THE EFFECT OF CHEMICAL TREATMENT ON THE PULP AND PAPER PROPERTIES OF BANANA (*Musa sp.*) STEM AND ITS EFFECT ON BLENDING WITH SECONDARY FIBERS

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by

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FARHANA MAHAMUD PAUZI

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LIST OF ABBREVIATIONS

2FI	Two-factor Interaction
A	Alkali concentration
AD	Air dry
ANOVA	Analysis of Variance
CCD	Central Composite Design
cm	centimeter
DP	Degree of Polymerization
g	gram
g/m^2	grams per square meter
kg	kilogram
kg/cm^2	kilograms per square centimeter
$KMnO_4$	potassium permanganate
kPa	kilopascal
$kPa.m^2/g$	kilopascal square meter per gram
L	litre
LOF	Lack of Fit
m	meter
min	minutes
mL	milliliter
mm	milimeter
$mN.m^2/g$	Millinewtons square meter per gram
MSS	Model Summary Statistics
$Na_2S_2O_3$	sodium thiosulphate
NaOH	sodium hydroxide

nm	nanometer
Nm/g	Newton meter per gram
No.	Number
OCC	Old Corrugated Containers
OD	Oven Dry
ONP	Old Newspaper
PRESS	Predicted Residual Sum of Squares
Prob. F	Probability of a larger F
psig	pounds per square inch gage
R.H.	relative humidity
R^2	Multiple Correlation Coefficient
R-square	Multiple Correlation Coefficient
RSM	Response Surface Methodology
S2	secondary layer
SCP	Semichemical Pulping
SMSS	Sequential Model Sum of Squares
Std	Standard
t	time
T	temperature

LIST OF SYMBOLS

%	percent
α	alpha
β	beta
γ	gamma
÷	divide
–	minus
+	plus
°C	degree centigrade
±	more or less

KESAN RAWATAN KIMIA TERHADAP SIFAT-SIFAT PULPA DAN KERTAS BATANG PISANG (*Musa sp.*) DAN KESAN PERCAMPURANNYA DENGAN GENTIAN SEKUNDER

ABSTRAK

Batang pisang (*Musa sp.*) dikaji untuk digunakan sebagai alternatif bagi menggantikan kayu untuk pengeluaran pulpa dan kertas. Pemulpaan separa kimia batang pisang melibatkan tiga pembolehubah pemulpaan (suhu: 30-90 °C, masa: 25-75 min, kepekatan alkali: 5-15%) dalam rawatan kimia. Reka bentuk eksperimen pemulpaan separa kimia telah direka dan sambutan sifat-sifat pulpa dan kertas terhadap pembolehubah pemulpaan telah dianalisis menggunakan reka bentuk komposit pusat (CCD) dalam metodologi respons permukaan (RSM). Tujuan kajian ini adalah untuk melihat pengaruh rawatan kimia dalam pemulpaan separa kimia batang pisang terhadap hasil, nombor kappa, tensil, pecahan, koyakan, lipatan dan kecerahan pulpa dan kertas. Kepekatan alkali mempunyai kesan yang utama pada sifat pulpa dan kertas batang pisang yang mana meningkatkan hasil pemulpaan, kekuatan tensil, kekuatan pecahan dan ketahanan lipatan. Suhu pemulpaan berada di tempat kedua dan masa perawatan nampaknya mempunyai keutamaan yang rendah. Dengan menggunakan kaedah fungsi kebolehcapaian, keadaan pemulpaan yang optimum didapati pada masa rawatan sebanyak 66 min, suhu memasak 61 °C, dan alkali (NaOH) kepekatan 15% (w/w bahan mentah asas). Pemulpaan optimum menyebabkan penurunan hasil sebanyak 20% jika dibandingkan dengan nilai yang diramalkan. Nilai sifat-sifat kertas yang terhasil adalah kira-kira 15-16% lebih rendah daripada nilai yang diramalkan. Perbezaan antara nilai sifat-sifat kertas yang

diperhatikan dan yang diramal dianggap boleh diterima. Kaedah percampuran digunakan untuk memulihkan potensi pulpa kraft liner kitar semula yang hilang dengan menggunakan pulpa dara separa kimia batang pisang sebagai bahan penambahbaikan kekuatan. Penambahan 20% pulpa dara kepada pulpa yang dikitar semula adalah mencukupi untuk mengembalikan sepenuhnya kekuatan tensil, kekuatan pecahan dan ketahanan lipatan kertas. Nisbah percampuran optimum pulpa kitar semula kraft liner dan pulpa dara separa kimia batang pisang adalah pada 60:40 bagi mendapatkan kertas yang bersifat baik.

THE EFFECT OF CHEMICAL TREATMENT ON THE PULP AND PAPER PROPERTIES OF BANANA (*Musa sp.*) STEM AND ITS EFFECT ON BLENDING WITH SECONDARY FIBERS

