or hardwoods such as pine or eucalyptus, from non-woody fibers which comprise of kenaf, rosselle, bamboo and more while agro-waste fibers include pineapple leaves, oil palm empty fruit bunches, oil palm frond, oil palm trunks, rice husks, wheat straws, soy hulls and sago residues (Das et al., 2014, Simone et al., 2012, Nazir et al., 2013, Alemdar & Sain, 2008). Therefore, cellulose pulp is an appropriate raw material for nanocellulose fiber production.

The production of cellulose pulp

In order to obtain cellulose pulp, pulping and bleaching processes need to be accomplished (Eriksen et al. 2008; Lindström & Ankerfors 2009). Pulping means the process to transform the chip of raw materials into individual fibrous pulps form under identified conditions such as pressure, temperature and period (Smook 1992). The conditions are very crucial in order to lead the dissolution of a substantial amount of lignin which cemented the cell wall together. Lignin is a random polymer network that connecting two major biopolyme

components, cellulose and hemicellulose (Clark 1985). Unbleached pulps are obtained after completing the pulping process. These pulps will allow better bonding during the formation of customized paper products like tissue, paper or board. In general, there are three types of pulping process; namely chemical, mechanical and combination pulping processes which are applied according to the target pulp product applications (Smook 1992).

The next step is bleaching process that whitens the unbleached pulp with minimal degradation of cellulose. The effectiveness of bleaching is influenced much by previous pulping process, pulp fiber species and end usage of the bleached products (Smook 1992). A series of stages which is called bleaching sequences need to be carried out in several steps such as DEDED, DEPD and DEDEH in order to achieve the target value for cellulose pulp in terms of pulp viscosity, brightness and kappa number.

The characteristics of cellulose pulp

The composition of cellulose pulp varied based on the type of raw materials, type of pulping process and type of bleaching process as well. The composition of pulp from various sources are shown in Table 1.

Table 1. Chemical compositions of softwood and hardwood pulp (Spence et al. 2010).

Pulp type	Cellulose	Hemicellulose	Lignin
Softwood			
Unbleached softwood	65.2 ± 0.8	20.1 ± 0.1	13.8 ± 0.7
Bleached softwood	79.2 ± 0.2	20.0 ± 0.1	0.8 ± 0.1
Hardwood			
Unbleached hardwood	78.0 ± 0.5	19.3 ± 0.1	2.4 ± 0.4
Bleached hardwood	78.0 ± 0.2	20.3 ± 0.1	1.3 ± 0.1

Fully bleached pulp that is cellulose pulp can reach as high as 94 compared to unbleached pulp which is only 15 Elrepho units (Smook 1992).

Cellulose pulp for nanocellulose

Cellulose pulp has high potential to penetrate more various industrial modern technologies in terms of information technology, biotechnology and nanotechnology as well (Kim *et al.* 2015). For instance, cellulose is also a well-known material in nano-medical applications for treating renal failure and also for the making of wound care, encapsulation and implant material (Hoenich 2006). Vigilant process for both pulping and bleaching must be carried out in such a way that crystalline or amorphous portions are preserved which finally will be tailor-made to certain production.



Chipping of bamboo in order to obtain 2-3 cm width of chip diameter to ease the penetration of chemical during pulping process.



Pulp digester is used for pulping process.



Unbleached pulp obtained after pulping process accomplished.



The pulps after a sequence of bleaching stages completed which the brightest is the cellulose pulp.

Conclusion

The availability of cellulose from many part of plants and it tremendous characteristics will greatly enhance the production of nanocellulose for high technology application in worldwide areas.

References

- 1) Alemdar, A. & Sain M. (2008). Isolation and characterization of nanofibers from agricultural residues Wheat straw and soy hulls. Bioresource Technology. 99: 1664–1671.
- 2) Clark, d'A.J. 1985. Pulp technology and treatment for paper. Miller Freeman Publications, Inc. San Francisco.
- 3) Das, A.M., Ali, A. A. & Hazarika, M.P. 2014. Synthesis and characterization of cellulose acetate from rice husk: Eco-friendly condition. Carbohydrate Polymers. 112: 342–349.
- 4) Eriksen, Ö., Syverud, K. & Gregerson, Ö. 2008. The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. Nord. Pulp Pap. Res. J. 23: 299–304.
- 5) French, A. D., Bertoniere, N. R., Brown, R. M., Chanzy, H., Gray, D., Hattori, K. & Glasser, W. In Kirk-Othmer Encyclopedia of Chemical Technology 5th ed., Seidel, A., Ed., John Wiley & Sons Inc. New York, 2004, Vol. 5.
- 6) Hoenich, N. 2006. Cellulose for medical applications: past, present and future. Bioresources. 1(2):270-280.

- 7) Kim, J.H., Shim, B.S., Kim, H.S., Lee, Y.J., Min, S.K., Jang, D., Abas, Z. & Kim, K. 2015. Review of nanocellulose for sustainable future materials. International Journal of Precision Engineering and Manufacturing-green Technology. 2(2): 197-213.
- 8) Lindström, T. & Ankerfors, M. 7th International Paper and Coating Chemistry Symposium, June 10–12, 2009. Hamilton, Canada.
- 9) Nazir, M.S., Wahjoedi, A.B., Yussof, A.W. & Abdullah Mohd., A. 2013. Eco-friendly extraction and chacterization of cellulose from oil palm empty fruite bunches. BioResources. 8 (2): 2161–2172.
- 10) Payen, A. Compt. Rend. 7:1052 (1838).
- 11) Simone, M.L., Rehman, R.N., Maria, I.G., Nachtigall, S.M.B. & Bica Clara I.D. 2012. Chlorine-free extraction of cellulose from rice husk and whisker isolation. Carbohydrate Polymers. 87: 1131–1138
- 12) Smook, G.A. 1992. Handbook for pulp and paper technologists. Angus Wilde Publications. Vancouver.
- 13) Spence, K. L., Venditti, R. A., Habibi, Y., Rojas, O. J. & Pawlak, J. J. 2010. The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties. Bioresource Technology. 101(15):5961–5968.



NANOCELLULOSE AND ITS POTENTIAL USE IN BIOMEDICAL

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Introduction

Cellulose is the most widely available organic polymer, representing about 1.5 trillion tons of the total annual biomass production, and is considered as an almost inexhaustible source of raw material for the increasing demand on environmentally friendly and biocompatible products [1]. Cellulose can be extracted from the wood, plants, tunicate, bacteria and algae (Figure 1). Nanocellulose materials can be divided into three broad categories, depending on the cellulose nanofibers origin (Table 1).

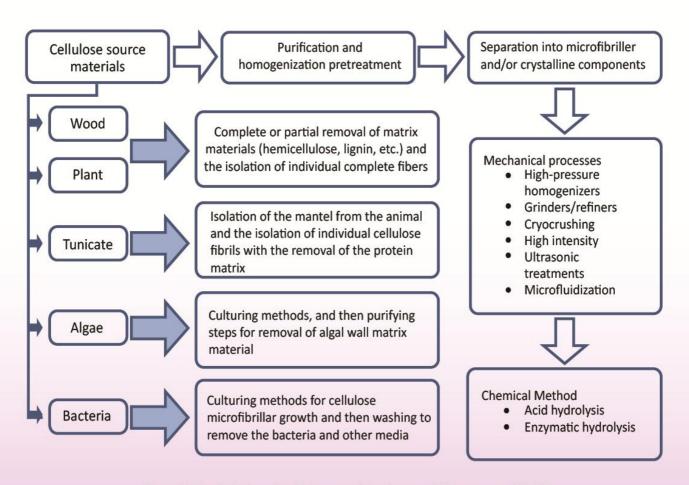


Figure 1. The isolation of cellulose particles from cellulose source [1], [2]

Acronyms	Name	Details	Toxicological experiment
WF PF	Wood fiber Plant fiber	-Hierarchical structure -Low crystallinity (43–65%)	Low toxicity potential Low environmental risk
MEC	Microcrystalline cellulose Microfibrillated cellulose	-Porous -B10–50 mm in diameter -high cellulose content, -higher crystallinity -aggregate bundles of multi-sized cellulose microfibrils that are strongly hydrogen bonded to each other -Usually the MCC aggregates are broken up into smaller micron-sized rod-like particles (1–10 mm in length) prior to use in composites -Produced via mechanical refining of highly purified WF and PF pulpsused as a thickening agent in the food and cosmetics industries. multiple elementary fibrils each consisting of 36 cellulose chains arranged in the lb crystal structure, - high aspect ratio (10–100 nm wide, 0.5–10's mm in length) -B100% cellulose -both amorphous and crystalline regions.	Low toxicity potential Low environmental risk Low toxicity potential Low environmental risk
NFC	Nanofibrillated cellulose	-consists of 36 cellulose chains arranged in crystal structure square cross-section, -high aspect ratio (4–20 nm wide, 500–2000 nm in length), -B100% cellulose -both amorphous and crystalline regions.	Low toxicity potential Low environmental risk
AC	Algae Cellulose	AC particles are the microfibrils extracted from the cell wall of various algae by acid hydrolysis and mechanical refining. The resulting microfibrils are microns in length, have a large aspect ratio (greater than 40) with a morphology depending on algae.	Low toxicity potential Low environmental risk
BC BNC	Bacteria Cellulose Bacteria Nano Cellulose	-large aspect ratio (greater than 50) - morphology depending on the specific bacteria and culturing conditions -Acetobacter microfibrils have a rectangular cross-section (6–10 nm by 30–50 nm), terminating surfaces of (010)t, and (100)t with (100)t being the largest facet,73 and have primarily la crystal structure - altering the culture conditions (stirring, temperature, and additives) it is possible to alter the la/lb ratio and alter the width of the micro- fibrils	No evidence of cytotoxicity No evidence of toxicity in vitro and in vivo Non-toxicity and non-immunogenicity
t-CNC	Tunicate cellulose nanocrystals	-produced from the acid hydrolysis of tunicates - ribbon-like shaped t-CNCs have a height of B8 nm, a width of B20 nm, a length of 100–4000 nm (typical aspect ratios 70–100) -B100% cellulose-highly crystalline (85–100%) -contain a high fraction (76–90%) of Ib crystal structure -highly crystalline and have the largest aspect ratio of any CNC.	Low toxicity potential Low environmental risk

Table 1. The different terminologies used to describe cellulose and cellulose nanoparticles and toxicology experiment results [3]

Bacterial Nano cellulose (BNC)

BNC is a pure cellulose made by bacterial fabrication via biochemical steps and self-assembling of the secreted cellulose fibrils in the medium [2]. The BNC has a fibrillar nanostructure, and its performance including high purity, ultrafine network structure, and high mechanical properties making it suitable for biomedical applications (see Figure 2) [4]. Shaping of the BNC materials in the culture medium can be controlled by the type of cultivation that changes chain sizes, origin of strains that produced different proportion of crystalline phase of BNC, and type of bioreactor[5].

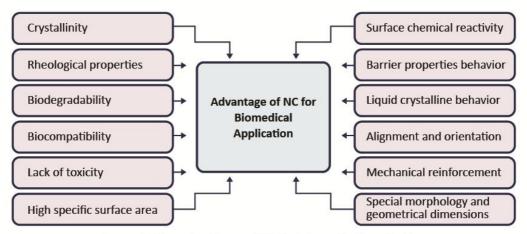


Figure 2. The advantages of NC for biomedical application

Biomedical application of NC

Recently, Nanocellulose has been called as the eyes of biomaterial highly applicable to biomedical industry which includes skins replacements for burnings and wounds; drugs releasing system; blood vessel growth; nerves, gum and duramater reconstruction; scaffolds for tissue engineering; stent covering and bone Figure 3 shows some applications for Nano cellulose within biomedical field[5].

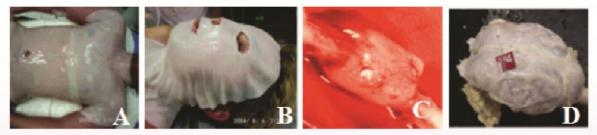


Figure 3: Biomedical applications of nanocellulose (A) and (B) never dried nanocellulose membrane; (C) artificial blood vessels; (D) dura mater reconstruction[6][7][8][9][10] [11]

References

- 1. Plackett, D. A review of nanocellulose as a novel vehicle for drug delivery. Nord. Pulp ... 2014, 29, 105–18.
- 2. Lam, E.; Male, K. B.; Chong, J. H.; Leung, A. C. W.; Luong, J. H. T. Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trends Biotechnol.* 2012, 30, 283–90.
- 3. Lin, N.; Dufresne, A. Nanocellulose in biomedicine: Current status and future prospect. Eur. Polym. J. 2014, 59, 302-325.
- 4. Jorfi, M.; Foster, E. J. Recent advances in nanocellulose for biomedical applications. J. Appl. Polym. Sci. 2014, 41719, n/a-n/a.
- 5. Kim, J.-H.; Shim, B. S.; Kim, H. S.; Lee, Y.-J.; Min, S.-K.; Jang, D.; Abas, Z.; Kim, J. Review of nanocellulose for sustainable future materials. Int. *J. Precis. Eng. Manuf. Technol.* 2015, 2, 197–213.
- 6. Gatenholm, P.; Klemm, D. Bacterial nanocellulose as a renewable material for biomedical applications. MRS Bull. 2010, 35, 208-214.
- 7. De Olyveira, G. M.; Manzine Costa, L. M.; Basmaji, P.; Xavier Filho, L. Bacterial Nanocellulose for Medicine Regenerative. J. Nanotechnol. Eng. Med. 2011, 2, 034001.
- 8. Siqueira, G.; Bras, J.; Dufresne, A. Cellulosic Bionanocomposites: A Review of Preparation, Properties and Applications. *Polymers (Basel)*. 2010, 2, 728–765.. 9. Kalia, S.; Dufresne, A.; Cherian, B. M.; Kaith, B. S.; Avérous, L.; Njuguna, J.; Nassiopoulos, E. Cellulose-Based Bio- and Nanocomposites: A Review. *Int. J. Polym. Sci.* 2011, 1–35.



NANOCELLULOSE FIBER PRODUCTION FROM OIL PALM EMPTY FRUIT BUNCH BY ELECTROSPINNING

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Introduction

Malaysia is one of the top producers of palm oil in the world, which contributes to the huge plantation area of oil palm trees, with total area of 50,000 km², or about 15% out of 77% of total agricultural land. It is estimated that about 44 million tons of solid residues are produced during the palm oil extraction, comprises of 54% empty fruit bunch (OPEFB), 30% shell and 18% oil palm mesocarp fiber (OPMF) (Chiew and Shimada, 2013). This value is expected to rise by the year 2020 as this industry keeps expanding year by year. With regard to this matter, the infinite supply of oil palm biomass creates abundant of renewable resources for various bioproducts manufacturing such as biocomposite, biofuel, biochar, biocompost and many more. According to National Biomass Strategy 2020, carbon emission can be reduced by replacing renewable biomass to non-renewable materials as a raw material. This could also contribute to the Gross National Income with the value approximately more than RM30 billion, as well as creating about 66,000 jobs. This data shows that the oil palm industry can create many opportunities and social benefits for the locals. In addition, the government has also launched several initiatives since last few years to capitalize the biomass potential as well as to demonstrate Malaysia commitment towards addressing global warming and climate change caused by the palm oil industry.

With the growing concern on environmental sustainability, various oil palm biomass can be fully utilized as a feedstock for various products manufacturing and this includes oil palm mesocarp fiber (OPMF) and oil palm empty fruit bunch (OPEFB). Particular attention has been given for the production of high-value products from these biomass. One potential product is nanocellulose fiber (NCF). According to Chen et al. (2011), NCF is a polymer fiber with dimension of 100 nanometer (nm) or less with extremely high specific area, high porosity and excellent pore interconnectivity. In fact, NCF shows great effect in enhancing the mechanical strength of material as they have good tensile strength, high permeability

and crystallinity as well as high thermal resistance as compared to neat polymer. These properties impart NCF to be used for several applications ranging from consumer products to high-tech industrial applications. Therefore, with the infinite supply of oil palm biomass throughout the year, there is high possibility to produce NCF in Malaysia for commercial purpose, which indirectly ensures maximum potential utilization of oil palm biomass.

Prior to NCF production, oil palm biomass need to be extracted to remove hemicellulose, lignin and other impurities, to leave only cellulose component (Jawaid and Abdul Khalil, 2011). The presence of hemicellulose and lignin may affect the quality of NCF as these two components may influence the crystallinity of NCF (Kang et al., 2013). There are a few pretreatments can be applied to remove these unnecessary components which can be divided into biological, chemical and mechanical pretreatments. Chemical pretreatments have been found to be the most effective method to leave approximately 98% of cellulose fraction compared to other pretreatments.

Cellulose fibrillation can be conducted by several techniques such as electrospinning, steam explosion, high pressure homogenization and ultrasonication. Electrospinning is one of the most promising techniques to produce high amount of NCF. The main challenge in preparing NCF from any polymer solution by electrospinning is to find the appropriate conditions that will allow for the formation of a stable and continuous fiber spinning (Freire et al., 2011). There are three main factors affecting fiber formation by electrospinning; which are process parameters, solution parameter and ambient conditions. The use of co-solvent such as dimethyl formamide (DMF) can successfully improve NCF production from electrospinning as it can improve spinnability, surface tension and viscosity of the cellulose solution.

In this study, OPEFB fiber was treated with 5% sodium chlorite (NaClO3) at 70°C for 90 minutes, followed by 6% potassium hydroxide (KOH) at room temperature for 24 hours aimed at cellulose extraction. The OPEFB cellulose was then dissolved in ionic liquid, 1-ethyl-3-methylimidazolium chloride with an addition of imethyl formamide (DMF) as a co-solvent prior to lectrospinning. Electrospinning was conducted by applying a high voltage (10-20 kV) to the metallic needle (0.1 cm i.d.) which was connected to a syringe filled with the appropriate cellulose solution. Solution rate was set at 0.5 ml/h with the distance of the needle to the collector was approximately 10 cm.

Dissolution of Lignocellulosic Material in Ionic Liquid

To evaluate the dissolution of OPEFB cellulose in the ionic liquid at room temperature, samples were collected periodically and analyzed using an optical polarized microscope. Based on Fig. 1, it is seen that the solubilization was not completely achieved. Original OPEFB sample (Fig, 1 a) failed to dissolve in ionic liquid due to the presence of high amount of lignin in the fiber. High amount of lignin inhibits the dissolution of sample in ionic liquid due to the limitation of hydroxyl interaction between ionic liquid and lignin (Kang et al., 2013). Complete cellulose dissolution under constant agitation and temperature was achieved for OPEFB cellulose (Fig. 1 b).

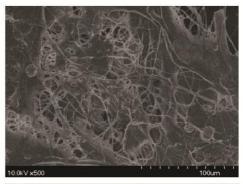




Figure 1. Dissolution of original OPEFB (a) and OPEFB cellulose (b) in 1-ethyl-3-methylimidazolium acetate after 24 H.

Electrospinning of OPEFB cellulose

The production of nanofiber by electrospinning from dissolved OPEFB cellulose fibers in ionic liquids was greatly affected by the addition of co-solvent. DMF was proven as a good co-solvent to enhance the processing parameters. According to Hardelin *et al.* (2012), the addition of co-solvent provided better spinnability and hence, better fiber can be obtained. The morphology of electrospun OPEFB cellulose nanofiber from dissolved cellulose in ionic liquid with and without the addition of DMF is depicted in Fig. 2. It is clearly shown in the micrograph that the addition of 10% (w/w) DMF gave better fiber formation with homogeneous distribution of nanofiber (Fig 2 a).



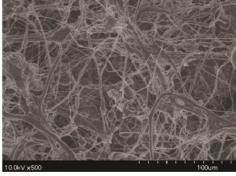


Figure 2. Morphology of electrospun OPEFB nanofiber from polymer solution in 1-ethyl-3-methylimidazolium acetate. With the addition of co-solvent (a), and without the addition of co-solvent (b).

Electrospun micrograph of OPEFB cellulose nanofiber was observed by field emission — scanning electron microscopy (FE-SEM) as shown in Fig.3. Results showed that electrospun OPEFB NCF had size less than 300 nm. This shows that the nanofiber could be produced from OPEFB and the size obtained was comparable to those NCF produced from several sources as shown in Table 1.

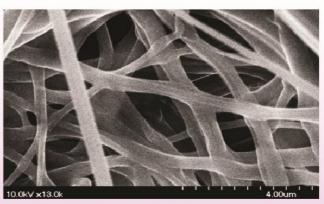


Figure 3. SEM image of electrospun nanofiber from OPEFB.

Table 1 shows cellulose nanofiber produced from electrospinning of various fibers such as hemp, pulp and commercial cellulose. It is seen that the size of the NCF obtained was comparable to that OPEFB NCF.

Table 1. Electrospun nanofiber from various sources.

Cellulose fiber	Ionic liquid	Voltage	Size of nanofiber	Images
Commercial – Sigma Aldrich (Freire <i>et al</i> . 2011)	1-ethyl-3- methylimidazolium acetate	25kV	450 -550 nm	335 m A335m A535m A555m A555m
Hemp (Kang <i>et al</i> . 2013)	1-ethyl-3- methylimidazolium acetate + DMF (90:10)	35kV	100 - 500 nm	(e)
Pulp (Hardelin <i>et al.</i> 2011)	1-ethyl-3- methylimidazolium acetate + DMF (90:10)	10-50kV	300 - 600 nm	
OPEFB (This study)	1-ethyl-3- methylimidazolium acetate + DMF (90:10)	25kV	100 - 300 nm	239/x139

Conclusion

This study shows that OPEFB could be appropariate bioresource for NCF production through electrospinning, with great spinnability. NCF produced herewith having diameter size of 100 to 300 nm, and these values are comparable to the previous reports. The use of 10% DMF as co-solvent successfully improved the fiber formation through electrospinning. Results obtained herewith could promote green utilization of biomass which may reduce waste generation and creating new industries sustainable development.

References

Chen, W., Yu, H., Liu, Y., Hai, Y., Zhang, M., Chen, P., 2011. Isolation and characterization of cellulose nanocellulose fibers from four plant cellulose fibers using a chemical-ultrasonic process. Cellulose 18, 433-442. doi:10.1007/s10570-011-9497-z

Chiew, Y.L., Shimada, S., 2013. Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer e A case study of Malaysia. Biomass and Bioenergy 51, 109-124. doi:10.1016/j.biombioe.2013.01.012

Jawaid, M., Abdul Khalil, H.P.S., 2011. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. Carbohydrate Polymer 86, 1-18. doi:10.1016/j.carbpol.2011.04.043

Hardelin, L., Thunberg, J., Perzon, E., Westman, G., Walkenstrom, P., Gatenholm, P. 2012. Electrospinning of Cellulose Nanocellulose fibers from Ionic Liquids: The Effect of Different Cosolvents. Journal of Applied Polymer Science. 125: 1901-1909.

Kang, Y., Ahn, Y., Lee, S.H., Hong, J.H., Ku, M.K., Kim, H., 2013. Lignocellulosic Nanofiber Prepared by Alkali Treatment and Electrospinning Using Ionic Liquid. Fibers and Polymers 14, 530-536. doi:10.1007/s12221-013-0530-8

Freire, M.G., Teles, R.R., Ferreira, R.A.S., Carlos, D., Coutinho, A.P., 2011. Electrospun nanosized cellulose fibers using ionic liquids at room temperature. Green Chemistry. 3173-3180. doi:10.1039/c1gc15930e.

Abdullah, N., Sulaiman, F., 2013. The oil palm wastes in Malaysia, in: Biomass Now - Sustainable Growth and Use. pp. 75-100. doi:10.5772/55302 Basiron, Y., Weng, C.K., 2004. The Oil Palm and its Sustainability. J. Oil Palm

Res. 16. 1-10.

Brinchi, L., Cotana, F., Fortunati, E., Kenny, J.M., 2013. Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications. Carbohydr. Polym. 94, 154–169. doi:10.1016/j.carbpol.2013.01.033

Chang, F., Lee, S., Toba, K., Nagatani, A., Endo, T., 2012. treatment and its application for nanocomposite 393-403. doi:10.1007/s00226-011-0416-0 Chen, W., Yu, H., Liu, Y., Chen, P., Zhang, M., Hai, Y., 2011. Individualization of cellulose nanocellulose fibers from wood using high-intensity ultrasonication combined with chemical pretreatments. Carbohydr. Polym. 83, 1804-1811. doi:10.1016/j.carbpol.2010.10.040





POTENTIAL OF NANOFIBRILLATED CELLULOSE FROM KENAF BAST USING ULTRASONIC APPROACH

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Introduction

Nanofibrillated cellulose (NFC) is a material which comprises of nanosized cellulose fibrils with high aspect ratio. The usual dimensions are below 100 nm in width and length up to several micrometers (Zimmermann *et al.* 2010). The dimensions depend on the various factors such as raw materials and mechanical processes of NFC (Abdul Khalil *et al.* 2014). In recent years, productions of NFC are greatly being focused due to potential in many areas especially in nanocomposite (Virtanen *et al.* 2014).

Kenaf (Hibiscus cannabinus) is one of the non-woody plants that is applied as cellulose sources to produce NFC (Kuramae et al. 2014). Other non-woody plants that have been studied are listed as abaca, sisal, flax, hemp and jute (Alila et al. 2013). The chemical composition of kenaf bast is around 63.5 % cellulose, 17.6 % hemicellulose and 12.7 % lignin (Janoobi et al. 2009). Fig. 1 exhibit the physical look of kenaf bast, unbleached kenaf bast pulp and bleached kenaf bast pulp.



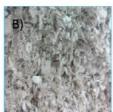




Fig. 1. A-Kenaf bast, B-Unbleached kenaf bast pulp and C- Bleached kenaf bast pulp

Recently, the ultrasonic method has been applied to produce nanocellulose (Mishra et al. 2012). The important process called cavitation occurs where ultrasonic energy is transferred to cellulose chains. This refers to the formation, growth and violent collapse of cavities in water (Tischer et al. 2010). Consequently, the ultrasonic collision can gradually disintegrate or collapse the micron-sized cellulose into nano-sized fibers (Fig. 2).

Morphology of the fibers

The FESEM and STEM images on the morphology of the kenaf bast cellulose (KB-Cellulose) before and after ultrasonic treatment can be shown in Fig 3. It can be seen that before ultrasonic treatment the surfaces of cellulose bleached fibers exhibited even and plain. This is caused by the removal of impurities (Fig. 3A). The images show a mixture of micro-sized fibers and nano-sized fibrils with web-like structures, and the diameter of the kenaf bast nanofibrillated cellulose (KB-NFC) was in the range of 9-20 nm (Fig. 3B & 3C). The cavitation process plays an important role to disintegrate the fibers from micron to nano size (Qian et al. 2012).

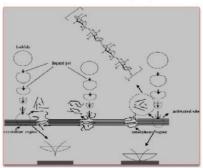


Fig. 2. Schematic diagram of ultrasonication process (Li, Yue & Liu, 2012)

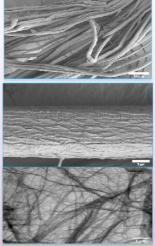


Fig. 3. (A) - (B) FESEM images of KB-Cellulose before ultrasonic treatment and (C) STEM image of KB-Cellulose afterultrasonic treatment at 20 kHz in frequency and 700 W output power for 60 min.

Viscosity Analysis

Table 1 shows the viscosity values of KB-Cellulose and KB-NFC, 12.70 cP and 9.03 cP, respectively. The calculated degree of polymerization (DP) was 1,058.36 (KB-Cellulose) and 833.76 (KB-NFC). The deterioration in viscosity value of NFC is highly due to fibrillation during the ultrasonic treatment. Lignin content also could probably affect the viscosity value. Higher lignin content may decrease the viscosity value as well. The value of DP strongly correlates with the aspect ratio of the fibrils. Lower DP means that more shorter fibrils and constant diameter are obtained (Zimmermann *et al.* 2010).

Sample	Viscosity (cP)	Degree of Polymerization (DP)
KB-Cellulose	12.70	1,058.36
KB-NFC	9.03	833.76

Conclusions

Nanofibrillated cellulose from kenaf bast was successfully produced using ultrasonic treatment at 20 kHz in frequency and 700 W output power. FESEM and STEM images revealed the existence of NFC from kenaf bast in the range of 9-20 nm diameters. Conclusively, higher crystallinity led to higher thermal stability and lower viscosity of NFC. Such property has very good and high potential to be used in various applications such as reinforcing material in the matrix.

References

Abdul Khalil, H.P.S., Davoudpour, Y., Nazrul Islam Md., Mustapha, A., Sudesh, K., Dungani, R., & Jawaid, M. (2014). Production and modification of nanofibrillated cellulose using various mechanical processes: a review. *Carbohydrate Polymers*, 99, 649-665.

Alila, S., Besbes, I., Vilar, M.R., Mutjé, P., & Boufi, S. (2013). Non-woody plants as raw materials for production of microfibrillated cellulose (MFC): a comparative study. *Industrial Crops and Products*, 41, 250-259.

Janoobi, M., Harun, J. Shakeri, A. Misra, M. & Oksman, K. (2009). Chemical composition, crystallinity, and thermal degradation of bleached and unbleached kenaf bast (Hibiscus cannabinus) pulp and nanofibers. *BioResources*, 4(2), 626-639.

Kuramae, R., Saito, T., & Isogai, A. (2014). TEMPO-oxidized cellulose nanofibrils prepared from various plant holocelluloses. *Reactive and Functional Polymers*, 85, 126-133.

Li, W., Yue, J. & Liu, S. (2012). Preparation of nanocrystalline cellulose via ultrasound and its reinforcement capability for poly(vinyl alcohol) composites. *Ultrasonic Sonochemistry*, 19(3) 479-485.

Mishra, S.P., Manent, A.S. Chabot, B. Daneault, C. (2012). Production of nanocellulose from native celulose – various options *utilizing ultrasound*. *BioResources*, 7(1), 422-436.

Qian, Y., Qin, Z., Vu, N.M., Tong, G., & Chin, Y.C.F. (2012).Comparison of nanocrystals from tempo oxidation of bamboo, softwood, and cotton linter fibers with ultrasonic-assisted process. *BioResources*, 7(4), 4952-4964.

Tischer, P.C.S.F., Sierakowski M.R., Westfahl, H., & Tischer, C.A. (2010). Nanostructural reorganization of bacterial cellulose by ultrasonic treatment. *Biomacromolecules*, 11(5), 1217-1224.

Virtanen, S., Vartianen, J., Setälä, H., Tammelin, T., & Vuoti, S. (2014). Modified nanofibrillated cellulose-polyvinyl alcohol films with improved mechanical performance. *RSC Advances*, 4, 11343-11350.

Zimmermann, T., Bordeanu, N., & Strub, E. (2010). Properties of nanofibrillated cellulose from raw materials and its reinforcement potential. *Carbohydrate Polymers*, 79(4), 1086-1093.

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PREPARATION AND CHARACTERIZATION OF FIBROUS CELLULOSE/POLYPYRROLE NANOCOMPOSITES

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Introduction

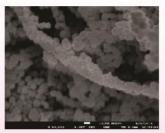
Polypyrrole has been one of the most widely studied polymers in the area of conductive polymers because of its environmental stability, physical and electrical properties [1]. The properties of conducting polymers such as redox activity, ion exchange, ion discrimination capacities and corrosion protection are highly dependent on the synthesis procedure as well as on the nature of dopant, monomer and solvent [2]. Polypyrrole is one of the conductive polymers readily synthesized from a range of aqueous and non-aqueous solvents and have many potential advantages such as low cost and low potential oxidation. All these properties made polypyrrole as a good candidate in many potential applications such as electronic and electrochromic devices, light-weight batteries, membrane separation, sensors, drug delivery, rechargeable batteries, and chromatographic stationary phases [3,4]. However, it is an infusible, improcessable polymer which has relatively poor mechanical, and processability properties. Because of that, the study on the new approaches, to synthesize conductive polymers composite with enhanced mechanical and electrical properties is still continuing. In recent years, composite materials of cellulose and conductive polymers have received significant attention. It has been shown that polypyrrole (PPy) can be uniformly coated on cellulose fibers from commercial filter paper by a chemical polymerization-induced adsorption process [5]. More recently, it was demonstrated that pyrrole was in situ polymerized on the individual cellulose fibers extracted from the Cladophora green [6]. Microfibrillated cellulose (MFC), was first developed in the early 1980s, by high-shear mechanical homogenization in water. The word "fibril" has been used by various researchers to describe relatively long and very thin pieces of cellulosic material [7]. Due to the mild character of the enzymatic hydrolysis, the cellulose fibers in MFC are substantially longer than Cellulose nanocrystal (CNC) which produced by acid hydrolysis In this research, composite of

Polypyrrole-Microfibrillated Cellulose (PPy-MFC) was prepared in the presence of different surfactant. Microfibrillated celluloses (MFC) are generally considered to be fibrils with diameters in the range of 10-100 nm liberated from larger plant based cellulose fibers. Conducting Polypyrrole (PPy) composites were synthesized via chemical polymerization method using different concentration of Pyrrole, MFC, and Ammonium persulfate (NH4)2S2O8 as oxidant.

Results and Discussion

2.1. Field Emission Scanning Electron Microscopy (FE-SEM)

The morphologies of resulting composites were greatly depend on the monomer concentration and surfactant chain length. The FE-SEM micrographs of polypyrrole exhibited the presence of globular, micrometer-sized particles with a bulky and non-porous structure. However, the composite of PPy-MFC showed an open porous structure of fiber with average size of nanometer (Fig 1).



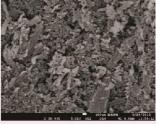


Figure 1: FESEM micrographs of PPy-MFC, AND PPy-MFC-CTAB at 50,000 x magnification

Ribbon-like polypyrrole nanostructures were prepared by chemical polymerization of pyrrole in the presence of long-chain cationic surfactant, Cetyltrimethylammonium bromide (CTAB), whereas no polypyrrole nanostructure was obtained in the presence of anionic surfactant of Sodium dodecylbenzenesulfonate (SDBS). The composite of PPy-MFC prepared in the presence of CTAB, nanofibers presented the mean diameter of 71.27 nm that showed a value between the size of PPy-MFC and PPy-CTAB.

2.2. Transmission Electron Microscopy)

The size of nanostructure, and fiber size distribution was studied by Transmission electron microscopy (TEM). Figure 2 shows the TEM images of PPy-MFC prepared from solution containing 0.03M pyrrole and 0.025M MFC.

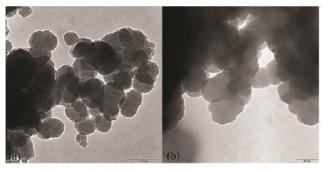


Figure 2: TEM images of PPy-MFC at magnifications of (a) 16, 000 and (b) 20,000

The composite of PPy-MFC prepared in the presence of CTAB as shown in Figure 3, nanofibers presented the mean diameter of 71.27 nm that showed a value between the size of PPy-MFC and PPy-CTAB.

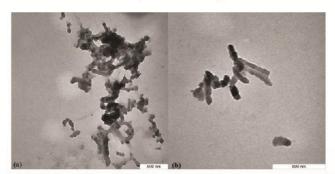


Figure 3: TEM image of PPy-MFC-CTAB at magnifications of (a) 40, 000 and (b) 80,000

Reaction between cationic surfactant of CTAB with anion of oxidizing agent which is persulphate ion acted as templates for the formation of ribbon-like polypyrrole nanostructures. However, anionic surfactant of SDBS cannot serve as a template for the polymerization of pyrrole probably because of its rule as counterions in the polymer chains.