ABSTRACT

Banana (*Musa sp.*) stem is studied to be used as the alternative to replace wood for the production of pulp and paper. Semichemical pulping of banana stem involved three pulping variables (temperature: 30–90°C, time: 25-75 min, alkali concentration: 5-15%) in chemical treatment. The experimental design of semichemical pulping was computed and the response of pulp and paper properties to the pulping variables was analyzed using a central composite design (CCD) of response surface methodology (RSM). The aim of the study is to observe the influence of chemical treatment in the semichemical pulping of banana stem on the yield, kappa number, tensile, burst, tear, fold and brightness of pulp and paper. The alkali concentration had a predominate effect on banana stem pulp and paper properties which improves the pulp yield, tensile strength, burst strength and folding endurance. The cooking temperature took the second place and the treatment time seems to have low priority. By applying the desirability function method, the optimal pulping conditions were found to be a treatment time of 66 min, cooking temperature of 61 °C, and alkali (NaOH) concentration of 15% (w/w basis raw material). The optimal pulping resulted in a decrease of yield by 20% when compared to the predicted value. The resulting paper properties value were approximately 15-16% lower than the predicted value. The difference of observed and predicted values of paper properties was considered acceptable. Blending method is used to recover the

lost potentials of kraft liner pulp by using semichemical banana stem pulp as the upgrading strength material. The addition of 20% virgin pulp to the secondary pulp is sufficient to completely restore the tensile strength, burst strength and folding endurance of the paper. The optimum ratio of blending recycled kraft line pulp and semichemical banana stem pulp point to 60:40 in order to have good paper properties.

CHAPTER 1

INTRODUCTION

1.1 Background

Paper products are integrated into nearly every aspect of our daily lives. It is undeniably important to the society. The industry is dominated by the Asia-Pacific region which witnessed more than 40 % growth rate in 2011, due to high demand in paper consumption. Approximately 90 % of this paper is produced from wood pulp (Annonymous, 2013a; Ai and Tschirner, 2010).

The rising demand in paper product consumption which is about 400 million metric tonne per year (2012) creates additional pressure on the world's forest resources since more wood need to be cut to satisfy the demand (Annonymous, 2014a). Along with this matter, the increased awareness of pressuring the environment led many researchers worldwide to focus their researches on finding the potential alternative raw material for papermaking from non-wood resources (Latibari *et al*., 2011).

There are four different non-wood fiber resources which paper can be made; agricultural crop residues (bagasse and straw), fiber crops (kenaf and jute), wild plants (sisal and bamboo) as well as textile and cordage wastes (cotton and linen scraps) (Annonymous, 2009; Annonymous, 2011). Banana stem is categorized as agricultural crop residues as the stem was thrown away after harvesting the fruits. Agricultural crop residues received a strong interest as the alternative raw materials for papermaking. They are fast-growing plants compared to wood trees that take a long replanting time.

1.2 Justification

The natural forests are extremely rich with their treasure. They are among the oldest living systems on earth. Sadly, the forests are in the process of being extinguished by logging. Until the world population reached 3 billion the means the earth provided were adequate (Tomek, 2011). However, the world population has reached 7.12 billion in 2013(Annonymous, 2014a). This present population growth together with industrial growth has caused all the limited resources to be outstripped by human demands. The forests were cleared for agricultural land, while the trees were chopped down for building houses, firewood and wood for fuel. Adding to that, paper and packaging materials are produced from the wood pulp.

Apparently, many people are comforted by the fact that they can afford to waste. The world's paper products consumption is calculates to be 398.92 million metric tonnes in the year 2012, where 54 % of the value is for packaging purposes and 27 % is used for printing and writing (Annonymous, 2014a). To satisfy the demands, the world's total paper production had increased to 403 million metric tons in 2013 from 399 million metric tons in 2012, with Asia as the largest paper producer accounts for 182 million metric tons (Annonymous, 2014b). According to Rogers (2005), every American discards over 200 pounds (90 kg) of rubbish a year, which includes junk mails. It takes on average 17 trees to make a ton of paper (Rogers, 2005). The misuse of natural and human means not only affects the world's population, but also shortens the world's resources.

As of the 2010 census, the population of Malaysia was 28.33 million and the number is increasing to 30.02 million in 2014. The total pulp, paper and paperboard production in 2014 was 1.943 million metric tons while the net paper and board consumption in that year was 3.178 million metric tons (Annonymous, 2014a). Therefore more wood resources were needed and this action can cause the deforestation where the trees were cut down to satisfy the increasing demand.

Actions have been conducted to reduce the possibility of deforestation such as importing the wood pulp and recycling methods but they are costly. Thus the researchers and manufacturers are searching for other alternative to be used as pulp sources.

In pulp and paper industry, nonwood plant materials have been proposed to be used as an alternative and as a way to preserve natural forest. Pulps from nonwood species is preferable because it provides good fiber for paper manufacturing with properties close to wood fibers.

Nonwoods have lower lignin content than wood and generally it is easier to delignify nonwoods, as they have lower activation energies (Ververis *et al.*, 2003). Producing paper from nonwood fiber would help in reducing the need to procure pulpwood from natural forests and for large-scale plantations. Under certain climatic conditions, nonwood fiber production may be a reasonable alternative to tree plantations.

In this research, banana stem was chosen as the raw material. It is one of the agricultural wastes that are produced after harvesting the fruits. In Malaysia, banana plantation is calculated to take about 15 % of the total acreage under fruits (Nik Mohd. Masdek, 2003; Hays, 2009; Quintana *et al*., 2009). Abdul Khalil *et al.* (2006) state the area for banana plantation in Malaysia alone is estimated to be 34 thousand hectars. Banana stem has high content of fibrous material and has been used for composite materials (Quintana *et al*., 2009). Therefore, by utilizing these wastes, it is hoped to be a way of disposing the waste instead of forgo them.

Banana stem is composed of plenty parenchyma, which consists of hemicelluloses. If banana stem undergo chemical pulping, lots of hemicelluloses will be removed and the yield will be low. Thus, adding mechanical pulping process enable the yield to be preserved. Kumar and Kumar (2011) believe banana stem can give a high quality fiber with high yield if the preparation of the material is adequate.

Many improvements in pulping techniques have been developed during recent years. These have resulted in improved quality and yield as well as reduction in time, chemicals, labor, and maintenance cost. Semichemical pulping is defined as a two-stage pulping process, involving chemical treatment to soften or remove some part of lignin or fiber-bonding substance and mechanical refining to complete the separation of the fibers (Smook, 1992; Jahn, 2013). The method includes the intermediate range of pulp yields between mechanical and chemical pulping.

There are five different methods of semichemical pulping. They are bisulphite, sulphite, neutral sulphite, kraft, and soda semichemical pulping (Smook, 1992). In this study, soda semichemical pulping was chosen. Besides the expectation to get a high pulp yield, this process is expected to have a reduction in time labor, chemicals and maintenance cost. Sodium hydroxide (NaOH) alone was used in the brief chemical treatment stage before undergo mechanical defibration. The yield of semimechanical pulp is reported to be 60 – 75 % (Smook, 1992; Jahn, 2013), but as the banana plant is a nonwood material and has a parenchyma stem, the yield is expected to be lower.

In general, the properties of pulp and paper would change with different pulping condition used. Pulp and paper properties are influenced by pulping conditions such as alkali concentration, cooking temperature, as well as treatment time. The good combination between the pulping condition factors above can produce pulp and paper with good and strong properties. Thus, this study is important to examine the factors that is necessary to obtain the required banana stem pulp and paper properties. As the study will concentrate more on the chemical treatment of the banana stem, the mechanical process will remain constant. A central composite design (CCD) in response surface methodology (RSM) is used to ease the experimenting process and statistical analysis.

Blending of pulps was done to recover the original papermaking potential as much as possible. Blending with different fibers relies on the interaction between the two types of fiber to enhance the paper performance. The blending of virgin fibers with secondary fibers will help to increase the paper properties.

1.3 Objectives

The objectives of the research are as follows:

1. To study the effect of chemical treatment on pulp and paper properties of semichemical pulping conditions of banana stem using central composite designs (CCD) of response surface methodology (RSM).
2. To determine the optimum conditions of semichemical pulping of banana stem on its pulp and paper properties using central composite designs (CCD) of response surface methodology (RSM).
3. To study the effects of blending between semichemical banana stem fiber (virgin pulps) and kraft liner paper fiber (secondary pulp) on paper properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Paper

Paper and fiber-based products play important roles in our daily lives. The increasing demands and the requirements of these paper and products are in line with the increasing of human population, their quality of life and the country's rapid development and progress.

Paper can be defined as the crossing network of cellulose fibers bonded to each other. Until recently, there are various criteria for paper produced in accordance with the requirements of the users. To fulfill the user's product specifications, there are various types of fiber, cooking methods as well as treatments that can be used.

2.1.1 Paper industry development

Paper is an evolution of various other materials used as a medium for recording, storing and conveying information from ancient times. Among these are pieces of clay, pottery, stone, metal, bone, wood, bamboo, papyrus and vellum. Asia has been using pieces of wood or bamboo as information media. Meanwhile, the Sumerian, Babylonian and Mesopotamian have been using pieces of clay as their media. As for the Egyptian, Greek and Roman, they use papyrus scrolls and the Persians, Arabs and Jews use animal skin scrolls (Atchison and McGovern, 1983).

A.D. 105 often cited as the year which papermaking was invented. In that year, Ts'ai Lun, an official of the Imperial Court reported the invention of paper to Chinese Emperor (Annonymous, 2006). Early Chinese paper have been made from a suspension of mashed pieces of mulberry bark, cloth and hemp waste in water, washed, soaked and beaten to a pulp with wooden mallet. A paper mold, probably a sieve of coarsely woven sloth stretched in a four-sided bamboo frame, was used to dip up the fiber slurry from the vat and hold it for drying (Annonymous, 2006; Annonymous, 2013c). The secret of papermaking remained in China for 650 years, until Arabs learned the art from Chinese prisoners of war. The process was brought to Europe in the 12^{th} century – but the method of making paper from wood was lost along the way. Rags were used instead (Annonymous, 2013c).

The word paper is derived from the name of the reedy plant papyrus. Papyrus or its scientific name *Cyperus papyrus* is a kind of water plant which grows abundantly along the Nile River in Egypt and can also be found in Ethiopia, Jordan and Sicily. The height of this plant can exceed to 3 meters. Papyrus is made from the sliced sections of the flower stem of the papyrus plant pressed together and dried, and then used for writing or drawing. The process appeared in Egypt in 2400 B.C. (Atchison and McGovern, 1983; Bellis, 2015). However, true paper is made of pulped cellulose fibers like wood, cotton or flax (Bellis, 2015).

2.1.2 Paper usage

The use of paper is widespread today. Many daily affairs associated with the fiber or paper products. Generally, it can be divided into 3 functional groups, namely:

1) Communication, information and literature.
2) Commercial (Packaging), industrial use and construction.
3) Personal or sanitary purposes.

Table 2.1 shows the definitions for some commonly used paper grade on those 3 functional groups (Smook, 1992).

Table 2.1 : The term of paper grades.