2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectra showed that pyrrole was polymerized successfully on the MFC fibers and when an anionic surfactant was used to prepare the composites; it served as counter ion for the PPy chains. The infrared absorption spectra of PPy, MFC, CTAB and a composite prepared from solution containing 0.06M PPy, 0.1% MFC and 12cmc of CTAB.are shown in Figure 12. The characteristic peaks of polypyrrole at 1022.74 cm⁻¹ (C–H in-plane), 1138.29 cm⁻¹ (C–N stretching), and 1525.41 cm⁻¹ (ring vibration), confirmed the formation of

polypyrrole doped by oxidizing agent which was Ammonium persulfate (NH4)2S2O8. The peak at 3327.46 cm⁻¹ and 2913.16 cm⁻¹ which are due to O-H and C-H stretching in MFC indicating the polymerization of Pyrrole on the surface of MFC. The peak at 1307.09 cm⁻¹ which is related to C-O and C-H bending in MFC, is another evidence of presence of MFC in the structure of PPy-MFC-CTAB composite. The absorption at 1698.66 cm⁻¹ was assigned to the C=C ring stretching of pyrrole in benzoic form. A sharp peak at 909.26 cm⁻¹ is characteristic peak of CTAB inside structure of composite.

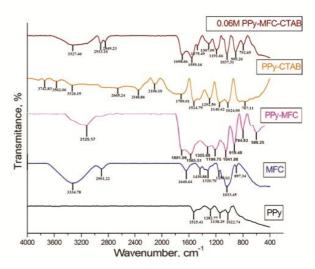


Figure 4: The FT-IR spectrum of PPy, MFC, PPy-MFC, PPy-CTAB, and composite prepared from solution containing 0.06M Pyrrole, 0.1% MFC and 12cmc of CTAB.

References

[1] Abdi, M. M., Ekramul Mahmud, H. N. M., Kassim, A., Mat Yunus, W. M., Talib, Z. A., & Haron, M. J. (2010). Synthesis and characterization of a new conducting polymer composite. *Polymer Science* - Series B, 52(11-12), 662-669.

[2] Pron, A., & Rannou, P. (2002). Processible conjugated polymers: From organic semiconductors to organic metals and superconductors. *Progress in Polymer Science (Oxford)*, 27(1), 135-190.

[3] Ansari, R., (2006). Polypyrrole conducting electroactive polymers: Synthesis and stability studies, E-Journal of Chemistry, 3(13), (186-201).

[4] Liu, Y., Chu, Y., & Yang, L. (2006). Adjusting the inner-structure of polypyrrole nanoparticles through microemulsion polymerization. Materials Chemistry and Physics, 98(2-3), 304-308.

[5] Eriksen, Ø., Syverud, K., & Gregersen, Ø. (2008). The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. *Nordic Pulp and Paper Research Journal*, 23(3), 299-304.

[6] Mihranyan, A., Nyholm, L., Garcia Bennett, A. E., & Strømme, M. (2008). A novel high specific surface area conducting paper material composed of polypyrrole and cladophora cellulose. Journal of Physical Chemistry B, 112(39), 12249-12255.

[7] Alemdar, A., & Sain, M. (2008). Isolation and characterization of nanofibers from agricultural residues - wheat straw and soy hulls. *Bioresource Technology*, 99(6), 1664-1671.

BIOPLASTICS: MOVING TOWARDS SUSTAINABILITY

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Introduction

Bioplastics (BPs) is expanding from biodegradable biomass-based/bio-sourced/renewable sources plastics. Biopolymers and bioplastics can refer to: 1) bio-based and biodegradable plastics like PLA, PHA and starch acetate (SA); 2) bio-based, non biodegradable plastics like polyamides and bio-based PE; 3) synthetic biodegradable polymers, e.g. PCL, PBS and PVA; 4) conventional plastics. Biodegradability of BPs has been widely publicized in society and the demand for packaging is rapidly increasing among retailers and the food industry at large. However, there is little consensus on actual impacts of BPs production. This topic therefore aims to identify current strengths and weaknesses and future threats and opportunities and leverage points for bioplastics industry in a move towards sustainability?

Compelling measures for the BP industry include: having a consensus in BPs applications based on strategic sustainable development, universal labelling and recycling systems for BPs, government strategic policies to encourage research into new technologies in improving biodegradability and energy efficiency in manufacturing. In today's world, there are almost incomplete? Without plastics, but most of these materials have been derived from petroleum based and currently with increasing of fuel costs, potential scarcity and customer demands for alternatives. These concerns generate new research using alternative raw materials in production of Bioplastics (BPs).

There are three major ways to synthesis bioplastics; (1) using natural polymer, (2) using bacterial polyester fermentation, and (3) using chemical polymerization. Movement towards sustainability of BPs growth slowly since there are some limitation on the application of biodegradable plastics?. Currently, the production of raw materials for BPs is much smaller than ordinary plastics due to technical issues and very low demand in the marketplace. The raw materials for BPs may come from crop biomass that can face competition pressures from agricultural and biofuels interests. These considerations make it difficult to claim that BPs is "truly" sustainable products. Bioplastics can be produced from two categories of plastics. The first category is plastics derived from renewable biomass sources of carbon (as opposed to fossil fuels), such as hemp and soy bean

oil, corn and potato starch andcellulose or molecules produced by microbes. Second, biodegradable plastics made of biomass or fossil fuels (European bioplastics, 2007), but not all biodegradable plastics are made of biomass. Biodegradable plastics are plastics that can decompose into carbon dioxide, methane, water, inorganic compounds, or biomass via microbial assimilation (the enzymatic action of microorganisms) in a compost facility. Polylacticacid (PLA) plastics is one example of biodegradable plastic?? That have been successfully commercialized and applied most in many different fields. A number of fossil fuel-based polymers such as Polybutylenexacinate (PBS) and Polyglycolic acid (PGA) certified biodegradable and compostable (Bioplastics Supply Chains, 2004).

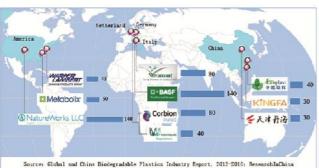
Global market situation of Bioplastics

Consumer awareness towards eco-friendly products has increased tremendously in recent years. Hence, the growth of bioplastic packaging market worldwide is expected to be huge. The bioplastic packaging market is expected to be contributed by the utilization of eco-friendly products to replace the chemically derived synthetic products. In fact, chemical manufacturers have already started investing in the development of bio-based chemicals in order to reduce their dependency on petrochemical supply. This move increases the availability of bio-based raw materials and further encourages the growth of bioplastic packaging products. In light of the increasing environmental awareness towards, one of the industries that will greatly apply the bioplastic packaging is the textile industry. However, oil price is also a factor to be concerned with. Low oil price will have a negative impact on the growth of bioplastic packaging market. Oil prices will fall if its production is high, especially in Russia and Middle East. This is one of the many factors that make the future of bioplastic packaging market more challenging and unpredictable. Bio-based resins such as poly lactic acid (PLA), PHA, bio-PP, and bio-PET are used to produce bioplastic packaging materials. These resins give the bioplastic products the needed tensile strength and improved impact resistance, allowing their applications in various areas such as in

electronic industries, food and beverages, and in the production of cooking utensils. Emerging countries such as BRICS will likely observe the growth of bioplastic packaging market demand due to the growth of domestic electronics as well as food and beverage industries. The changing lifestyle in Middle East, India, and China due to increasing disposable income leads to the higher demand of convenience foods, which contributes towards the growth of bioplastic packaging market. Similarly, India, China and Brazil are experiencing the growth of their pharmaceutical industry due to the increasing foreign investments and local demand for medical drugs, which also amplifies the market demand for bioplastic packaging.

Europe has a set of strict regulations associated to the use of non-recyclable plastics and higher environmental awareness to apply sustainable packaging. Therefore, it is expected to have one of the highest market demands for bioplastic packaging. The European government policies such as Europe 2020 strategy also promote bio-economy. Through these initiatives, taxes for bio-based products are reduced and public authorities are encouraged to give preference towards procurement of bio based products.

Figure 1: Global and China Bioplastics Industry Report (Research in China, 2013 - 2016



In 2012-2013, the global bioplastic production and demand reached 1-1.5 million tons per annum. However, so far poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and plastarch material (PSM) are only the types of bioplastics that are being mass-produced. In 2013, 87% of the global bioplastic capacity was contributed by PLA, PBS, and PSM. In 2013, the market demand for bioplastics in Europe was 54% of the global demand and the market demand for bioplastics in North America was 28%. The major producers of bioplastics in the world are NatureWorks (US) with 140 kt/a capacity, BASF (Germany) with 140 kt/a capacity, Novamont (Italy) with 80 kt/a capacity, and Purac (Netherlands) with 80 kt/a. China is also a major supplier of bioplastics, accounting for 20% of the world production capacity. China's bioplastics production capacity grew at the

rate of more than 21% in 2009–2013. Supportive government policies and expanding range of applications contributed to its growth and encouraged local companies to engage in the business of manufacturing and developing bioplastics.

Conventional vs. Biodegradable Plastics

Conventional Plastics

- There are two broad categories of plastic materials: thermoplastics and thermosetting plastics. Thermoplastics can be heated up to form products and then if these end products are re-heated, the plastic will soften and melt again. This gives them the potential to being recycled. In contrast, thermoset plastics can be melted and formed, but once they take shape after they have solidified, they stay solid and, unlike thermoplastics, cannot be remelted. Hence, they cannot be recycled.
- Global production of plastics in 2012 rose to 288 million tonnes a 2.8% increase compared to 2011.
- Around 5-8% of the world's oil production is used for plastics production.
- Producing 1kg of plastics generates about 3-6kg of CO2 (including production and incineration); whereas recycling of plastic saves on average about 2.5kg CO₂ per kg of plastic.
- China remains the leading plastics producer with 23.9%, and the rest of Asia (incl. Japan, 4.9%) accounts for an additional 20.7%. CO2 emissions for Asia from plastics production can be estimated between 385 and 770 million tones.
- In the US, packaging applications accounted for 43% of total plastics produced in 2012. In Europe, packaging applications are the largest application sector for the plastics industry and represent 39.4% of the total plastics demand. Recycling and energy recovery rates for plastics packaging in Europe are higher than for other plastics, 69.2% compared to 61.9% for all plastics.
- Recyclability depends on the type of plastics.
 Recyclable types of plastics (thermoplastics) include: expanded polystyrene (EPS), polyolefins, polyethylene teraphtalate (PET), polystyrene, polyurethanes (PUR), polyvinyl chloride (PVC).

Biodegradable Plastics

 Biodegradable plastics can be divided into two types: plastics derived from renewable raw resources, called bioplastics, and plastics made from petrochemicals with biodegradable additives which enhance biodegradation.

- Biodegradable plastics are plastics that can be decomposed by bacteria or other living organisms.
 Biodegradable means that an object can be broken down biologically to the point where microorganisms can completely metabolize them to carbon dioxide (and water). However, the conditions under which these plastics decompose are often very specific and depend on the composition of the plastic.
- There are many different types of biodegradable plastics, which are at different stages of development. Over the past couple of years, biodegradable plastics have steadily increased their market share. For example, in the years 2000 to 2008, the worldwide consumption of biodegradable plastics based on starch, sugar, and cellulose—so far the three most important raw materials—increased by 600%. As of 2013, 5-10% of the plastic market focused on biodegradable polymer derived plastics.
- Life cycle analyses show that bioplastics can reduce CO2 emissions by 30-80 percent compared to conventional plastics (depending on the material and application). However, taking the whole range of biodegradable plastics, life cycle assessments that were undertaken to determine whether the carbon, fossil fuel and water usage in these materials is more efficient than polymers made by conventional plastics have resulted in mixed findings.
- Asia has the biggest share in global biodegradable plastics production (36.2%), followed by South America (28.1%), and Europe (22.8%).



Figure 2. Logos used in Japan for products derived from biomass. (a),Biomass Plastics' logo indicating that the plastic material consists of at least 25 wt% biobased content. This logo is authorized by the Japan Bio-Plastics Association (JBPA); (b) ,Biomass Products' logo indicating that part or all of the raw materials is derived from biomass. This logo is authorized by the Japan Organics Recycling Association (JORA) (Copyright permitted by both associations). Add source e.g., (John, 2000)

Sustainability and sustainable development

According to Plastics Europe (2008), the use of conventional plastic is resource efficient. Its application in various products and services has made our lives easier in many ways. However, it causes many environmental problems such as non-biodegradable wastes, greenhouse gases, and the potential emission of hazardous substances including dioxin. Thus, it has been a target of criticism by environmentally-associated organizations.





US Composting

Figure 3. Logos of European and United State Composting Council Add source

Some companies in the chemical industry took the initiatives to deal with the environmental issues associated to their products and manufacturing processes. For instance, a polyvinyl chloride (PVC) manufacturer based in UK known as Hydro Polymers started working together with The Natural Step (TNS) to achieve sustainability. They started to have dialogues with the customers, suppliers, and other stakeholders with regard to how to attain sustainable production of PVC as well as other chemicals (Leadbitter, 2002). The move by Hydro Polymers was successful and it was later followed by Imperial Chemical Industries (ICI). ICI utilized the Sustainability Life Cycle Assessment (SLCA) tool, which is based on the FSSD and the theory of Strategic Life Cycle Management introduced by Ny et al. (2007), to assess the sustainability performance of their products (ICI, 2007).

Life Cycle Analysis (LCA)

LCA is a method of assessment to compare the performance of alternative products and systems. Furthermore, it calculates the consequences of a process, system, or product on the environment. In ASTM D7075, it has been outlined that the LCA method involves different stages including setting the goal, analyzing the inventory, assessing the impact, and making interpretation. In setting the goal, the reasons and scope of the study is defined. This includes its breadth and depth. During the analysis of the inventory, environmental inputs (e.g. raw material, land, energy,

and water) and outputs (releases to water, air and land) related to the product and its whole life cycle is identified and quantified. In assessing the impact, the inventory input—output flows are characterized based on a series of environmental impacts (e.g. global warming, resource depletion, ozone thinning, human toxicity, ecological toxicity, eutrophication, acidification, and the degradation of landscapes as well as ecosystems). In making interpretation, the environmental impacts are combined and the results are described following the goals of the LCA study (Conshohocken and Narayan, 2004). The terminology and concepts stated in ASTM D7075 follows the ISO Standards 14040—14043.



Figure 4. Life Cycle Analysis of Bioplastic (Life cycle Inventory, 2003)

For the compostable packages, the waste management approaches may involve recycling, landfilling, or combustion. To ensure the overall eco-balance, the final disposal system is the main concern, especially if it involves biodegradable wastes. If bio-based wastes undergo composting and the compost is then applied on land, the value is higher because it will accumulate significant emission and energy credits for sustainable agriculture. In earlier LCA studies of biodegradable packaging, the ecotoxicity, eutrophication, and land use are some of the impact factors being emphasized (ISO 14043, 2000).

EPA has outlined three factors that should be included in the evaluation of greenhouse gas emissions for a polymer system. The first factor that should be analyzed is the emissions of greenhouse gases within the entire life cycle of the polymer, which also includes the emissions from the utility and from the disposal action. The second one is the impact of manufacturing and disposing the material on carbon sinks. The final analysis is about how much the disposal option can recover

energy that can be used to replace electricity and reduce the emissions of greenhouse gases from the utility. However, there is some amount of uncertainty in evaluating the impact of biodegradable polymers on greenhouse gas emissions. In fact, the studies greenhouse gas emissions and carbon sequestration related to landfilling are scarce. LCA has some limitations in evaluating the total environmental impact assessment of a compost system because some parameters such as reductions fertilizers and water in soil as well as improvement in soil conditions could not be measured or characterized with values (Life Cycle Inventory, 2003).

Barlaz et al. (2003) assessed the environmental impacts of solid wastes disposal alternatives. According to them, energy recovery will be reduced if organic waste management system is shifted from landfilling to composting because the composting process uses energy and increases greenhouse gas emissions. However, due to the lack of data, the characterization of complete environmental consequences of composting could not be obtained. Some of the offsets could be in the form of nutrient content in compost-amended soil, reduced pesticide use, reduced fertilizer application, reduced irrigation, and avoided manufacture of erosion control products, or avoided harvest and transportation of peat.

In another study, Komilis and Ham (2004) introduced a model for municipal solid waste composting and yard waste facility known as life cycle inventory (LCI) model. This model was based on lab experiments to identify some emissions that were not present and it took into account the production of compost as a low and high value product. Three organic streams were considered, i.e. yard waste, mixed paper, and food waste. For these categories of operation, 77% of the total capital cost was spent for the building and the odor control system. Also according to them, the solid waste decomposition actually produced more than 90% of the CO2 emission. However, after trying to characterize the emissions, indicators are required to assess and compare the composting facilities systematically

Conclusion

The use of bioplastics as packaging is expanding in the fields of medical, food and beverage, and other consumer goods. As we know, bioplastics are biodegradable and thus composting is now an alternative disposal method for these packaging materials. The companies involved are only focusing on how these bioplastics are good because they are made from eco-friendly renewable resources and how they can reduce fossil fuel consumption. Regardless, most of these eco-friendly bioplastics are still being disposed in

landfill together with other non-biodegradable packaging materials due to the lack of composting and recycling programs. Therefore, a more systematic procedure in disposing these bioplastics is required, with the enactment of state or federal regulations to keep everything in line.