GRADE	TYPE	DEFINITION
PRINTING	Newsprint	Paper machine products consist of mechanical pulp (mostly), typically used to print newspapers.
	Catalog	Is a print of low weight, but usually contain fillers.
	Rotogravure	Usually refers to the uncoated printing paper, may contain fillers.
	Broadcasting	High calendaring paper and coated magazine paper. The raw stocks are mainly made up of mechanical pulp, but for the best grade use chemical pulp.
	Bank note, documents	High grade permanent paper, usually made from rug source
	Bible	Low weight, full load paper or a rug made from chemical pulp.
	Bond, ledger	High quality paper used for letterhead or storage. Consisting of rug or chemical pulp.
	Stationery	Good performing paper, mild and bulk. Usually using chemical pulp, rag use for better quality.
INDUSTRY	Bag	High-strength paper, usually consists of unbleached craft softwood pulp that were beaten at high degree.
	Linerboard	Low-weight board which is used as a liner on the corrugated board. Also used for wrapping paper. Consisting of high product kraft pulp, unbleached with the quality of the upper layer is better for printing.
	Medium corrugated	Used for layer in corrugated board. Usually consists of high products of semichemical hardwood pulp on the 9 points thickness.
	Construction paper	Printing paper produced in high grammage and bulk, used for kindergarten and arts.
	Greaseproof	Dense paper and non-porous made from sulphite pulp beaten to a high degree.
	Glassine	Resulting from the greaseproof paper stock by damping and casting high pressure during calendaring. The smooth and translucent paper is used as a special protective wrapper and converted into a wax paper.
TISSUE	Sanitary tissues	This classification includes facial tissues, toilet paper, sanitary products and table napkins. Its main feature is the softness and absorbency. The high percentage consists of chemical pulp beaten in low degrees.
	Evaporated tissue	Low-weight tissue, well-structured (5 g/m^2) produced from kraft pulp beaten to a high degree, used as a dielectric capacitor. Basically using the same raw materials for carbonation grades stocks and (with wet strength treatment) is used for tea bags.
	Towel	Absorbent paper is usually made from kraft pulp beaten to a low degree by the addition of mechanical pulp. Rapid absorption and water storage capacity is the main function. There is also the addition of wet strength resins to avoid wet disintegration.
	Wrapping tissue	This design includes a wide variety of tissues made to wrap and pack. Its main characteristics are strength, good shape and clean. Grammage is between 16 - 28 g/m^2.

Printing paper category has the highest demand among the functional groups found in Table 2.1. As stated, there are many types of paper that fall within the printing category. Each type of paper has different characteristics. Depending on the demand and the usage, manufacturing methods of these papers also differ (Payne, 1997). The main criteria required for printing paper is runability. Recycled paper usually does not have a good runability. Therefore, most of the factory blends the recycled fiber with virgin fiber at ratio of 3:7 to resolve the issue.

2.1.3 Paper properties

Generally the paper properties can be divided into 5 specific groups, namely physical, optical, chemical, electrical and microscopical. Typically, the paper will only be tested by a physical, optical and chemical groups based on the required paper properties. Properties such as tensile, burst, tear, fold, density, weight and thickness fall in physical properties. Opacity, brightness and color are tested for optical properties, while alpha-cellulose content, pentose, ash, starch and moisture are for chemical properties.

Cellulose is the predominant material in the paper, thus its properties influenced most of the paper properties. The main properties of cellulose that affect the paper are:

i. absorb water - paper will absorb water unless it is treated
ii. white –paper is white unless it contains lignin (as impurity) or dye
iii. hydroscopic –paper is hydroscopic and will take and remove moisture with the changes in relative humidity
iv. flexible – paper is flexible
v. combustible – paper can be burned

Pulping process and papermaking affect cellulose by enhancing the desired properties and reducing the unwanted properties. The type of fiber used, cooking duration, bleaching process and degree of interfiber bonding had a major influence to physical and optical properties (Retulainen, 1998). All of these factors had to be controlled to acquire desired paper properties.

2.1.4 Paper formation

The uniformity of fibers and other solid components scattered in a paper determines formation of paper. Practically, formation of paper is determined by placing it under the light to observe the uniformity of the fiber scattering structure. Roughly we can evaluate the paper whether the paper is formed evenly or not. A good paper formation will show a neat texture, compact and uniform fiber scattering (Page, 1989).

Generally, during water removal process either draining or drying, surface tension will form a strong force that condense and draw fibers for closer contact (Page, 1989). Surface tension force is low when the amount of water is sufficient to fill the empty spaces between fibers in web. The surface tension will slowly increase starting at 11-12% of solid content in the water. At this moment, air forms a large part in the media in which the fibers are suspended and causing the area between the air-water rise quickly. Paper is said to form at solid content of 25-30%. As the amount of solids increases, air-water interfaces are broken up and inter-fiber bonding starts to dominate. Hydrogen bonding starts to dominate at solids contents above 50% (van de Ven, 2008)

2.2 Banana

Banana is a common name for herbaceous flowering plants of the genus *Musa* of the family *Musaceae*. There are other family aside from *Musaceae* and often been combined with each other resulting better species for various purposes. Some species such as *Musa Basjoo* of Japan and *Musa Ornata* from Pakistan to Burma are grown only as ornamental plants or for fiber, while *Musa Textilis* of Philippines is grown for its fiber that makes strong ropes. Banana species are cultivated in Ethiopia for fiber and for foods derived from young shoot, base of stem and corm (Simmonds, 1966). Figure 2.1 shows the banana plant.

Figure 2.1: Banana plant.

Normally *Musaceae* is tall and sturdy and often mistaken for a tree due to the main upright stem composed of a bundle of leaf stem that grows to 6 to 7.6 m tall. The strength of the trunk is derived from the curvature of the leaf stems, and the way they overlap. Narrower stem mean less overlap thus potentially less strength. The leaves and bracts that are spirally arranged and overlapped could grow up to 2.7 m long and 60 cm wide. The male and female flowers which responsible in producing edible fruits, are separated within one inflorescence. The fruits may have seeds but they never develop. A typical banana plant grows in nine to 18 months before harvested (Simmonds, 1966; Hays, 2009). Figure 2.2 shows the banana plant structure.

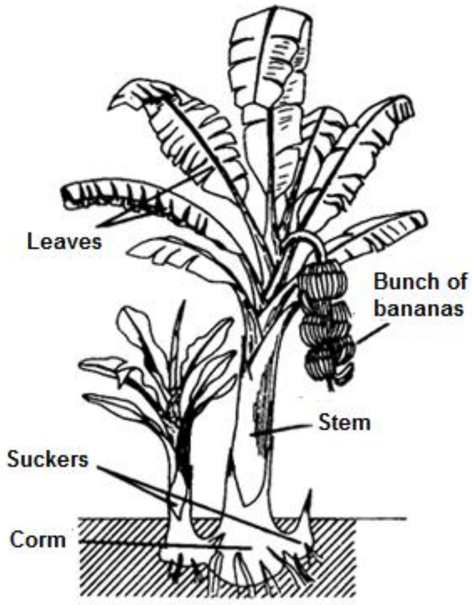


Figure 2.2: Banana plant structure (Annonymous, 2013b).

The most-edible banana comes from the two wild species *Musa Acuminata*, originally from Malaysia and *Musa Balbisiana,* originally from India and it has been vastly cultivated for edible fruit production (Hays, 2009). World banana producers were Ecuador, Costa Rica, Philippines and Columbia which contribute 33% of world production (Anem, 2012a). It is the fourth most important crop in the developing countries after rice, wheat and corn. Banana remains the second in Malaysia, amounting to about 15 % of the total acreage under fruits (Nik Mohd. Masdek, 2003; Hays, 2009; Quintana *et al*., 2009). There are only a few large banana plantations in Malaysia. Anem (2012b) stated that there is 29 thousand hectare of banana planted in

2012 producing 294 thousand metric ton of fresh banana with total value estimated about RM 294.5 million. Banana plantations are concentrated in Johor, Pahang, Selangor, Perak, Sabah and Sarawak. In Malaysia, bananas are planted as a cash crop for domestic market and also for export (Nik Mohd. Masdek, 2003; Anem, 2012b).

After harvesting the fruit, the plant is cut down and thrown away mostly as waste. (Quintana *et al*., 2009) mentioned that 88.84 % from the total biomass production is discarded and many of this waste namely bunch, stem and leaves have high content in fibrous material. The fibers of this waste material have been used for composite materials as a reinforcing agents and fiber-cement composites (Quintana *et al*., 2009; Bilba *et al*., 2007; Zuluaga *et al*., 2009; Miller, 2010). The use of renewable agricultural waste crops as nonwood cellulosic fibers would be great advantage for countries with limited wood forests, and would increase the profit of farmers in developing countries (Ganan *et al*., 2004; Kumar and Kumar, 2011).

Banana stem made of the rolled bases of leaves, which may be two or three meters tall. The sheaths are crescentics and highly packed together to form the stem that function as the trunk to support the plant. In cross-section of the stem (Figure 2.3), about half of the area exposed is air-space formed by longitudinal canals separated radially by parenchymatous septa in which vascular bundles are embedded. Horizontally, the canals are separated each 2 - 6 mm by thin septa which are made of parenchyma and stellate aerenchyma. Vascular bundles consist of vessels and tissues that carry or circulate fluids (sap) through the body of the plant. They are scattered right through the ground tissue of the sheath but are distinctly dense towards the outer surface (Wilson and White, 1986; Simmonds, 1966).

Figure 2.3: Cross section of banana stem.

Under electron micrographs, the cell walls are distinctly visible and have linear fibrillar arrangement. The stem consists of high content of fibrous material and high quantity of gum and mucilage. A chemical study on banana stem has shown that these fibers contain high holocellulose (cellulose and hemicelluloses) content and low lignin levels (Bilba *et al*., 2007). Despite low lignin content, the delignification of banana stem appears difficult (Kumar and Kumar, 2011). Table 2.1 shows the chemical properties of banana stem.

Table 2.2: The chemical properties of banana stem in previous work.

Properties	Goswami *et al*., 2008	Bilba *et al*., 2007	Kumar and Kumar, 2011
Lignin (%)	17.25 - 18.21	15.07	11.0
Cellulose (%)	57.8 - 62.2	31.27	43.6
Hemicellulose (%)	15.2 - 17.5	14.98	-
Ash (%)	1.6 - 2.5	8.65	7.1

2.3 Secondary fiber

Secondary fiber is defined as any fibrous material that has already undergone a manufacturing process and is being recycled as the raw material for another manufactured product (Smook, 1992). The increasing usage of secondary fiber may reduce the dependency on forest resources as well as lessen landfill loadings by assigning minimum content levels of secondary fiber for certain paper grades, notably newsprint.

Secondary fiber plants are usually located in high population density area, where a reliable supply of waste material can be more easily collected and transported. There are five basic grades of wastepaper that are generally accepted by the paper industry; namely mixed paper, old newspaper (ONP), old corrugated containers (OCC), pulp substitutes and high-grade deinked (Smook, 1992). Pulp substitutes are more favorable because they mainly consist of unprinted paper and boards that has not been coated or contaminated in any way. Thus they can be utilized directly in the papermaking process for certain products.