Although the market share of the bioplastics is small, they have potential in reducing the environmental impact and in becoming an important group of materials with a wide range of properties and applications. The major countries in the research and production of bioplastics that would profit from this developing market are Germany and Europe. However, the actual impact of bioplastics on the environment have not yet been fully studied and understood because this technology is still considered new. The available studies suggest that bioplastics have the capability of increasing the efficiency of the resources and reducing the environmental impacts, but it is still too soon to provide any concrete conclusions regarding this new material. More extensive researches are certainly required.

From the energy aspect, recycling of the bioplastics seems to be a better option than composting. However, the sorting and cleaning processes that are required in recycling make it less practical. Therefore, composting would be the better alternative. The current issue is that neither of these alternatives is actually available. Currently, the most significant benefit of using bioplastics is solely for marketing purposes. In actuality, instead of creating a sustainable packaging option, a new waste disposal problem is being created. However, if the issue of waste disposal and the life cycle of the bioplastics are fully addressed and understood, compostable bioplastic packaging would absolutely be a valuable packaging alternative. One of the simplest ways to do this is by mixing them together with manure, food, or yard waste facilities. Some of the countries that are already in position to exploit these materials are Germany and Canada.

References

Allsopp, M., Walters, A., Santillo, D., Johnston, P. (2006). Plastic Debris in the World's Oceans. Greenpeace International, Amsterdam, Netherlands.

ASTM. "D7075-04. Standard Practice for Evaluating and Reporting Environmental Performance of Biobased Products".

Beucker, S.; Fichter, K.; Marscheider-Weidemann, F. (2007): Fallstudie Biokunststoffe, Analyse der Leistungsfähigkeit in "grünen" Zukunftsmärkten, Case Study in the project Green Future Markets.

Bohlmann, G. M. (2004). Biodegradable packaging life-cycle assessment. Environmental Progress, 23, 342.

Barlaz, M. A., Kaplan, P. O., Ranjithan, S. R., Rynk, R. (2003). Comparing recycling, composting and landfills. Biocycle, 44, 52.

Conshohocken, P A., Narayan, R. (2004). Drivers and Rationale for Use of Biobased Materials Based On Life Cycle Assessment (LCA) in: Global Plastics Environmental Conference, Atlanta.

European Committee for Standardization. (1997). "ISO 14040:1997 Environmental Management-Life Cycle Assessment- Principals and Framework", EN, Brussels, Belgium.

Komilis, D., Pham, R. K. (2004). Life-cycle inventory of municipal solid waste. Journal of Environmental Engineering. 130, 1390-1400.

Life Cycle Inventory and Life Cycle Assessment for Windrow Composting Systems. (2003). Department of health conservation, University of New South Wales, Sydney, Australia.

http://www.grandviewresearch.com/industry-analysis/bioplastic-packaging-market

Bioplastic Packaging Market Analysis, Market Size, Application Analysis, Regional Outlook, Competitive Strategies, and Forecasts, 2015 To 2022.

http://www.marketresearchreports.biz/analysis-details/global-and-china-biodegradable-plastics-industry-report-2013-2016.

 $http://www.powershow.com/view1/8b813ZDc1Z/Biodegradable_Plastics_Produced_by_Microorganisms_powerpoint_ppt_presentation$

http://www.unep.org/ietc/Portals/136/Conventional % 20 vs % 20 biodegradable % 20 plastics.pdf

ISO (1998). "14041:1998. Environmental Management – Life Cycle Assessment – Goal and Scope Definition and Inventory Analysis", ISO, Geneva, Switzerland. ISO (2000). "14042:2000. Environmental Management – Life Cycle Assessment – Life Cycle Impact Assessment", ISO, Geneva, Switzerland.





USE OF OIL PALM BIOMASS FOR POLYHYDROXYALKANOATES BIOPOLYMER PRODUCTION

Hidayah Ariffina,b* and Mohd Ali Hassanb

Summary

The palm oil sector generates 80 million dry tonnes of biomass in Malaysia alone. There is increasing potential to utilise oil palm biomass, especially those associated with the daily harvesting of the fresh fruit bunch, which are available at the palm oil mills as business-as-usual without any additional collection costs, for higher-value uses such as for biopolymers. The National Biomass Strategy 2020 estimated that 12 million dry tonnes of oil palm biomass will likely be utilised for wood products and bioenergy. An additional 20 million tonnes could be mobilised for use as biofuel pellets and bio-based chemical industries. Since many of the biomass technologies are fast maturing and becoming more economically feasible, the trend for oil palm biomass utilisation to value-added and sustainable products such as biopolymers will continue to rise.

Keywords: Oil palm biomass, value-added products, biopolymers

Introduction

It is estimated that 11% of Malaysia gross national income (GNI) is contributed by the agriculture sector, and from that figure, more than half (8%) is contributed by palm oil sector. Malaysia has been well recognized as the leader of palm oil export globally due to its favourable agro-ecological conditions for crop growth and development. A total area of 5.1 million hectares was planted with oil palm trees as of December 2012, with nearly 100 million tonnes of fresh fruit bunch (FFB) processed which yielded 20 million tonnes of crude palm oil (CPO) (MPOB, 2013). This large production of palm oil resulted in huge generation of waste and wastewater from the palm oil industry. It was reported that four kg of solid biomass is generated for every kg of palm oil produced. On the other hand, palm oil mill effluent (POME) is generated at 50 % of the total amount of FFB processed (Yacob et al., 2006). There have been many studies on the utilization of solid and liquid biomass from palm oil industry for biopolymers production. By adopting the research outcome to the industry, sustainable palm oil production could be created as the biomass will not only be able to be discarded efficiently, but it also may contribute to extra income to the industry and give positive impact socially by creating new job opportunities. Furthermore, efficient utilization of oil palm biomass for such bioproducts will also contribute to sustainable production of energy and materials since renewable feedstock are being used.

Oil Palm Biomass

Oil palm biomass are by-products from palm oil industry, which cover both by-products from the oil palm plantation and palm oil mills. Six types of oil palm biomass have been recognized from the industry, with palm oil mill effluent (POME) as the only liquid biomass. Table 1 shows the types of oil palm biomass, production site, annual generation of biomass and current uses.

It is estimated that the above figure will increase annually and by 2020, the total amount of solid and liquid biomass will reach 85-110 and 70-110 million tonnes, respectively (Agensi Inovasi Malaysia, 2012). Due to the abundance of the biomass, improper treatment of the biomass may create other issues. For example, most of the OPF, OPT and OPEFB are currently discarded at the plantation for nutrient recycling and mulching. However, too large amount of biomass discarded at the plantation will invite snakes and rodents. On the other hand, anaerobic treatment of POME using open pond system will generate methane which adds to the generation of greenhouse gas from the industry. Therefore, efficient treatment and utilization of the biomass are needed in order to ensure sustainable production of palm oil.

Oil palm biomass consists of mainly carbohydrate in the form of cellulose and hemicellulose. On the other hand, liquid biomass from palm oil mill, i.e. POME contains substantial amount of oil and grease, COD, total solids and nitrogen (Mumtaz et al., 2010). Even though carbon compound in both solid and liquid biomass is in different form, but in overall the high carbon content of both solid and liquid biomass of oil palm indicate that the biomass are suitable to be used as feedstock for the production of value added products such as bioenergy, bio-based chemicals and biopolymers.

Table 1. Oil palm biomass (data adopted from National Biomass Strategy 2020)

Type of biomass	Production site	Amount generated* (million tonnes)	Availability	Current uses
Oil palm fronds (OPF)	Plantation	46	Daily	Discarded at the plantation for soil mulching
Oil palm trunks (OPT)	Plantation	14	At the end of plantation lifecycle (every 25 years)	Discarded at the plantation
Oil palm empty fruit bunch (OPEFB)	Mill	7	Daily	Soil mulching, incinerated
Oil palm mesocarp fiber (OPMF)	Mill	7	Daily	Fuel for boiler
Oil palm shell (OPS)	Mill	4	Daily	Fuel for boiler
POME	Mill	60	Daily	Anaerobic treatment and discharged to the river

^{* 2010} data. Dry weight basis, except for POME.

Polyhydroxyalkanoates biopolymer from oil palm biomass

Biopolymers refer to polymer materials derived from bio-based and renewable resources; such as bioplastics, biocomposites and lignocellulosic materials. Polyhydroxyalkanoates (PHA) is an interesting biopolymer as it is being produced by microorganisms intracellularly as carbon and energy reserve materials when they are under stress conditions (Anderson and Dawes, 1990). PHA can be generally classified into short-chain-length (scl) and medium-chain-length (mcl), depending on the number of carbons of the alkyl side chains. scl-PHA possessing alkyl side chains having up to two carbons, while mcl-PHA has at least three carbons on the side chains. Due to the difference in the total number of carbons, these PHAs have different requirement of substrate in fermentation. The scl-PHA requires simpler substrate such as sugars and volatile fatty acids (VFA).

There have been many reports on the production of PHA from oil palm biomass, both solid and liquid. Palm oil mill effluent (POME) for instance, is a good substrate for the production of PHA as it contains substantial amount of VFA. POME is generated as wastewater during sterilization of oil palm fresh fruit bunches (FFB), clarification of palm oil and effluent from hydrocyclone operations. With high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), POME requires pre-treatment before being discharged into the

environment. An anaerobic treatment method for POME which is coupled with the production of organic acids for subsequent use in PHA fermentation has been successfully developed (Hassan et al., 1996; 1997; 2002; 2006). It has been reported that the integration of POMEtreatment and PHA production will sufficiently provide a zero discharge system for palm oil mills. Depending on the scale of operation, concentration of clarified organic acids obtained from treated POME varied from 50-100 g/L. The acids consisted a mixture of acetic, propionic and butyric acids (Hassan et al., 1996). The combination of these acids make POME suitable for the production of scl-PHA, especially poly(3hydroxybutyrate-co-3-hydroxyvalerate), PHBV copolyymer. PHBV is generally better in terms of mechanical nd thermal properties compared to its homopolymer, poly(3-hydroxybutyrate), PHB.

Apart from the above studies, there have also been reports by other researchers on the production of PHA from POME. Salmiati and co-workers (2007) reported on the production of PHA from mixed microbial culture in POME. It was found that PHA accumulation in the bacteria reached 40% during the fermentation. Indeed, the use of POME as substrate for PHA production does not only contribute to the use of renewable carbon source for PHA production, but it also helps in the treatment of wastewater from palm oil mill. The 2-in-1 process helps to create sustainable production of PHA from oil palm biomass.

Recently, oil palm frond (OPF) juice has been introduced as another feedstock candidate for fermentation (Zahari et al., 2012a). OPF juice contains nearly 80 g/L of sugars, of which 70% is glucose. OPF juice is advantageous as fermentation feedstock due to its daily availability; on top of its easy processing, whereby only simple pressing is needed for obtaining the sugars. OPF juice has been utilized for the production of PHA (Zahari et al., 2012a and 2012b) and it was found that the use of OPF juice as substrate yielded higher PHA production compared to sugars having similar sugars commercial concentration. The higher PHA production was contributed by other minerals and vitamins presence in the OPF juice, which enhanced the bacterial growth and PHA production.

Types and properties of PHAs produced from oil palm biomass are comparable to those produced from other feedstock. The summary of the PHA properties from various carbon sources is shown in Table 2. PHB produced from OPF juice had higher molecular weight (MW) compared to other PHB produced from other substrates, and had similar mechanical properties compared to that produced from pure fructose. The properties of PHBV produced from POME organic acids on the other hand were varied according to the composition of 3HV fractions (Zakaria et al., 2010), however in overall high molecular weight of PHBV is achievable by using organic acids derived from POME. This shows that oil palm biomass can be a good fermentation substrate for the production of PHA. A detailed economic analysis to study the feasibility of PHA production from POME organic acids was reported by Hassan and co-workers (1997). It was concluded that coupling anaerobic treatment of POME with PHA production would reduce the price of PHA to less than 1 USD / kg, compared to the normal price at 6 USD / kg. The results from the study showed that the use of POME for PHA production is economically feasible, with additional advantage to the environment.

Table 2. Properties of PHA produced from various carbon sources.

Type of PHA	Carbon source	Mw (kDa)	Tm	Tensile strength (MPa)	Elongation to break (%)	Reference
РНВ	Fructose	NA	177	43	5	Doi, 1990
	Maple sap	507	177	NA	NA	Yezza et al., 2007
	Mixture of commercial sugars (glucose, sucrose and fructose)	713	NA	NA	NA	Zahari et al., 2012a
	Sodium acetate	523	153	31	22	Reddy et al., 2009
	OPF juice	812	162.2	40	8	Zahari et al., 2012a,b
PHBV	Glucose	540	166	35	45	Reddy et al., 2009
	Glycerol	610	171	37	69	Reddy et al., 2009
	Glucose + propionic acid	990 - 1300	NA	NA	NA	Liu et al., 2009
	NA	NA	145	20	50	Tsuge, 2002
	POME organic acids	400 - 1000	139 - 156	NA	NA	Zakaria et al., 2010

Conclusions and future perspectives

The present trend towards green and sustainable products with low carbon footprints will undoubtedly provide the push for the development of technologies related to the utilisation of biomass resources for value-added products. In conclusion, we can expect increased research and development efforts in the near future which will soon lead to more utilisation of oil palm biomass for sustainable and cost-effective biopolymers production.

References

Agensi Inovasi Malaysia. National Biomass Strategy: New wealth creation for Malaysia's palm oil industry (2011).

S. Yacob, M.A. Hassan, Y. Shirai, M. Wakisaka, and S. Subash, *Baseline study of methane emission from anaerobic ponds of palm oil mill effluent treatment,* Sci. Total. Environ. 366 (2006), pp. 187-196.

M.A. Hassan, Y. Shirai, N. Kusubayashi, M.I.A. Karim, K. Nakanishi, and K. Hashimoto, *The production of polyhydroxyalkanoate from anaerobically treated palm oil mill effluent by Rhodobacter sphaeroides*. J. Ferment. Bioeng. 83 (1997a), pp. 485-488.

A.J. Anderson, and E.A. Dawes, Occurrence, metabolism, metabolic role, and industrial uses of bacterial polyhydroxyalkanoates, Microbiol. Rev. 54 (1990), pp. 450-472.

M.A. Hassan, Y. Shirai, N. Kusubayashi, M.I. Abdul Karim, K. Nakanishi, and K. Hashimoto, Effect of organic acid profiles during anaerobic treatment of palm oil mill effluent on the production of polyhydroxyalkanoates by Rhodobacter sphaeroides, J. Ferment. Bioeng. 82 (1996), pp. 151-156.

M.A. Hassan, Y. Shirai, H. Umeki, H. Yamazumi, S. Jin, S. Yamamoto, M.I. Abdul Karim, K. Nakanishi, and K. Hashimoto, *Acetic acid separation from anaerobically treated palm oil mill effluent by ion exchange resins for the production of polyhydroxyalkanoate by Alcaligenes eutrophus*. Biosci. Biotechnol. Biochem. 61 (1997b), pp. 1465-1468.

M.A. Hassan, Y. Shirai, M. Inagaki, M.I. Abdul Karim, K. Nakanishi, and K. Hashimoto, Economic analysis on production of bacterial polyhydroxyalkanoates from palm oil mill effluent, J. Chem. Eng. Jpn. 30 (1997c), pp. 751-755.

M.A. Hassan, O. Nawata, Y. Shirai, N.A. Abdul Rahman, L.Y. Phang, A.B. Ariff, Abdul and M.I. Karim, A proposal for zero emission from palm oil industry incorporating the production of polyhydroxyalkanoates from palm oil mill effluent, J. Chem. Eng. Jpn. 35 (2002), pp. 9-14.

M.A. Hassan, A process for treatment of palm oil mill effluent and for conversion of the palm oil mill effluent into biodegradable plastics, Malaysian Patent. MY123658A. (2006).

T. Mumtaz, N.A. Yahaya, A.A. Suraini, N.A. Abdul Rahman, L.Y. Phang, Y. Shirai, and M.A. Hassan, *Turning waste to wealth-biodegradable plastics polyhydroxyal-kanoates from palm oil mill effluent: Malaysian perspective.* J. Clean. Prod. 18 (2010), pp. 1393-1402.

M.R. Zakaria, H. Ariffin, N.A. Mohd Johar, A.A. Suraini, H. Nishida, Y. Shirai, and M.A. Hassan, *Biosynthesis and characterization of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer from wild-type Comamonas sp. EB1722*, Polym.

Z.U. Salmiati, Z. Ujang, M.R. Salim, M.F. Md Din, and M.A. Ahmad, Intracellular biopolymer productions using mixed microbial cultures from fermented POME, Water Sci. Technol. 56 (2007), pp. 179-185.

M.A.K.M. Zahari, M.R. Zakaria, H. Ariffin, M.N. Mokhtar, J. Salihon, Y. Shirai, and M.A. Hassan, *Renewable sugars from oil palm frond juice as an alternative novel fermentation feedstock for value-added products*, Biores. Technol. 110 (2012a), pp. 566-571.

M.A.K.M. Zahari, H. Ariffin, M.N.M. Mokhtar, J. Salihon, Y. Shirai, and M.A. Hassan, Factors affecting poly(3-hydroxybutyrate) production from oil palm frond juice by Cupriavidus necator (CCUG52238T), J. Biomed. Biotechnol. (2012b), pp. 125865. 8 pages.

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COCONUT COIR FOR PULP AND PAPER

Mohamad Jani Saad*

Introduction

Coconut is grown in more than 90 countries around the world. In Malaysia, coconut occupied about 115,000 hectares of land which is most planted in Johor, Perak and Selangor (Table 1). Coconut was ranked 4th place after palm oil, rubber and rice in term of land acreage. Coconuts are typically grown in tropical countries. The coconut husk is abundantly available as cheap residue from coconut production. The husk comprises 30 wt.% coir fibres and 70 wt.% pith, which can be separated for traditional coir fibre applications in woven carpets, ropes, brushes and matting. This can be achieved by retting procedures or mechanical decortication (Van Dam et al. 2004).