Other wastepaper must be cleaned up to remove contaminants. Kraft liner paper or recycled linerboard is one of the products made from recycled old corrugated container (secondary fiber) (Chung, 2002; Smook, 1992). It is sufficient for secondary pulps that are used for inner plies of a multi-ply paperboard or for corrugating medium to undergo separation and/or dispersion of such contraries as adhesives, glues, waxes, plastic laminates, etc. But for printing grades, it is necessary to have more selective removal of contaminants, including deinking, for a suitable papermaking stock preparation (Smook, 1992).

During each recycling, significant losses of both fibers substance and strength occur and hence numbers of recycling are limited. Some investigators have suggested that a fiber can be recycled only four times before the loss in quality becomes too great for effective reuse (Smook, 1992). Figure 2.4 illustrates the relative effects of repeated recycling of newsprint on individual fiber strength and on the bonding strength between fibers. Both strength indices decrease, but the bonding between fibers shows more loss. The fibers become less flexible and less permeable to water with each drying and slushing cycle. Therefore they do not conform as well as virgin fibers. Cumulative loss of hemicelluloses from the fiber surfaces also contributes toward reduced bonding.

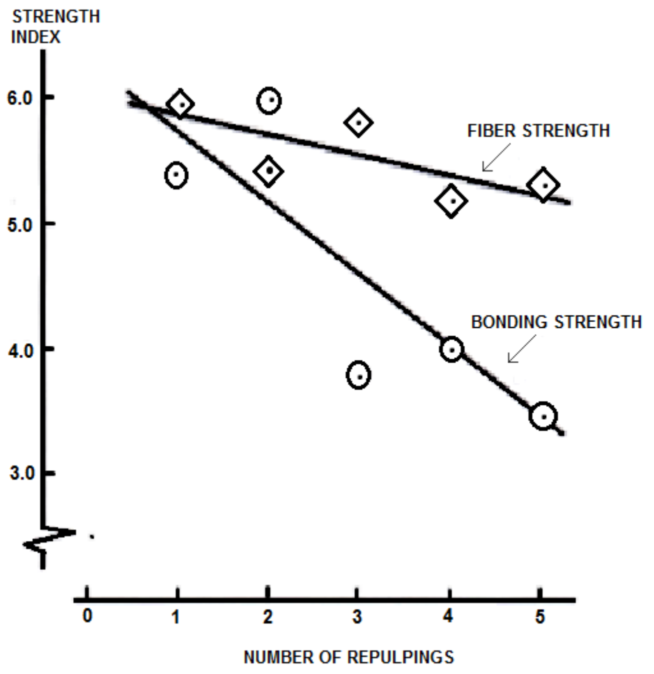


Figure 2.4: Effect of multiple recycling on fiber and bonding strengths of newsprint (Smook, 1992).

Secondary fibers have notably different characteristics when compared to virgin pulps. Regardless of how they have been processed, secondary pulps always contain some residual contamination that will have an impact on papermachine operation. Thus, it must be processed in such a way that not only coarse contaminants, but also printing inks, stickies, fines and fillers do not enter into the process. Waxes, glues, inks, and a variety of dissolved solid found in secondary pulp tend to build up in the systems. They precipitate and agglomerate at various points along the papermachine. For example, ink and clay may agglomerate into larger particle in the white water system and eventually end up visible dirt in the paper product. Stickies and hot melts are prone to precipitate on fabrics and dryer surfaces.

Secondary fibers on mixing with certain amount of primary fibers ensure the strength and other properties of the paper. For effective use of secondary fiber it is necessary to collect, store, sort and then classify the materials suitable enough for various quality grades. New developments in fiber processing are essential to create a sustainable equilibrium between future demands of fiber resources and recycle possibilities to produce quality product so as to ensure smooth operation of paper machine (Anil and Kathirvelu, 2010).

2.4 Lignocellulosic fiber

Lignocellulosic material primarily made up of cellulose, hemicelluloses, lignin and small amounts of extractives. Sources of lignocellulosics include wood, agricultural residues, water plants, grasses, and other plant substances. Cellulose and hemicelluloses are sometimes referred to collectively as holocellulose. Cellulose is a complex carbohydrate that forms the main constituent of the cell wall in most plants.

Lignin is an aromatic polymer that strengthens plant tissue by binding cellulose fibers. This functional mix of chemical species determines the chemical and physical properties of wood (Johnson, 2007).

Most lignocellulosics have similar properties even though they may differ in chemical composition and matrix morphology. The chemical compositions of a lignocellulose fiber vary according to the species, growing conditions, methods of fiber preparations and many other factors (Testova, 2006).

2.4.1 Cellulose

Cellulose which is the major structural component of wood cells is the most abundant organic substance on the Earth. Depending on species and growing conditions, it is the main constituent of wood as it makes up 40% – 50% of the wall mass. It occurs mostly in the secondary cell wall and commonly in association with hemicelluloses and lignin.

In plant fibers, the substance cellulose determines the character of the fiber and permits its use in papermaking. Cellulose is a carbohydrate composed of carbon, hydrogen and oxygen. Chemically, hydrogen and oxygen elements present in cellulose is the same proportion by weight as they combine to form water (H-O-H). This property of cellulose is essential in papermaking as it allows swelling in water to provide an increased natural bonding affinity for it and other similar carbohydrates in the plant commonly referred to as hemicelluloses (Smook, 1992).