Coir is a natural fibre extracted from the husk of coconut and used in products such as floor mats, doormats, brushes, mattresses, etc. Technically, coir is the fibrous material found between the hard, internal shell and the outer coat of a coconut (Wikipedia 2012). The brown

Product Evaluation Discussion

Pulp and paper products were some product that can be produced using coir fibres. Even though coir has high lignin at 30% (Table 2), it still can be turned into paper. The coir fibre pulp was chemically analysed; pulped by chemical-mechanical pulping (CMP) process and bleached by elementary chlorine free (ECF) process with four stages of chlorine dioxide (D) and alkali extraction (E). Sheets or paper were made from the unbleached and bleached coir fibre pulp. The results in Table 3 showed that in the papermaking process, the coconut coir has chemical properties that can be successfully pulped by the CMP and bleached by the ECF processes. The DEDED sequences can be used in bleaching the coir pulps. The bleached pulp produced paper with better tensile index, burst index, tear index, folding endurance as well as brightness properties but has lower opacity compared to the unbleached pulp. The bleaching process also improved the bonding strength of the coir fibre in the paper due to removal of lignin. fibre is obtained by harvesting fully mature coconuts when the nutritious layer surrounding the seed is ready to be processed into copra and desiccated coconut (Wikipedia 2012). The fibrous layer of the fruit is then separated from the hard shell manually or using dehusking machine.

To date, relatively little attention has been given to the use of coconut husk which can create environmental problem if no right disposal is practised. Practically, the utilization of coir can create economic and environmental advantages (Abdul Khalil *et al.* 2006). The fibres are renewable, nonabrasive, cheaper, available in abundance and show less health and safety concern during handling and processing (Zulkifli *et al.* 2008). These advantages can be of great potential in converting the coir fibres into various products especially pulp and paper manufacturers.

Conclusion

Coir fibre has chemical properties that can be exploited for successful pulp and paper production. The DEDED sequences can be used in the bleaching process of coir pulps. The results showed that bleaching of coir fibre pulp produced paper with better tensile index, burst index, tear index, folding endurance as well as brightness properties with lower opacity than the unbleached pulp. This is mainly due to the removal of the lignin in the coir fibre during the bleaching process which increased the bonding strength of the coir fibre paper.



Coconut tree and coir

	2011		2012		2013	
	Planted (ha)	Production (mt)	Planted (ha)	Production (mt)	Planted (ha)	Production (mt)
Johor	21124	81597	22384	88146	23055	92553
Perak	15064	123537	15958	137368	16437	144237
Selangor	10521	154591	11271	166721	11609	175057
Kedah	1650	8445	1856	7754	1912	8141
Kelantan	5587	26207	6077	29593	6259	31072
Melaka	2990	26658	3155	26233	3250	27544
N.Sembilan	1273	4262	1449	5384	1493	5653
Pahang	1772	8016	1827	6590	1882	6920
Perlis	560	1903	579	883	597	927
P.Pinang	1942	16697	2113	18059	2176	18962
Terengganu	4335	8952	2428	7117	2501	7473
Peninsular	66819	460865	69098	493849	71171	518541
Malaysia		\$4000 000000000000000000000000000000000	and Alexandria (ACC)	500 St. 000 CC.	Newton Den & Chief	
East Malaysia	39493	101690	42995	112681	44285	118315
Malaysia	106312	562555	112093	606530	115456	636856

Table 1: Coconut production and plantation in Malaysia 2011-2013 (Unit Perangkaan, Jabatan Pertanian Semenanjung Malaysia 2013)

	Ash	Extractive	Holocellulose	α-cellulose	Alkali	Hot water	Lignin	Pentosan	Silica
Coir	2.14	2.66	70.5	37.4	17.3	2.55	32.1	22.0	0.5

Table 2. Chemical components of coir (Rushdan 2002)

	Apparent density (g/cm³)	Tensile index (Nm/g)	Burst index (kPa.m²)	Tear index (mNm²/g)	Folding (no)	Opacity (%)	Brightness (%)
Unbleached paper	0.37a	18.33a	1.85a	7.05a	8.57a	99.60a	16.28a
Bleached paper	0.44b	30.56b	3.35b	11.78b	67.43b	85.46b	82.87b

Table 3. Strength and optical properties of coir paper (Mohamad Jani S. 2014 Means with the same letter within the same column are not significantly different at 5%











Coconut coir

Paper from coconut coir

Some product from coir paper

Particleboard of coconut coir

References

- 1. Abdul Khalil, H.P.S., Alwani, S.M. and Mohd Omar, A.K. (2006). Chemical composition, anatomy, lignin distribution, and cell wall structure of Malaysian plant waste fibers. BioResources 1(2): 220 232
- 2. Mohamad Jani S. 2014. Effect of bleaching on coir fiber pulp and paper properties. Journal Tropical Agriculture and Food Science. 42 (1), 51-61.
- 3. Rushdan, I. (2002). Chemical composition of alkaline pulps from oil palm empty fruit bunches. Oil Palm Bull. 44: 19-24
- 4. Unit Perangkaan Jabatan Pertanian Semenanjung Malaysia 2013. Statistik Tanaman (Sub Sektor Tanaman Makanan) 2013.
- 5. Van Dam, J. E.G., Van den Oever, M.J.A., Keijsers, E.R.P. (2004). Production process for high density high performance binderless boards from whole coconut husk. Industrial Crops and Products, 20: 97-101.
- 6. Wikipedia (2012). Coir. Retrieved in 9 May 2013 from http://en.wikipedia.org/wiki/Coir
- 7. Zulkifli, R., Mohd Nor, M.J., Mat Tahir, M.F., Ismail, A.R. J. and Nuawi, M.Z. (2008). Acoustic properties of multi-layer coir fibres sound absorption panel. Appl Sc. 8(20): 3709-3714



IMPROVED OXYGEN DELIGNIFICATION: A WAY TO ENHANCE TOTALLY CHLORINE-FREE BLEACHING SELECTIVITY

Leh Cheu Peng* and Chong Yin Hui

Why is totally chlorine-free bleached pulp not prevalence?

The application of totally chlorine-free bleaching (TCF) is well recognised for its environmental compatibility. However, its application is less well-established in comparison to conventional chlorine-based bleaching due to the TCF bleached pulp demonstrates relatively lower brightness and strength properties. Oxygen delignification (O-stage) plays an important role in establishing TCF bleaching and it is commonly used as the first bleaching stage in the pulp bleaching sequence. As compared to the conventional first bleaching stage—chlorination stage (C) followed by alkaline extraction (E), the bleaching selectivity between delignification and cellulose degradation of an O-stage is relatively lower. After the CE stage, up to 90% of the lignin can be eliminated from the pulp with merely slightly cellulose degradation; however, a reduction of kappa number of 50% or even lower by an O-stage is accompanied by a significant loss in pulp viscosity (Beyer et al., 1999; Smook, 1992). As a result, the TCF bleaching performance is restricted.

Improved Oxygen Delignification

For attaining a more efficient TCF bleaching, many studies have been carried out to improve the selectivity of the O-stage by two approaches which are either modifying the process or implementing a pretreatment. For the former approach, peroxide reinforced oxygen bleaching—OP -stage is one of the well-known modified O-stages, which is performed by adding hydrogen peroxide (H2O2) in the O-stage. It has been verified that OP stage is able to enhance the degree of delignification, a boost in brightness, lower brightness conversion, and maintain pulp viscosity at an acceptable level. In addition, the consumption of bleaching chemicals can be reduced with the application of the OP-stage as well (Ng et al., 2011). Nevertheless, according to Parthasarathy et al. (1990), only a small amount of H2O2 (less than 0.5% on oven dry pulp) should be added to avoid serious loss of pulp viscosity.

For the second approach, it is believed that a simple pretreatment may activate the residual lignin in the pulp and thus enhance the degree of delignification in the subsequent O-stage. For instance, pretreating of pulp with peracetic acid (PAA) exercises a "stimulating" effect on O-stage as the reactive species generated by PAA—hydrosonium ion (OH+) can react with both phenolic andon-phenolic types of lignin (Fossum and Marklund 1988; Kishimoto et al. 2003). With the capability of degrading non-phenolic lignin by PAA, therefore enhances lignin reactivity during succeeding stages (Obst et al. 1979; Minja et al. 1998).

New Findings of Improved Oxygen Delignification

The H2O2 reinforced oxygen delignification (OP-stage) even though shows better performance than the ordinary O-stage, its beneficial effects is limited as only a small amount of H2O2 addition is allowed for the avoidance of serious cellulose degradation. Thus, in order to gain the full advantage of H2O2 upon delignification and pulp brightness, H2O2 charge higher than 0.5% may be required. With this in mind, an OP-stage with H2O2 charge more than 1.0% was first studied by using oil palm empty fruit bunch (EFB) soda-anthraguinone pulp (Ng et al., 2011). Different from ordinary Op-stage, a small amount of anthraquinone (AQ)—less than 0.05% (on the basis of oven dry pulp weight) was added into the OP system and it was found that the resultant pulp from the modified OP-stage (known as AQ aided H2O2 reinforced oxygen delignification, OPAq-stage) exhibited the highest selectivity (2.26) as shown in Table 1.

The research was continued and further verified by using commercial mixed tropical hardwood brown kraft pulp (supplied by Sabah Forest Industries Sdn. Bhd., SFI). It was found that the effective reduction of kappa number (K_n) by the optimum O-stage was limited to about 38%, and the pulp viscosity was 18.7 cP with selectivity less than 0.60 and ISO brightness of ca. 43% (Table 1). The selectivity of the O-stage on mixed tropical hardwood kraft pulp was improved by adding H2O2 (Op stage), as it offered a greater effect on Kn reduction, but inevitable, it induced more serious cellulose degradation. In order to minimize the drop of pulp viscosity, an OPAq-stage was applied by adding a small amount of AQ. The OPAq-stage with the optimum amount of AQ was of retaining higher pulp

Thus, with the same amount of alkaline charge, the selectivity of all of the OPAq-stages was greater than that of O stage and Op stage. It was also found that an excessive amount of AQ was not applicable as there are no positive effect to K_n reduction, pulp viscosity, selectivity and pulp brightness. Again, the result verified that the addition of AQ in an OP-stage enabled the employment of H₂O₂ with a higher amount to gain better K_n reduction and brightness increment without compromising on unwarranted drop of pulp viscosity.

	С	ondition		Result				
Type of	NaOH	H2O2	AQ	Kappa Number	Pulp Viscosity	Kappa Number Reduction	Selectivity	Brightness
Sample	%	%	%		cP	%		%
958	2.5	78	-	8.2	11.6	42.3	1.76	55.11
EFB	2.5	2	20	6.2	11.3	56.3	2.16	66.63
	2.5	1.4	0.02	6.5	12.4	54.2	2.26	61.92
	2	=	-	10.4	18.9	36.6	0.52	42.58
Hardwood	2.5	40	-	10.2	18.7	37.8	0.53	43.15
	2	1.4	-	8.6	18.1	47.6	0.64	53.00
	2.5	1.4	-	7.3	17.5	55.6	0.71	52.02
	2	1.4	0.04	9.2	21.7	44.2	0.83	50.30
	2.5	1.4	0.04	8.4	20.4	48.7	0.8	52.56
	2.5	1.4	0.06	8.4	18.8	48.7	0.69	52.04

Table 1 Study of O-stage, Op-stage and OpAQ stage on EFB and hardwood kraft Pulp

On the other hand, the application of a simple UV radiation pretreatment prior to the O-stage and OP-stage was also capable of enhancing the selectivity in comparison to the ordinary O-stage and OP-stage (Figure 1). As shown in Table 2, the improvement of bleaching selectivity of O-stage was attributed by the increase of Kn and retaining of pulp viscosity. It was noted that the Kn reductions of both O-stage and OP-stage increased from 37.8% and 55.5% to 53.7% and 59.1%, respectively, after the UV pre-treatment. Moreover, the UV treated pulps also showed higher resistant to alkaline degradation during the subsequent bleaching stage and resulted in a higher pulp viscosity after O-stage and retained an acceptable pulp viscosity after OP-stage.

In order to verify the effect of UV pre-treatment, spectroscopy analysis of Fourier transform infrared (FTIR) was carried on the pulp before and after pre-treatment. Based on the FTIR spectra, it was found that advantages of photo pretreatment were causing structural and /or functional groups changes in both carbohydrates and lignin. Consequently, the carbonyl-induced degradation of carbohydrates (random cleavage ofglycosidic bonds in cellulose chain) was

diminished and thus, increased the selectivity by protecting the cellulose from carbonyl-induced degradation and stimulating more lignin degradation (Chong et al. 2015).

Besides selectivity, the application of an UV pretreatment was also enhanced the brightness increment of the pulps. For O-stage, the addition of the pre-treatment increased about 5 units of the pulp brightness in comparison to the unpretreated one, whereas the brightness of the UV pretreated OP bleached pulp attained brightness up to 60% ISO. In short, it can be concluded that application of a simple UV pretreatment, the Kn reduction can be improved up to 48% for O-stage and only no more than 5% for Op-stage. Although the protective effect was more prominent in the O-stage than the Op-stage, the latter could achieve about 12 units higher brightness.

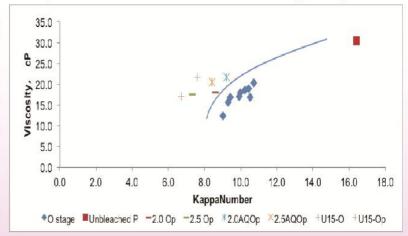


Figure 1: Selectivity curve of ordinary oxygen delignification and various improved oxygen delignification.

No	PAA Charge (%)	Temp. (°C)	Time (min)	Type of Oxygen Bleaching	Kappa Number	viscosity (cP)	Selectivity	Kn (%)	Brightness (ISO, %)
		Unb	leached P		16.4	30.4			36
<u>0</u> 2	_	_	-	2.0 Op	8.6	18.1	0.64	47.6	51
70	-	. 	-	2.5 Op	7.3	17.5	0.71	55.5	52.02
=	(-	-	- 2	.0AQOp	9.2	21.7	0.83	44.2	50.30
-	140	-	- 2	.5AQOp	8.4	20.4	0.80	48.8	52.22
U15-0	2	_	30	0	7.6	21.7	1.01	53.7	47.77
U15-Op) -	1.7	30	Op	6.7	17.1	0.73	59.1	60.31

Table 2: Effect of additive and pre-treatment on oxygen delignified hardwood kraft pulp

Conclusion

Maximizing of bleaching selectivity as well as pulp brightness in the first stage of TCF bleaching sequence should become an important conception nowadays. The major intention of shifting the pulp bleaching technology from conventional chlorine-based to TCF is to minimize the environmental pollution caused by pulp and paper industry. In the production of high brightness pulp (90% ISO brightness and above), a series of bleaching stage is required and the number of bleaching stages basically will increase proportionally to achieve a higher brightness. Thus, to produce a brighter pulp, more chemicals, energy and cost are required and at the same time the strength property of the pulp and paper produced might be diminished, especially by using TCF bleaching sequence with relatively low selectivity. Hence, in the context of environmental conservation, due to the implementation of government policy, printing and copying A4 papers with the brightness of 70-75% ISO brightness made from chlorine-free bleached pulp and up to 70% recycled paper are well accepted in Japan. This indicated that the acceptance of the paper consumers towards lower brightness paper products (70-80% ISO brightness) is a key factor to promote TCF bleached pulp and paper products as pulps with 70% ISO brightness can be produced by a short TCF bleaching sequence with no more than four bleaching stages. Moreover, by implementing the improved O-stage in a TCF bleaching sequence, it is believed that an even shorter bleaching sequence with three stages or lesser can easily attain the desired brightness without sacrificing pulp viscosity.

Acknowledgments

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References

Beyer, M., Lind, A., Koch, H., and Fischer, K. (1999). "Heat-induced yellowing of TCF-bleached sulphite pulps - Mechanistic aspects and factors that influence the process," *Journal of Pulp and Paper Science* 25(2), 47-51.

Chong, Y. H., Daud, W. R. W., and Leh, C. P. (2013). "Effect of hydrogen peroxide and anthraquinone on the selectivity and hexenuronic acid content of mixed tropical hardwood kraft pulp during oxygen delignification," *BioResources* 8(2), 2547-2557. DOI: 10.15376/biores.8.2.2547-2557.

Chong, Y. H., Daud, W. R. W., Poh, B. T., and Leh, C. P. (2015). "Application of Photo, Peracetic Acid, and Combination Pre-treatments in Improving Totally Chlorine-Free Bleaching Selectivity," *BioResources* 10(3), 4110-4125. DOI: 10.15376/biores.10.3.4110-4125

Fossum, G., and Marklund, A. (1988). "Pretreatment of kraft pulp is the key to easy final bleaching," *TAPPI Journal* 77(11), 79-84.

Kishimoto, T., Kadla, J. F., Chang, H.-m., and Jameel, H. (2003). "The reactions of lignin model compounds with hydrogen peroxide at low pH," *Holzforschung* 57(1), 52-58. DOI: 10.1515/HF.2003.008

Minja, R., Kleppe, P., and Moe, S. (1998). "Improving the pulp yield by using PS/AQ and/or two-stage oxygen delignification," *Breaking the Pulp Yield Barrier Symposium Proceed.*, TAPPI, Atlanta, GA, pp. 213-217.

Ng, S. H., Ghazali, A., and Leh, C. P. (2011). "Anthraquinone-aided hydrogen peroxide reinforced oxygen delignification of oil palm (Elaeis guineensis) EFB pulp: A two-level factorial design," *Cellulose Chemistry and Technology* 45(1-2) 77-87.

Obst, J. R., Landucci, L. L., and Sanyer, N. (1979). "Quinones in alkaline pulping: β - ether cleavage of free phenolic units in lignin," *TAPPI Journal* 62(1), 55-59.

Parthasarathy, V. R., Klein, R., Sundaram, V. S. M., Jameel, H., and Gratzl, J. S. (1990). "Hydrogen-peroxide-reinforced oxygen delignification of Southern Pine kraft pulp and short sequence bleaching," TAPPI Journal 73(7), 177-187. Smook, G. A. (1992). Handbook for Pulp and Paper Technologists (3rd Edition), Angus Wilde Publications, Vancouver, BC.

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CHARACTERIZATION OF KENAF FIBRE-RETTING WASTEWATER

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Introduction

Kenaf, or known as *Hibiscus cannabinus L*. plants in scientific name is categorized under *Malvaceae* family that is close to the cotton and hollystock plants. Kenaf (Figure 1) is known to live in tropical and subtropical atmosphere and it can grow rapidly which in turn contribute to the high production yields. This plant is acknowledged for its potential as a source to produce plant-based raw material and also capable to absorb carbon dioxide (CO₂) higher than other plant.



Figure 1: Kenaf Plants

Kenaf possesses a lot of potential for specific use including its utilization as a green composite for textile. The whole stalk of kenaf (bast and core fibres) has been identified as a promising fibre source for paper pulp. The bast and core can be pulped together or individually depending on the pulping process and the type of paper pulp to be produced (Kaldor, et al., 1990). Bast-fibres contained in kenaf plant play an important role as a raw material for plant-based or bio-composite products. Production from bio-based feedstock is estimated to increase from 5% to 12% in 2010 and continues to rise up to 18% in 2020 and reach 25% in 2030 (Alexander et al, 2005). This number shows a good progress in reducing human dependability to petroleum based Nevertheless, for certain applications, bast-fibres cannot be used directly as a raw material because it needs to be separated into individual fibre. This individual fibre can be obtained through retting process. Retting process can be defined as a slow degradation process that can take up a few days to complete. There are various types of retting, for example using chemical, dewwater-retting. Commonly water-retting procedure is selected because it is simple and often produced as a good quality fibre. Typically water used in the process will be released to the watercourse without any treatments. According to Zhang et al. (2005) and as reported by Yu & Yu (2007), retting is defined as treatment degrading the pectin-rich middle lamella connecting adjacent fibre cells to release bast fibres. Retting method play an important role in producing a good quality of fibres. Effective retting involves degradation of pectin and other cementing materials, which act as binding agents between the individual bast fibres as well as between fibre bundles and the epidermal and core tissues (Morrison III et al., 1999). If the fibres are under-retted, it will produce coarse fibres and a lot of non-fibres fractions still adhere, whilst over-retted fibres will produce low strength fibre due to an excessive thinning of bundles or microbial attack on cellulose (Alexander et al., 2005)

Large amount of water in fibre separation (retting) process is required to obtain the fibres. At present, industrial sector are producing fibres in large quantity through water-retting process, hence, the process generating enormous amount of wastewater from the separation process. According to Mondal & Kaviraj (2008) as reported by Huda et al. (2012), 10,000kg of jute requiredapproximately 432m³ of water in water-retting process. Since kenaf and jute are from same family known as Malvaceae, the retting process might be similar. In the future, amount of wastewater will be increased tremendously when the amount of fibre production will be greater than before as kenaf become one of the commodities in Malaysia. The condition of wastewater that turbid and produces odour makes it unacceptable by public. This problem can be resolved with an appropriate treatment process. Hence, effective wastewater treatment process is necessitated to protect the environment, to fulfil the standard required by authority and also to help to recover water resource.

Characteristics of kenaf retting wastewater

Kenaf retting wastewater samples were analyzed according to procedure provided by APHA (2005). The results of wastewater characterization were listed in Table 1. The values of parameter were varied depend on different conditions of kenaf in terms of moisture content. The wastewater characteristics were compared with the allowable limit that regulated by Department of Environment (DOE), Malaysia. It is

important to identify either the wastewater is allow to be released into water stream or required further treatment. Table 1 also shows the allowable limit of pollutants that can be released into watercourse. Standards A and B are referred as area point of effluent release before water intake and after water intake point, respectively.

Table 1: Analyses results from the wastewater characterization (Zawani, 2015)

Parameter	Value	Unit	Allowable Limit			
rarameter	value	Unit	A B		Unit	
pH	3.5 - 5.5	8-1	6.0-9.0	5.5-9.0	NA	
Total Solids (TS)	2200 - 2400	mg/L	¹ NA	NA		
Total Suspended Solids (TSS)	200.0 - 500.0	mg/L	50	100	mg/L	
Volatile Suspended Solids (VSS)	150.0 - 300.0	mg/L	NA	NA		Remarks
Chemical Oxygen Demand (COD)	2000 - 2500	mg/L	80	300	mg/L	
		5550 E	80	200	mg/L	
Biological Oxygen Demand (BOD ₅)	70.0 – 230.0	mg/L	20	50	mg/L	
Colour	1000 - 1200	PtCo	100	200	ADMI	
Turbidity	180.0-280.0	NTU	NA	NA		
Sulphate	200.0 - 250.0	mg/L SO ₄ ²⁻	NA	NA		for pulp mill effluent
Sulphide	290.0 - 400.0	μg/L SO ²⁻	0.5	0.5	mg/L	for other industry effluent
Phosphorus	30.0 - 40.0	mg/L	NA	NA	01	
Ammoniacal Nitrogen	4.0 - 20.0	mg/L NH3-N	10	20	mg/L	
Nitrite	0.15 - 0.35	mg/L NO2-N	NA	NA	J.	
Nitrate	4.5 - 7.0	mg/L NO3-N	NA	NA		

¹ NA – Not Available

Inorganic Compound

Presences of heavy metals in wastewater were determined using ICP-OES. Table 2 lists several types of inorganic compounds existed in the sample. The presence of these elements possibly comes from the soil at plantation or from the fertilizer used. All inorganic compounds detected in the samples were lower than permissible limit set by DOE regulations.

Table 2: List of inorganic compound identified in the sample (Zawani, 2015)

Element	Concentration,	Standard	Allowable Limit (mg/L)			
	mg/L	deviation	Α	В		
Calcium	20.36	0.134	NA	NA		
Magnesium	34.37	0.217	NA	NA		
Manganese	0.313	0.0053	0.20	1.0		
Zinc	0.108	0.0007	2.0	2.0		
Kalium	237.9	0.60	NA	NA		
Arsenic	0.0077	0.0074	0.005	0.05		
Ferum	1.096	0.0088	1.0	5.0		

Organic Compound

Organic compounds were analyzed by GC-MS. In total there were 30 types of organic compounds detected in the sample and the results are tabulated in Table 3. Most of the compounds detected were fatty acids that exist abundantly in the plant and also important for the growth of the plant. These fatty acids possibly influence the pH value of wastewater samples.

² American Dye Manufacturer Institute

Table 3: List of specific organic compound detected in the sample(Zawani, 2015)

No.	Name of compound	No.	Name of compound
1	Tetradecanoic acid	16	9,12-octadecanoic acid
2	Dodecanoic acid	17	Methyl ester
3	Undecanoic acid	18	Stearolic acid
4	Pentadecanoic acid	19	9-octadecynoic acid
5	Pentacyclic acid	20	Acetic acid
6	N-hexadecanoic acid	21	Ethanoic acid
7	Hexadecanoic acid	22	Glacial acetic acid
8	Z-9-tetradecanoic acid	23	Butanoic acid
9	Eicosanoic acid	24	Butyric acid
10	Arachid acid	25	N-butyric acid
11	Octadecanoic acid	26	2-propanone
12	2-(2-hydroxethoxy)ethyl ester	27	Undecanoic acid
13	Z-8-methyl-9-tetradecanoic acid	28	n-decanoic acid
14	Oleic acid	29	Dodecanoic acid
15	9-octadecanoic acid	30	Ethylacetic acid

References

Alexander, B., Mishra, S., & Lampke, T. (2005). Plant Fibers as Reinforcement Green Composites. In L. K. Mohanty, Amar; Misra, Manjusri; T. Drzal (Ed.), Natural Fibers, Biopolymers, and Biocomposites (p. 896). CRC Press.

APHA, A. P. H. A. (2005). Standard methods for the examinations for water and wastewater. Washington DC: APHA.

Huda, A. H. N., Tajuddin, R. M., Ahmad, Z., & Nazrin, O. M. (2012). Determination of optimum debark time in retting process of kenaf fibre production. *International Sustainabilty and Civil Engineering Journal*. 1(2): 14–18.

Kaldor, A., Karlgren, C. & Verwest, H. (1990). Kenaf - a fast growing fiber source for papermaking. TAPPI. 73: 205-208.

Mondal, D. K. & Kaviraj, A. (2008). Ecotoxicological effects of jute retting on the survival two freshwater fish and two invertebrates. *Ecotoxicology*. 17: 207-211. Morrison, III, W. H., Akin, D. E., Archibald, D. D., Dodd, R. B., & Raymer, P. L. (1999). Chemical and instrumental characterization of maturing kenaf core and bast. *Industrial Crops and Products*. 10(1): 21–34.

Morrison, W. H., Akin, D. E., Ramaswamy, G., & Baldwin, B. (1996). Evaluating Chemically Retted Kenaf Using Chemical, Histochemical, and Microspectrophotometric Analyses. *Textile Research Journal*. 66(10): 651–656.

Nieschlag, H., Nelson, G., Wolff, I. & R.E. Perdue, J. (1960). A search for new fiber crops. TAPPI. 43: 193-201.

Samudro, G. & Mangkoedihardjo, S. (2010). Review on BOD, COD and BOD/COD ratio: a triangle zone for toxic, biodegradable and stable level. *International Journal of Academic Research*. 2(4): 235-239.

White, G. et al. (1970). Cultural and harvesting methods for Kenaf. Washington D.C.: USDA Prod. Res. Rpt.

Yu, H., & Yu, C. (2007). Study on microbe retting of kenaf fiber. Enzyme and Microbial Technology. 40(7): 1806-1809.

Zawani Z. (2015). Treatment of Wastewater from Kenaf Water-Retting Process. PhD Dissertation, Universiti Putra Malaysia.

Zhang, J. et al., 2005. The active component in the flax-retting system of the zygomycete rhizopus oryzae sb is a family 28 polygalacturonase. *J. Ind. Microbial. Biotechnol.* 32: 431-438.

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GREEN SYNTHESIS OF SILVER NANOPARTICLES USING CYCLODEXTRIN GLYCOSYLTRANSFERASE PRODUCED BY ALKALIPHILIC BACILLUS

Susan Azizia, Azin Amiria, Raha Abdul Rahimb, Farideh Namvarc and Rosfarizan Mohamada, c,*

Introduction

Cyclodextrin glycosyltransferase (CGTase) extracellular enzyme commonly produced by alkaliphilic Bacilli. In this article, we report a one-step synthesis of silver nanoparticles (Ag-NPs) through a green-method using CGTase as both reducing and stabilizing agents. Structural, morphological and optical properties of the Ag-NPs were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV-Vis spectroscopy. The formations of Ag-NPs with an absorbance band centered at 450nm were confirmed. A TEM image displayed that the nanoparticles are spherical in shape with size ranging from 10 to 25nm. The XRD pattern showed that the nanoparticles were crystalline in nature. The bio-formed nanoparticles are expected to have prominent-uses in pharmaceutical and biomedical areas.

Researchers in the field of nanotechnology are turning to 'Nature' to provide inspiration, for stimulating and innovative approaches of nano-production. Synthesizing new metallic nanoparticles based on the notion of green nanotechnology is obtaining momentum. Green nanotechnology mixes the principles of green engineering and green chemistry to produce safe and eco-friendly nanoparticles, which do not use toxic substances in their synthesis procedure [1]. The synthesis of nanoparticles of noble metals, such as Ag-NPs, is of excessive interest because of their unique characteristics. Manipulation of their shape and size creates unique properties that have potential applications in biomedical uses such as antibacterial, anti-HIV activity, controlling plant pathogens and as a biosensor and catalyst [2-5].

Current chemical and physical techniques for the production of Ag-NPs use hazardous substances, for example; hydrazine, dimethyl formamide (DMF) and sodium borohydride, as reducing agents, and may also need to use costly instruments. These approaches produce Ag-NP efficiently; nevertheless downstream processing to distinct the nanoparticles from the toxic compounds is high cost and time-consuming. The existence of even a slight trace of toxic compounds makes these Ag-NPs incompatible for pharmaceutical and biomedical applications.

Since 2000, the production of inorganic nanoparticles using bacteria [6], fungus [7] and plant extracts such as rose [8], for nanoparticle synthesis are under potent investigations [9]. The investigations can be a feasible substitute for the current physicochemical processes of producing nanoparticles [10]. Hence, in the present study, the CGTase was used for the production of the Ag-NPs. The CGTase is an extracellular, inducible enzyme produced by microbial cells and the alkaliphilic *Bacilli* strains are the best producers of the CGTase. In this paper, we report a simple, fast and cost-effective process to produce Ag-NPs that are stable with extended shelf life.

Methodology

Materials

AgNO3 (99.98%), which was applied as a silver precursor, was purchased from Merck (Darmstadt, Germany). The CGTase was produced using the previous method [11]. In the experiments, all reagents were of analytical grade and all the solutions were made using deionized water.

Synthesis of Aq-NPs

A volume of 25 mL of the CGTase was added to 0.1 mM AgNO3 aqueous solution under gentle stirring at 30°C for 1 h, and then it was kept at room temperature for another 2 h. The resulting solid product was collected by centrifugation at 8,000 rpm for 15 min and carefully washed with distilled water and dried at 45°C overnight.

Instrument

The crystalline structure of the sample was examined by XRD analysis, which recorded by a diffractometer (XPERTPRO) at room temperature at a voltage of 40 kV land current of 30 mA. The morphology and size of the sample were determined by HITACHI H-700 TEM. The pure sample was analyzed for its UV-visible spectrum using a UV-vis spectrophotometer (Lambda 25-Perkin Elmer) in the range of 200 to 800nm.

Results

Preliminarily, the synthesis of Ag-NPs was confirmed through visual assessment. The reaction solution turned to dark brown color from brownish-yellow color within 30 min specified the formation of Ag-NPs. The appearance of dark brown color may be owing to the excitation of surface plasmon resonance (SPR) effect and reduction of AgNO3 [12]. UV-Vis spectrum of reaction solution showed strong absorption peak with centering at 450 nm (Figure 1) specified the formation of Ag-NPs. This absorption is near to that seen for silver nanoparticles formed by different methods [13].

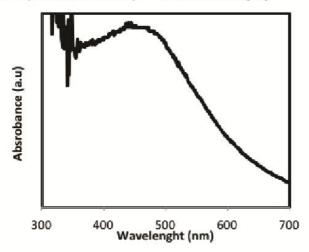


Figure 1. UV absorption spectrum of bioformed Ag-NPs.

The XRD pattern (Figure 2A) displays that the particles are crystalline. The lattice planes (111), (200), (220), and (311) were identified with the corresponding Bragg's angles of 37.95°,45.84°, 64.07°, and 76.43°, respectively, which confirm the face-centered cubic structure of the formed Ag-NPs. The TEM image Figure 2B shows the Ag-NPs formed were well dispersed with a spherical structures and a particle size ranging from 10 to 25 nm.

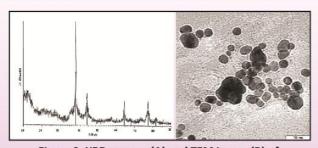


Figure 2. XRD pattern (A) and TEM image (B) of biosynthesized Ag-NPs.

Conclusions

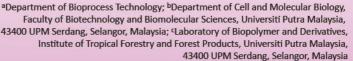
This article highlights on the development of a simple, eco-friendly and economic, biological procedure to synthesize Ag-NPs. The biosynthesized silver nanoparticles have spherical shapes, and the particle size ranges from 10 to 25 nm. The biosynthesized silver nanoparticles are expected to have important applications in pharmaceutical and biomedical fields.

References

- [1] Castro, L., Blazquez, M.L., Munoz, J.A., Gonzalez, F., Garcia-Balboa, C., Ballester, A., Biosynthesis of gold nanowires using sugar beet pulp. *Process Biochem.*, 2011, 46(5), 1076-1082.
- [2] Elechiguerra, J.L., Burt, J.L., Morones, J.R., Camacho-Bragado, A., Gao, X., Lara, H.H., Yocaman, M., Interaction of silver nanoparticles with HIV-1. *J. Nanobiotechnol.*, 2005, doi:10.1186/1477-3155-3-6.
- [3] Shiraishi, Y., Toshima, N., Oxidation of ethylene catalyzed by colloidal dispersions of polym(sodium acrylate)-protected silver nanoclusters. *Colloids Surf.* A., 2000, 169, 59–66.
- [4] Jain, P., Pradeep, T., Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. *Biotechnol. Bioeng.*, 2005, 90, 59–63.
- [5] Krishnaraj, C., Jagan, E.G., Ramachandran, R., Abirami, S.M., Mohan, N., Kalaichelvan, P.T., Effect of biologically synthesized silver nanoparticles on *Bacopa monnieri* (Linn.) Plant growth metabolism. *Process Biochem.*, 2012, 47(4), 651–658.
- [6] Kalishwaralal, K., Deepak, V., Ram Kumar Pandian, S., Gurunathan, S., Biological synthesis of gold nanocubes from *Bacillus licheniformis*. *Bioresour. Technol.*, 2009, 100(21), 5356–5358.
- [7] Du, L., Xian, L., Feng, J.-X., Rapid extra-/intracellular biosynthesis of gold nanoparticles by the fungus *Penicillium sp. J. Nanopart. Res.*, 2011, 13(3), 921–930.
- [8] Ghoreishi, S.M., Behpour, M., Khayatkashani, M., Green synthesis of silver and gold nanoparticles using *Rosa damascena* and its primary application in electrochemistry. *Physica*. E., 2011, 44(1), 97–104.
- [9] Nadagouda, M.N., Hoag, G., Collins, J., Varma, R.S., Green synthesis of Au nanostructures at room temperature using biodegradable plant surfactants. *Cryst. Growth Des.*, 2009, 9(11), 4979–4983.
- [10] Karn, B., The road to green nanotechnology. J. Ind. Ecol., 2008, 12(3), 263–266.
- [11] Azin, A., Rosfarizan, M., Raha, A.R., Rosli, M.I., Farideh, N., Joo Shun, T., Sahar, A. Cyclodextrin glycosyltransferase biosynthesis improvement by recombinant *Lactococcus lactis* NZ:NSP:CGT: medium formulation and culture condition optimization. *Biotechnol. Biotechnol. Equip.*, 2015, 29(3), 555-563.
- [12] Mulvaney, P., Surface plasmon spectroscopy of nanosized metal particles. *Langmuir*, 1996, 12, 788–800.
- [13] Lee, Ch.J., Karim, M.R., Vasudevan, T., Kim, H.J., Raushan, K., Jung, M.J., Kim, D.Y., Lee, M.S., A comparison method of silver nanoparticles prepared by the gamma irradiation and in situ reduction methods. *Bull. Korea Chem.* Soc. 2010, 31, 1993–1996.