Cellulose is a polysaccharide molecule containing thousands of glucose sugar molecules (Johnson, 2007). The glucose molecules ($C_6H_{12}O_6$) of the cellulose are produced by the tree through photosynthesis. Firstly, this monomer units are transformed into glucose anhydrides ($C_6H_{10}O_5$) and then linked through oxygen atoms end-to-end to form linear polymers $(C_6H_{10}O_5)n$. The number of monomers per macromolecules (*n*) indicates the degree of polymerization (DP) in cellulose. Typical value of *n* is 8,000 - 10,000 for wood cellulose in natural state (Testova, 2006). In addition, most papermaking fibers have weight-average DP in the range of 600 - 1,500. Inside the cell wall, macromolecules of cellulose linked laterally through hydrogen bonding forming long molecules called microfibrills.

All polymers are collections of structural repeat units. Figure 2.5 shows the chemical structure of cellulose. The recurring unit of cellulose is actually two consecutive glucose anhydride units, known as cellobiose unit. Furthermore cellulose molecule can be describe as a chain of D-glucose anhydride units bonded together by β(1,4) glycosidic linkages to form the dissacharide cellobiose molecule (Johnson, 2007). The macromolecules have both amorphous and crystalline parts (Figure 2.6). Crystallinity is a peculiar property of cellulose. Because of their close arrangement, the crystalline cellulose area have high resistant to chemicals and it favors preserving cellulose in chemical pulping processes. In and amongst this crystalline domain, there often occur unorganized amorphous regions of entangled cellulose molecules that are less resistant to chemicals. It is this dual morphology of cellulose that imparts both stiffness and flexibility properties to wood. Despite that, pure cellulose can be quite easily hydrolyzed to glucose under controlled acidic conditions.

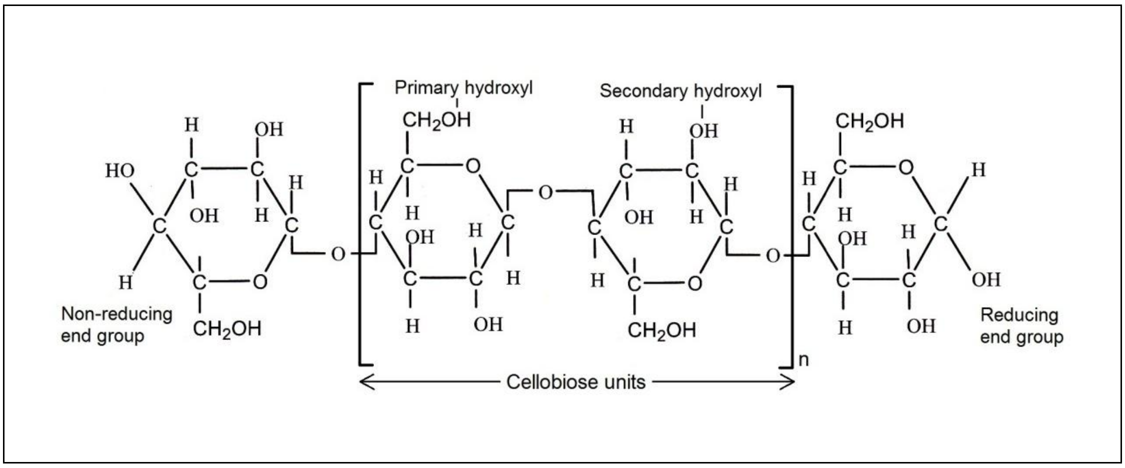


Figure 2.5: Cellulose chemical structure (Smook, 1992; Abdul Khalil and Rozman, 2004).

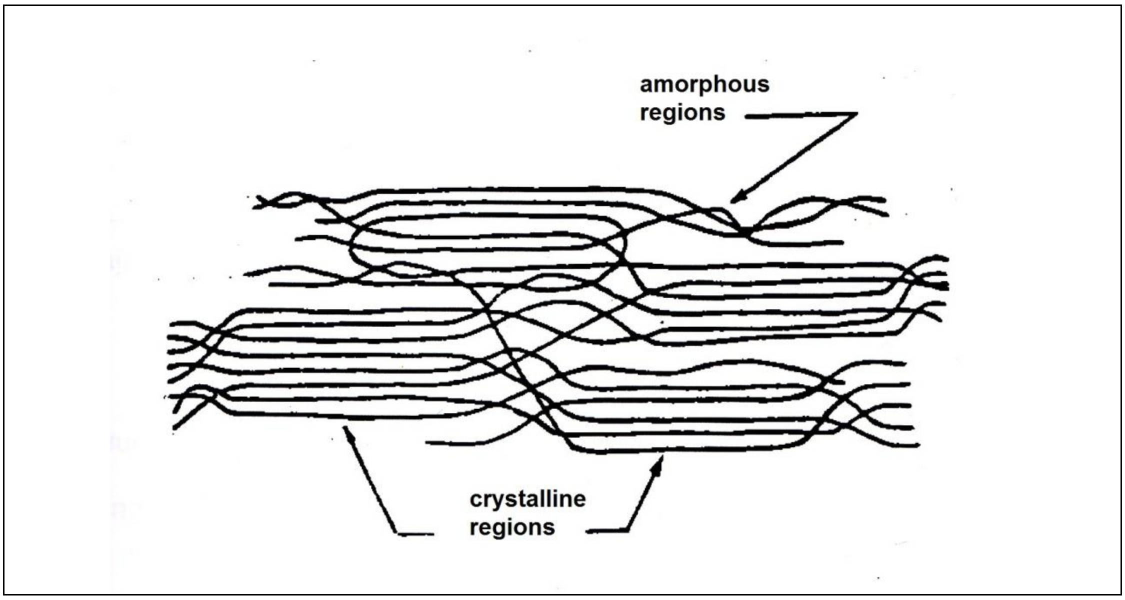


Figure 2.6: Schematic of molecular organization within a cellulose microfibril (Smook, 1992).