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HIGH ENERGY DENSITY SOLID BIOFUEL FROM OIL PALM BIOMASS

Chin Kit Ling and H'ng Paik San*

Introduction

Biomass is a primary source of renewable carbon that can be utilized as a feedstock for biofuels production in order to achieve energy independence. As one of the largest producers and exporters of palm oil, Malaysia has abundant availability of oil palm biomass (oil palm trunk and empty fruit bunch) as a promising source of lignocellulosic raw material. In nature, lignocellulosic biomass has high moisture content, low bulk energy density and is difficult to transport, handle, store and feed into existing combustion systems without When lignocellulosic biomass is pretreatments. for bioenergy, pretreatments employed lignocellulosic biomass are essential procedures for achieving higher efficiencies of fuel production or consumption [2]. For example, moisture content from the lignocellulosic biomass was driven off to enhance the combustion efficiency and prevent microbial degradation during storage [3]. While, in liquid biofuel production, acid pretreatments have been adopted widely to facilitate the conversion of hemicelluloses and cellulose into soluble sugars for lignocellulosic ethanol production [4,5,6].

In addition to the aforementioned methods, torrefaction of biomass is another notable pretreatment method that enables energy densification of biomass and biomass homogenization [7,8]. This pretreatment has been recommended as an efficient way to enhance solid biofuel properties by water removal, reduction of the hygroscopic range, and increased grindability. Torrefaction is a thermal pretreatment process by subjecting wood to temperature levels between 200 °C and 300 °C in the absence of oxygen. During this process, the cell walls are degraded and the nature of the resulting product lies between that of wood and

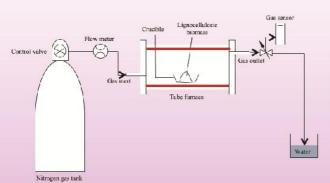


Figure 1: Schematic diagram of torrefaction experimental setup

charcoal. The residual product is in solid form, which is referred to as torrefied biomass. Torrefaction is influenced by many parameters including the composition and physical properties of the biomass and operating condition [8].

Torrefaction Pretreatment on Oil Palm Biomass

Without appropriate treatment, oil palm trunk (OPT) and empty fruit bunch (EFB) are not suitable to be fed into existing combustion systems because of its high moisture content, low bulk energy density and difficulties in transport, handling and storage. Biomass can be upgraded and used as a fuel by torrefaction process. The torrefied biomass is more suitable than raw biomass in terms of HHV, physical and chemical properties. The optimum conditions for the torrefaction of oil palm biomass were investigated with respect to the reaction temperature (Temp) and time (RT). The primary goal of torrefaction is to refine raw biomass to an upgraded solid fuel, of improved handling qualities and enhanced combustible properties comparable to those of the fossil coal. Regarding fuel efficiency, it is necessary to increase the energy density (HHV yield) of the biomass, requiring a growth of the ratio between HHV and mass. The HHV yield per raw material indicates the total energy conserved in the torrefied biomass. The HHV yield was calculated from the weight loss and HHV using Eq. 1 and expressed as a percentage of the HHV of untreated lignocellulosic biomass: HHVf is HHV of lignocellulosic biomass after torrefaction and HHVi, is HHV of lignocellulosic biomass before torrefaction.

HHV yield (%) = $(100 - \text{Weight loss}) \times (\text{HHVf/HHVi})$ (Eq. 1)

Our results clearly demonstrated an increased degradation of the material due to the combined effects of temperature and treatment time. While the reaction temperature had a strong impact on the HHV yield of torrefied oil palm biomass, the effect of reaction time was considerably lesser. As a whole, the torrefaction at 200°C just degraded a small amount of holocellulose and gave a mediocre effect on improving the energy properties. When biomass underwent the torrefaction at temperatures above 250°C, large amount of hemicelluloses and cellulose were degraded which

contributed to the increment of acid-insoluble material. Weight loss and HHV vary for different biomass types at the same operating conditions as the polymeric composition and reactivity differ. In consequence, each biomass type has its own set of operating conditions to achieve a high density solid biofuel. The torrefied biomass occurred more suitable than raw biomass in

terms of calorific value, physical and chemical properties. The results of this study could be used as a guide for the production of high density solid biofuel from oil palm biomass available in large amounts in Malaysia.

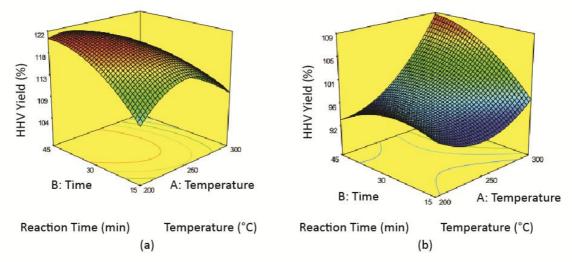


Figure 2: Response surface and contour plot of torrefaction temperature vs. reaction time on the HHV yield for; (a) EFB and (b) OPT.

Tem p (°C)	Untre ated	200			250			300		
RT (min)		15	30	4 5	15	30	45	15	30	45
OPT			0	-	0	-	0		0	
EFB		-	4						9	

References

- [1] Sims REH, Hastings A, Schlamadingerz B, Taylor G, Smith P. Energy crops: current status and future prospects. Glob Change Biol 2006;12:2054–76.
- [2] Tabil L, Adapa P, Kashaninejad M. Biomass Feedstock Pre-Processing-Part 1: Pre-Treatment. In: Aurélio Marco dos Santos Bernardes, editors. Biofuel's Engineering Process Technology, Croatia: InTech; 2011, p. 411-38.
- [3] Chin KL, H'ng, PS Chai, EW Tey BT, Chin MJ, Paridah MT, Luqman AC, Maminski M. Fuel characteristics of solid biofuel derived from Oil Palm biomass and fast growing timber species in Malaysia. Bioenerg Res 2012; published online 3 July 2012.
- [4] Chin KL, H'ng PS, Wong LJ, Tey BT, Paridah MT. Optimization study of ethanolic fermentation from oil palm trunk, rubberwood and mixed hardwood hydrolysates using Saccharomyces cerevisiae. Bioresource Technol 2010;101(9):3287-91.
- [5] Chin KL, H'ng PS, Wong LJ, Tey BT, Paridah MT. Production of glucose from oil palm trunk and sawdust of rubberwood and mixed hardwood. Appl Energ 2011:88: 4222-8.
- [6] Lloyd TA, Wyman CE. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. Bioresource Technol 2005;96:1967–77.
- [7] Yan W, Acharjee TC, Coronella CJ, Vásquez VR. Thermal pretreatment of lignocellulosic biomass. Environ Prog Sustain Energ 2009;28(3):435-40.
- [8] Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 2008;89:169-75.





RATIO MODELING FOR EFFICIENT BIODEGRADATION OFORGANIC SUBSTANCES IN LIGNOCELLULOSIC BIOMASS

H'ng Paik San*, Chin Kit Ling and Chai Ee Wen

Introduction

The organic waste in Malaysia can be grouped into domestic waste, agriculture residues, animal wastes and sewage sludge and wood chips. Agriculture residues accounted nearly 70% of total 70 million tons of organic waste discharged in Malaysia per year [1]. This follows by domestic waste 9.5%, and the rest make up the total percentage. Malaysia is enjoying the achievement as one of the world's largest palm oil producers, with total export volume of 18 million metric tons of crude palm oil per year [2]. However, the achievement comes at a price. Several studies pointed out that production of single ton of crude palm oil generate huge amount of by-products which include 1425 kg of empty fruit bunch (EFB), 300 kg of palm kernel shell (PKS), 150 kg of mesocarp fiber, 150 kg of decanter cake (DC), 300 kg palm kernel cake (PKC) and 3 ton of palm oil mill effluent (POME) with total solid content of 0.6% [3,4]. EFB make up the largest volume of organic material waste in term of weight over weight (w/w) basis (20.41 million tonnes/year). Ideally, EFB generated from palm oil production should be returned to the plantation to enrich the soil through the composting process. Nonetheless, long period for composting of EFB to reach maturity (up to 180 days) poses problems in the industrial scale composting due to high land area needed.

The composting process can be shortened to three to four weeks by co-composting with different organic materials. In co-composting, by combining the two or more organic materials, the benefits of each can be used to optimize the process and the product. The key for starting a successful matching ingredient for co-composting is to understand the physical and chemical characteristic of organic waste materials. Analysing organic waste materials for their physical and chemical characteristics helps in developing co-composting recipes.

Ratio Modeling of Matching Ingredients for EFB and Other Organic Materials for Efficient Biodegradation

This ratio modeling aims to provide recipes for starting a successful composting process and making good compost. The ideal composting are C/N ratio of the composting material between 20/1 and 40/1 [5].

Excessive or insufficient quantities of carbon or nitrogen greatly affect the composting process. High initial C/N ratio will cause a slower beginning of the process and the required composting time to be longer than usual [6,7] while low initial C/N ratio results in high emission of NH3 [7,8]. Maximum degradation efficiency is achieved through altering the C/N ratio. As mentioned, EFB is high in C/N ratio and require proper treatment for efficiency composting. Therefore, nitrogen source materials or co-composting substrates need to be added to the EFB compost pile to increase the compost efficiency. The nitrogen sources are important for microorganism to grow and reproduce. Carbon is the basic building block of life and is a source of energy. Given the proper C/N ratio, microorganisms are able to reproduce very quickly, thus, increase the composting rate. Based on the ratio of carbon to nitrogen, the organic waste materials can be separated into two groups; nitrogen source materials (C/N <30) and carbon source materials (C/N >30). In this section, a right ratio of EFB (C/N: 57.89) mixed with nitrogen source organic waste materials co-composting was discussed. POMS (C/N: 8.05), decanter cake (C/N: 23.71), PKC (C/N: 18.44), coffee grounds (C/N: 27.29), cocoa shell (C/N: 25.9), chicken manure (C/N: 6.1) and sewage sludge (C/N: 11.05) which grouped as nitrogen were formulated with EFB using Eq. 1 to develop co-composting recipes with C/N ratio of 30.

C/N ratio= Weight of Carbon in Material A + Weight of Carbon in Material B Eq. 1
Weight of Nitrogen in Material A + Weight of Nitrogen in Material B

To use the equation, carbon and nitrogen content of selected materials are required. C/N ratio of the mixture is calculated based on weight basis of carbon and nitrogen content of the materials. The calculation for C/N ratio is in dry weight basis.

Table 1 shows the mixing ratio for the selected organic waste materials. Theoretically, mixture I— VII are ideal mixing ratio for effective of co-composting of EFB with other organic materials. Results in Table 5 can be divided into two groups, mixture with EFB as major compost feedstock (ratio>50%) and EFB as minor major compost feedstock (ratio <50%). Mixtures having EFB ratio < 50% in the effective co-composting model (I, II and III) can be

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achieved by adding coffee grounds, cocoa shell and DC which are higher C/N ratio compared to other organic materials. Other nitrogen sources like POMS, sewage sludge, chicken manure and PKC with lower C/N ratio (< 20) lead to higher EFB (>50%) can be added in the compost pile. This will lead to more EFB able to be returned to the soil.

Adding single nitrogen source into the EFB compost will generate model with either little quantity of EFB (less than 10%) or huge amount of EFB (more than 70%). EFB with exceptionally low bulk density (66.98 kg/m³) should be put into consideration. The bulk density

indirectly provides a measure of the porosity. EFB with high porosity affects the water absorption in compost. If the water absorption too high, the composting temperature might not increase. Due to the physical characteristic of EFB, the percentage ratio of EFB in a co-compost pile should not be too high. Thus, other feedstock with higher bulk density should be added. In order to fully utilize the EFB, mixture with optimal EFB content should be considerate in the mixing ratio. Therefore, the ideal quantity of EFB in the co-composting should be in the ranged in 50 - 60%.

Table 1. The following mixing ratio is derived from the Eq.1 to achieve C/N ratio of 30.

Mixture	EFB (%)	Coffee Grounds (%)	Cocoa Shell (%)	Poms (%)	Sewage Sludge (%)	DC (%)	Chicken Manure (%)	PKC (%)
l.	7	93	.Tal	073	0=	.E.O	5 0	
II.	24	22	76	(2)	112	_		~
III.	37	-	_	-	-	63	-	-
IV.	57	35 5 5	. 	0.70	0.5	=0	3 5	43
V.	78	300	22	-	-	-	×=	-
VI.	78	1=	-	-	22	-	-	_
VII.	87	-	-	-	-	-	13	-

The new model for effective co-composting with two nitrogen sources and EFB presented in Table 2. EFB mixes with two nitrogen source create a practical mixing ratio with appropriate amount of EFB (50-60%) that

achieve the favourable C/N ratio and bulk density. In this study, Mixtures IV - VIII in Table 6 are considered to be the most effective mixing ratio for EFB co-composting.

Table 2. Mixing ratio of EFB co-composting with two nitrogen source.

Mixture	EFB (%)	Coffee Grounds (%)	Cocoa Shell (%)	Poms (%)	Sewage Sludge (%)	DC (%)	Chicken Manure (%)	PKC (%)
I.	17	37	46	-	.	9 <u>2</u> 9 3	-	-
II.	30	-	37	-	-	33	-	-
III.	37	36	72	-	_	<u>"</u>		27
IV.	50	37	-	13	_	_	_	-
V.	50	-	37	-	13	-	-	-
VI.	52	-	37	11	-	-	-	-
VII.	52	-	37	-	11	-	-	-
VIII.	56	36	-	-	-	-	8	-
IX.	68	-	i. .	12	-	_	-	20

Conclusion

The study on physical and chemical analysis of representative materials helps in selection of suitable organic materials for composting process. Most of the organic materials are not suitable to be composted alone due to impropriate C/N ratio. Organic waste materials with higher nitrogen content can mix with EFB in co-composting. The model presented here suggested that percentage of EFB ranged between 50-60% considered as ideal mixing ratio in effective co-composting. The ratio modeling of matching ingredients for EFB and other organic materials co-composting determined here can as foundation and starting point for any real composting process.



Heaps of EFB prepared for composting



Materials were mixed according to the ratio and heap using a bulldozer



Temperature Monitoring



Co-composting - was prepared by mixing EFB with two nitrogen source (according to the ratio)

References

- 1. P. Agamuthu and S.H. Fauziah, Biomass waste utilization and energy energy security in Malaysia, Second Meeting of Regional 3R Forum in Asia, Kuala Lumpur Malaysia. 2010.
- 2. P.W. Tay, P.S. H'ng, K.L. Chin, L.J. Wong, and A.C. Luqman, Effects of steeping variables and substrate mesh size on starch yield extracted from oil palm trunk, Ind. Crop. Prod. 44 (2013), pp. 240-245.
- 3. P.F. Rupani, R.P. Singh, M.H. Ibrahim, and N. Esa, Review of current palm oil mill effluent (POME) treatment methods: vermicomposting as a sustainable practice, World Appl. Sci. J. 10 (2010), pp. 1190-1202.
- 4. K.L. Chin, P.S. H'ng, E.W. Chai, B.T. Tey, M.J. Chin, M.T. Paridah, A.C. Luqman, and M. Maminski, Fuel characteristics of solid biofuel derived from oil palm biomass and fast growing timber species in Malaysia, Bioenerg. Res. 6 (2012), pp. 75-82.
- 5. T. Kaosol and S. Wandee, Co-composting between rubber waste with other wastes for reuse, GMSARN International Conference on Sustainable Development, Issues and Prospects for the GMS, Songkhla, Thailand, 2008.
- 6. M. Tuomela, M. Vikman, A. Hatakka, and M. Itavaara, *Biodegradation of lignin in a compost environment: a review*, Biores. Technol. 72 (2000), pp. 169-183. 7. G.A. Ogunwande, J.A. Osunade and L.A.O. Ogunjimi, *Effects of carbon to nitrogen ratio and turning frequency on composting of chicken litter in turned-windrow piles*, Agric. Eng. Inter: the CIGR Ejournal. X (2008).
- 8. S.M. Tiquia and N.F.Y. Tam, Fate of nitrogen during composting of chicken litter, Environ. Pollut. 110 (2000), pp. 535-541.

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ACHIEVEMENTS 2015

No.	ltem	Achievements
1	Patent Filed	1
2	Public Grant	RM1,421,626
3	Private Grant	RM739,000
4	International Grant	RM18,000
5	Journals	104 (Q1 + Q2 = 44)
6	Books	5



AWARDS 2015

RESEARCHER / STAFF NO. NAME OF AWARD CONFERRING BODY INTERNATIONAL Prof. Dr. Ahmad Ainuddin Nuruddin Best Presentation Award The 6th International Wildland Fire Conference Prof. Ir. Dr. Mohd Sapuan Salit SEARCA Regional Professional Chair Southeast Asian Regional Center for grantee for AY 2015/2016 Graduate Study and Research in Agriculture 3 Prof. Ir. Dr. Mohd Sapuan Salit SAE Fellow Grade of Membership **SAE International** Prof. Dr. Luqman Chuah Abdullah Malaysia's Rising Star Award Ministry of Higher Education and Thompson Reuters @SEARCA M SAE Fellow Grade of Membership MALAYSIA'S RISING STAR AT

NATIONAL

1	Prof. Dr. Paridah Md. Tahir	Star Awards 2015	Standards Malaysia, MOSTI
2	Prof. Dr. Luqman Chuah Abdullah	Best of The Best (Built Environment)	4th International, Invention, Innovation & Design (INDES 2015) UiTM Perak
3	Prof. Dr. Luqman Chuah Abdullah	Gold Medal	5th International, Invention, Innovation & Design (INDES 2015) UiTM Perak
4	Dr. Hidayah Ariffin	Bronze Medal	MTE



STUDENTS GRADUATED IN 2015

Name : Mohd Syahmi Bin Salleh

Matrix No: : GS25043

Programme : Master of Science Field of Study : Agricultural Technology

Thesis Title : Effects of Sewage Sludge and Livestock

Manure Vermicompost on Growth and

Yield of Maize (Zea Mays L.)

Supervisor : Prof. Dato' Dr. Nik Muhamad Nik Ab. Majid

Name : Nurul Hikmah Binti Zameli

Matrix No: : GS31079

Programme : Master of Science Field of Study : Nature Tourism

Thesis Title : Recreation Value of Domestic Visitors in

Kilim Karst Geoforest Park, Langkawi,

Malaysia

Supervisor : Dr. Syamsul Herman Bin Mohammad Afandi

Name : Nabil Fikri Bin Leemon

Matrix No : GS36378

Programme: Master of Science

Field of Study : Biocomposite Technology

Thesis Title : Comparative Performance Between

Natural Endospermum Diadenum (Miq.) Airy Shaw Wood and Treated Wood Impregnated with Nanoclay

and Phenolic Resin

Supervisor : Prof. Dr. Zaidon Bin Ashaari

Workshop on Dynamic Mechanical Analysis (DMA)

Date : 11 March 2015

Venue: Material Characterization Unit, INTROP, UPM

Laboratory of Biocomposite Technology (BIOCOMPOSITE) has organized a workshop on Dynamic Mechanical Analysis (DMA). The speaker for this workshop was Dr. Mohammad Jawaid, a Research Fellow in INTROP. The objective of this workshop was to provide knowledge on the application of DMA for characterizing various polymer and composite samples. DMA is one of the most powerful tools to study the behaviour of polymeric materials and it allows for a quick and easy determination of material properties. The workshop was attended by students and staff from Universiti Putra Malaysia (UPM), Universiti Tenaga Nasional (UNITEN) and Malaysian Nuclear Agency.



Workshop on High Impact Journal Writing and Publishing

Date : 3 - 4 June 2015

Venue: Gallery Room, Faculty of Engineering, UPM

The workshop was held on 3rd to 4th June 2015 at Gallery Room, Faculty of Engineering, Universiti Putra Malaysia. The total number of participants for this workshop was 53. The objectives of the workshop were to train, groom and encourage students and staff to publish their research finding in high impact journals. This workshop also provided opportunities to the research officers, science officers, and graduate students to gather and exchange ideas to improve their own writings for publication, and to contribute to the improvement of their KPI. This sharing session was presented by Prof. Ir. Dr. Mohd Sapuan Salit, a Professor and the Head of Laboratory of Biocomposite Technology, INTROP and Dr. Mohammad Jawaid, a Research Fellow at INTROP.



INTROP 2016 Strategic Planning Workshop

Date: 1 - 2 September 2015

Venue: Avillion Admiral Cove Hotel, Port Dickson, Negeri Sembilan.

A strategic planning workshop was organized by INTROP on $1^{\rm st}-2^{\rm nd}$ September 2015 at Avillion Admiral Cove Hotel, Port Dickson. The aim of the workshop was to strategize the action plans of each laboratory in achieving their 2016 Key Performance Indicator (KPI). The workshop was attended by 37 INTROP staff, consisted of INTROP management team, Head of Programme, Research Fellows, Post-Doctorals, Research Officers, Science Officers, Agricultural Officer, and supporting staff.





INTROP Family Day 2015
Date : 2 - 3 September 2015

Venue: Avillion Admiral Cove, Port Dickson, Negeri Sembilan.

INTROP's Staff Club (KSI) had successfully organized a Family Day on $2^{nd} - 3^{rd}$ September 2015 at Avillion Admiral Cove, Port Dickson. Among the activities conducted were BBQ Night, *Silat Lidah* or Tongue Twister and Berita *Kepala Tiga*. Self-Development activities were also carried out by inviting Assoc. Prof. Dr. Shamsul Bahri Mohd Tamrin and Mdm. Zainora Abdul Talib to deliver their talks on 'Ergonomic at Workplace' and 'Research Equipment Management', respectively. On the last day, the staff and family members enjoyed themselves with beach games and other outdoor activities. It was an enjoyable gathering of INTROP members after full year of hardwork.



Kursus Kenal R&D and Signing Ceremony between INTROP and KISAS

Date: 3 November 2015 Venue: INTROP, UPM

'Kursus Kenal R&D Bersama Pelajar KISAS' was held on 3 November 2015 at INTROP. The aim of the course was to introduce research environment and laboratory facilities to the students of Kolej Islam Sultan Abdul Aziz Shah (KISAS), as a preparation for the students for a series of national and international Research and Innovation contest. In conjunction with the course, a signing ceremony between INTROP and KISAS was held, as a show of commitment from both sides in developing mutual research and innovation activities. The agreement was signed by the Director of INTROP, Prof. Dr. Paridah Md. Tahir and the Principal of the college. KISAS has been accepted as 'Sekolah Angkat' INTROP for 3 years, beginning 2016 to 2018. To date, INTROP has assisted KISAS to win three prestigious awards - 1 gold, 1 special awards and 1 silver medal in two international innovation competitions. The contribution and support of INTROP Technical Coaches were honored in a ceremony by KISAS during their Curriculum Award on 17 October 2015. It is hoped that the program will continue to benefit both parties.





Training on Strategy of Model Building

Date : 17 - 18 November 2015 Venue : Meeting Room, INTROP, UPM

Laboratory of Sustainable Bioresource Management (BIOREM) has successfully organized analysis course facilitated by Dr. Jean Marc Roda, a Fellow Researcher in INTROP. The objective of the course was to highlight the theoretical, practical and analytical issues and discuss the level of calculation and limitations of the different approaches.

The course was held for 2 days inclusive of theory and practical. The outlines of the training for Day 1 were model building strategy which comprised analysis needs, context, model choice, theory, tools and softwares, while the 2nd day of training was on practice and validity of models, comprising of fitting, validation, extrapolation, use, limitations and decisions. This course was opened to Researchers related in the area.

The course received a good response from the participant and the next course on statistic building will be proposed in future for intermediate participant.



Workshop on Response Surface Methodology in Bioprocess

Date : 20 - 21 October 2015

Venue: InfoComm Development Centre, UPM

Response Surface Methodology (RSM) is a statistical methodology of constructing approximations of the system behavior using results of the response analyses calculated at a series of points in the variable space. This method is applied in various fields such as chemistry, physics, engineering as well as biotechnology to find the optimum response. The objective of these 2 days workshop is to provide both theoretical and practical aspects, especially for process optimization in the field of biotechnology. The speakers of this workshop were Assoc. Prof. Dr. Rosfarizan Mohamad from INTROP, Dr. Tan Joo Shun from Universiti Sains Malaysia and Dr. Nagasundara Ramanan Ramakrishnan from Monash University. This workshop has attracted 44 participants from various government agencies such as UPM, USM, UiTM, MPOB, MARDI and and NAHRIM and also from private agencies such as TNB Research Sdn. Bhd, Felda Global Ventures (FGV), UCSI University and Malaysia University of Science & Technology.



INTROP Research Colloquium Date : 1 - 2 December 2015 Venue : RHR Hotel, UNITEN.

INTROP Research Colloquium (IRC 2015) was successfully organized on 1-2 December 2015 at RHR Hotel, UNITEN. The event was officiated by Prof. Dato' Dr. Azmi Lila, the Deputy Vice Chancellor (Research and Development) of Universiti Putra Malaysia. Seventy-two researchers attended the IRC 2015, including lecturers, research officers and post graduates from INTROP. A total of 65 presentations were being presented, of which 45 and 20 were oral and poster presentations, respectively. The presenters were from the laboratories of BIOREM, BIOCOMPOSITES and BADs; representing upstream, midstream and downstream research area. The colloquium received positive response from the participants due to its focused and beneficial content. Three best winners for each oral and poster slots were announced at the end of the colloquium. It is hoped that IRC 2015 was beneficial to all INTROP researchers, and has been a platform to gain knowledge and share research ideas.



10th World Bamboo Fair

Date: 17 - 31 September 2015 Venue: Damyang, Korea

INTROP has successfully participated in the 10th World Bamboo Fair 2015 (WBF 2015), Damyang Korea. Damyang is a county in South Korea which is known as bamboo centre of Korea. It was a great pleasure to join such an established and prestige world exhibition. The main purpose of INTROP's participation was to showcase some of the innovations and products from bamboo besides fostering international networking and promoting UPM as a potential destination for further studies. The products being exhibited at this event were those produced by Bamboo Research Group in INTROP under the project *Advanced Processing in Bamboo Industry towards Wealth Creation in Rural Communities* which is funded by the University Putra Grant. The research studies involved two of the most available bamboo species in Malaysia namely *Gigantochloa schortechchinii* and *Bambusa vulgaris*. Five products were displayed throughout the exhibition: (i) Superior paper from bamboo (ii) Enzymatic treated paper from bamboo (iii) V-Grooving Method for bamboos (iv) Bamboo and hybrid-bamboo laminations (v) Bio-fuel pellets from bamboo.



NEW MEMBER

1) Name: Dr. Hidayah Ariffin

Post: Head of Laboratory, Laboratory of Biopolymer and Derivatives (BADs), INTROP

Email: hidayah@upm.edu.my

 Field of specialization: Bioprocess Engineering, Environmental Technology and Biopolymer

- 3) Recent achievement at International level:
 - Organizing Committee, Asian Congress on Biotechnology 2015 (ACB2015)
 - Organizing Committee, 3rd International Symposium on Applied Engineering and Science 2015 (SAES2015)
 - Reviewer for Journal articles published by Elsevier, John Wiley & Sons.
- 4) Recent research projects:

Duration	Funding	Theme	Position
2014-2017 (on-going)	Fundamental Research Grant Scheme (FRGS), MOE	Improved use of superheated steam for controlled hydrolysis of polyhydroxyalkanoates towards oligoesters production	Project leader
2016-2017 (on-going)	Geran Putra IPS (GP-IPS), UPM	Nanocellulose production from oil palm mesocarp fiber	Project leader
2014-2018 (on-going)	SATREPS project, MOE	Chemical-free Pre-treatment of Oil Palm Biomass for Fermentable sugars, Nanofiber and Biocomposite	Sub-Project leader

5) How do you feel to be a part of INTROP's family?

I joined INTROP in 2013 as a Research Associate, and was appointed as a Head of Biopolymer and Derivatives (BADs) Laboratory in July 2015. It is such a pleasure to be a part of INTROP, particularly BADs since my research interest is in biopolymer and biomass. Since INTROP's focus is on natural fiber and biomass research, this institute has a group of experts in the field. It is such a nice feeling to be surrounded with those working in the same area.

6) What are your future strategies as a Head of Laboratory in INTROP?

Insha Allah, my strategy particularly for BADs is to make the laboratory as the leading laboratory in bio-based polymer study. At present, several projects have been identified as signature projects for BADs, namely nanocellulose, specialty paper and bioresin. Of course there are several other projects in the list, but at the beginning we would like to focus on these three products. As a start, BADs is planning for a Nanocellulose Workshop in early 2016. I also would like to invite more researchers from UPM and other universities to become Research Associates of BADs, as I always believe that working in group is more impactful that working alone.

7) What is your opinion on INTROP's working environment?

To be honest, INTROP is a great workplace. It has a very nice working environment and pleasant officers. The close relationship among the staff creates a happy and enjoyable working experience. As a research institute, it consists of three laboratories with different areas, nevertheless that never dilutes the INTROP's niche area which is in tropical wood and natural fiber, as everyone is working together.

8) How do you see INTROP in 5 years?

Alhamdulillah, in these recent years INTROP has been among the top institutes in UPM. I foresee that INTROP has no problem to maintain this achievement and to continue its legacy as the leader in tropical wood and fiber research in future, Insha Allah. With the great staff and management team, Insha Allah INTROP will fly higher in the next 5 years.



GALLERY 2015



Separation of male gametes and female gametes. Kenaf Breeding Training (1-11 February 2015)



Japanese class with Ishikawa sensei. UPM Look East Mobility Program (1-11 February 2015)





At farewell party with down syndrome children from Twinkle Cats School. UPM Look East Mobility Program (1-11 February 2015)



in front of the Kyushu Institute of Technology, Japan. UPM Look East Mobility Program (1-11 February 2015)



Factory tour to TOTO Factory. UPM Look East Mobility Program (7 September 2015)



Damyang Cultural Centre. Introp Participation In 10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



World Bamboo Fair 2015, Damyang, South Korea. 10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



Explaning the products produced by INTROP. 10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



Bamboo products produced from V-Grooving method. 10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



Product Testing Laboratory (PTL), Laboratory of Biocomposite Technology (BIOCOMPOSITE) was audited by Department of Standard Malaysia (DSM). (7 September 2015)



Papers made from various non-woody fibers. 10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



Bamboo products produced from V-Grooving method.10th World Bamboo Fair 2015 (WBF2015) (17 - 22 September 2015)



MS ISO / REC 1725 Pre - Assessment Audit (7 September 2015)

SERVICES AVAILABLE AT INTROP

(Laboratory of Biocomposite)

NO	INSTRUMENT	APPLICATION	PERSON IN CHARGE	CONTACT NO
1	BRABENDER Internal Mixer MDF Glue Mixer	To melt-mix polymer samples with natural/ synthetic fillers at low volume.	Ms. Ana Salleza Md. Salleh	03-8947 1885
2	Thermoplastic Compression Moulding (40 tonne)	To melt-compress plastic/composite samples at low pressure.	Ms. Ana Salleza Md. Salleh	03-8947 1885
3	Hot Press (100 tonne)	To compress wood/composite samples at high pressure.	Ms. Ana Salleza Md. Salleh	03-8947 1885
4	Twin Screw Extruder	To melt-mix polymer samples with natural/ synthetic fillers at high volume.	Ms. Ana Salleza Md. Salleh	03-8947 1885
5	Various chipper and milling machines	To chip and grind wood and fiber sample	Ms. Ana Salleza Md. Salleh	03-8947 1885
6	Injection Moulding	To inject polymer/composite samples into a mould cavity.	Ms. Ana Salleza Md. Salleh	03-8947 1885
7	Universal Testing Machine (UTM) (30 kN)	To determine tensile/flexural properties of polymer/composite samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
8	Thermal Gravimetric Analyzer (TGA)	To determine thermal decomposition of samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
9	Differential Scanning Calorimeter (DSC)	To determine thermal behaviours of samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
10	Dynamic Mechanical Analyzer (DMA)	To determine mechanical-thermal properties of samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
11	Thermal Mechanical Analyzer (TMA)	To determine thermal-mechanical behaviours of samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
12	Impact Tester	To determine impact properties of polymer/composite samples.	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
13	Digital Image Analyzer	To visualize fibre/composite sample at low magnification (40x).	Mr. Mohd Lufti Mohd Tawil	03-8946 9615
14	Freezer Mill / Cryocrusher (excluding liquid nitrogen)	To crush leaf/fibre samples via cryogenic process.	Ms. Ana Salleza Md. Salleh	03-8947 1885



OSB resin Mixer



Injection Moulding Machine



Optical Microscope



Universal Testing Machine



Compression Moulding Machine



SERVICES AVAILABLE AT INTROP

(Laboratory of Biopolymer and Devivatives)

NO	INSTRUMENT	APPLICATION	PERSON IN CHARGE	CONTACT NO
1	Gas Chromatography Mass Spectrometry (GCMS)	Characterization of sample in components in samples (e.g. fatty acids, organic acids, biodiesel (FAME)	Mdm. Nor Azizah Haron	03-8947 1887
2	Pulp Digester	To convert wood/non-wood into pulp	Mdm. Nazlia Girun	03-8946 7009
3	Papermaking instruments (handsheet former)	To convert pulp into paper/board	Mdm. Nazlia Girun	03-8946 7009
4	Beater (PFI mill)	To beat pulp	Mdm. Nazlia Girun	03-8946 7009
5	Pulp Viscometer	To find the viscosity of pulp	Mdm. Nazlia Girun	03-8946 7009
6	Paper/board tensile machine	To find the strength of paper/paperboard	Mdm. Nazlia Girun	03-8946 7009
7	Chemical compositional analysis	To measure the composition of cellulose, hemicellulose and lignin	Mdm. Nazlia Girun	03-8946 7009
8	Canadian Standard Freeness	To measure the rate of drainage of a diluted pulp suspension	Mdm. Nazlia Girun	03-8946 7009







Disintegrator



PFI Mill (Beater)



Pulp Viscometer



Handsheet Former