Long-chain cellulose is known as alpha cellulose. Depending to the amount of alpha cellulose inside a cellulosic material, a paper with higher degree of durability and permanence can be produced. A number of shorter-chain polysaccharide, known collectively as hemicelluloses, also forms part of the woody structure of plants. Hemicelluloses (along with degraded cellulose) is further conveniently categorized according to DP: (1) beta cellulose with DP between 15 and 90 and (2) gamma cellulose with DP less than 15 (Smook, 1992; Abdul Khalil and Rozman, 2004).

2.4.2 Hemicelluloses

Hemicelluloses are a collective label for other polysaccharides comprised of photosynthetic sugars. The structures and function of these molecules differ from that of cellulose. Hemicelluloses contain a mixture of sugar molecules. By contrast to cellulose which is polymer only of glucose, the hemicelluloses are polymers of five different sugars. They are built up of pentose sugars D-xylose and L-arabinose with five-carbon atoms $(C_5H_8O_4)n$ units and hexose sugars D-glucose, D-mannose and D-galactose with six-carbon atoms $(C_6H_{10}O_5)n$ units. Hardwood and softwood species typically contain hemicelluloses with different combinations of these sugars (Abdul Khalil and Rozman, 2004).

Hemicelluloses constitute 25% - 35% of the cell wall mass. Hardwood species is somewhat contain more hemicelluloses than softwood species. They are heterogeneous low molecular weight polysaccharides and insoluble in water. The main distinguishing trait of hemicelluloses compared to cellulose is their relatively high accessibility to acidic and alkaline hydrolysis. This property allows them to be separated from the total carbohydrate fraction or holocellulose to gain essentially pure cellulose or alpha cellulose.

Hemicelluloses are not crystalline, but are highly branched with only100 - 200 monomer units. They are therefore shorter than cellulose and have low degree of polymerization. The molecules of hemicelluloses can be made up by variety of monosaccharides. Xylans form by polymerization of the anhydro forms of five-carbon sugars and 4-0-methyl-D-glucuronic acid. Galactoglucomannans form by polymerization of six-carbon sugars.

Depending on the plant species, hemicelluloses vary in structure and sugar composition. Although they do improve the strength of wood cells, hemicelluloses are not structural molecules in the way cellulose is. Because of their branched and polysaccharide natures, hemicelluloses act as an intermediary between cellulose and other structural polymer, lignin (Smook, 1992; Johnson, 2007).

Hemicelluloses play important role in papermaking as they assist in internal fibrillation of the fibers while promote swelling of fibers prior to grinding. During chemical treatment of wood to produce pulp, the amounts, locations and structures of the hemicelluloses usually change dramatically. The hemicelluloses are more easily degraded and dissolved under mild acidic conditions at higher temperatures than cellulose, so their percentage is always less in pulp than in the original wood. If hemicelluloses are preserved in cooking process, it gives higher yield of pulp (Smook, 1992; Testova, 2006).

2.4.3 Lignin

The term “holocellulose” is used to describe the total carbohydrate content of fibers. Along with polysaccharides, lignin is a structural polymer that contributes to the chemical and physical properties of wood. Lignin is vastly different from the sugar-based polymers in wood (Johnson, 2007). Its principal role is to form the middle lamella, the intercellular material which binds the fibers together. Additional lignin is also contained with the remaining cross-section of the fiber (Smook, 1992).

Lignin distinctively differentiates wood from other cellulosic materials found in the plant. It is a three-dimensional cross-linked amorphous polymer. These features contribute to the utility and the complexity of wood as a biomass feedstock. In all plants, lignin's basic structural units, or monolignins are based on various derivatives of phenyl propane molecule with various bonding combinations (Figure 2.7). Generally, lignin is composed of three monomers; that is, coumaryl, coniferyl, and sinapyl alcohols (Figure 2.8) (Abdul Khalil and Rozman, 2004). The three types of lignin monomers are differentiated by methoxy (-OCH_3) substitution at carbon three or five of the phenyl ring.

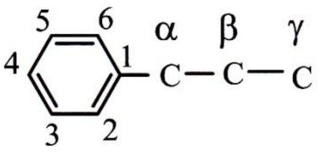
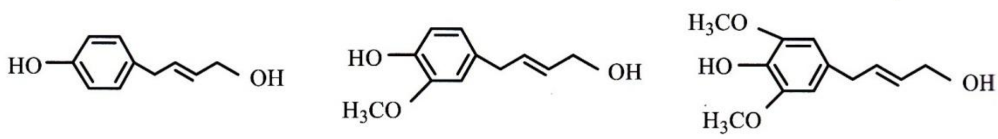


Figure 2.7: Phenyl propane unit (Abdul Khalil and Rozman, 2004).



I II III

Figure 2.8: Coumaryl Alcohol (I), Coniferyl Alcohol (II), and Synapyl Alcohol (III) (Abdul Khalil and Rozman, 2004).

Lignin content in wood can vary from 20% to 35%. There are two main types of lignin units: (1) guaiacyl, with one methoxyl group in phenol ring, and (2) syringyl, with two methoxyl groups. The lignin in softwoods (gymnosperms) is