SYNERGY BETWEEN CHEMICAL AND MECHANICAL ACTIONS IN THE ALKALINE PEROXIDE PULPING OF OIL PALM EMPTY FRUIT BUNCH

by

YUNITA MEGASARI BINTI DERMAWAN

Thesis submitted in fulfillment of the requirements for the Degree of Master of Science

April 2014

ACKNOWLEDGEMENT

Praise to ALLAH SWT, who has given me the opportunity to accomplish this thesis. I would like to dedicate this thesis for my parents and husband, who have given me all the love and great support during my studies.

I would like to thank to my supervisor, Dr. Arniza Ghazali, who have given me guidance, advices, encourage and great supports. Thank you to Prof. Wan Rosli Wan Daud for all the advices. Mr. Nasrullah R. C. L, thank you for introduced me to this school and for all your help and support. You have done a great job and I really appreciate it. I know it has been difficult through this period, but we got through it.

I would like to thank to all staff and lab assistant of School of Industrial Technology for giving me the opportunity to attend this school with full assistance and for the experiences that you have shared with me. Special thanks to Mr. Sadali bin Othman and Mr. Abu Mangsor Mat Sani for your great support during my lab works.

My brothers and sister, thank you for all your love, your kind attention and supports, I always miss the time we spend together. Thanks to Hasanah, Hafidz, Rosnah, Amin, and Azli who have made the toughest time so much easier. It is great to have such friend like you all by my side. 'All of my families and my friends in Aceh, thank you for always remember me and giving me your supports, I really miss you all.

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AP = Alkaline Peroxide

API = Alkaline Peroxide Impregnation

APMP = Alkaline Peroxide Mechanical Pulping

APP = Alkaline Peroxide Pulping

COD = Chemical Oxygen Demand

CMR = Chemical & Mechanical Refining

CSF = Canadian Standard Freeness

CTTRP = COD, TDS, Turbidity and Residual Peroxide

EFB = Empty Fruit Bunch

EPA = Environmental Protection Agency

MR = Mechanical Refining

LCR = Low Consistency Refining

MCR = Medium Consistency Refining

HCR = High Consistency Refining

LOP = Light Organic Product

OD = Oven Dried

PP = Plate Pattern

SEL = Specific Edge Load

SRE = Specific Refining Energy

SSL = Specific Surface Load

TDS = Total Dissolved Solids

TSS = Total Suspended Solids

LIST OF SYMBOLS

α = average intersecting angle

IL = length of refining impact

IN = number of refining impact

Ls = cutting speed of bars

Pe = effective power

Pn = no load power

Pt = total refining power

Wr = width of rotor bars

Wst = width of stator bars

SINERGI ANTARA TINDAKAN KIMIA DAN MEKANIKAL DALAM PEMULPAAN PEROKSIDA BERALKALI TANDAN BUAH KOSONG KELAPA SAWIT

ABSTRAK

Sinergi antara tindakan kimia dan mekanikal dalam sistem Pemulpaan Peroksida Beralkali (APP) diterapkan untuk menghasilkan pulpa dan kertas dari tandan buah kosong kelapa sawit (EFB). Dalam APP, kedua-dua proses pemulpaan dan pencerahan terjadi dalam satu proses. Proses ini didapati sesuai dijalankan selama 40 minit pada 70°C. Pelembutan dan pencerahan EFB didapati dilakukan sangat efektif dengan mensinergikan kekuatan peroksida beralkali dengan fibrilasi mekanikal daripada dua jenis corak bilah penghalus Andritz Sprout Bauer yang berbeza. Pengubahan kekuatan AP dilakukan dengan meningkatkan nisbah alkali ke peroksida dari 2:2.5%, 4:5% hingga ke tahap maksimum iaitu 8:10%. Selain daripada itu, kekuatan AP juga dapat ditingkatkan dengan menerapkan pengisitepuan AP dalam berbilang peringkat. Penerapan pengubahan ini pada EFB dan mendedahkan EFB setelah rawatan AP berikutnya kepada penghalusan menunjukkan bahawa kesan penghalusan dapat dipergiatkan oleh plat D2A505. Kesan tersebut amat besar sehingga pengubahan dalam kekuatan kimia ke tahap tertentu diselindungkan/dikeluarkan. Kesan daripada meningkatkan kekuatan kimia AP secara jelas digambarkan oleh refining dengan plat 12716, yang mana lebih bergantung kepada kekuatan kimia menghasilkan pemfibrilan yang mencukupi. Hal ini ditaksirkan oleh analisis pengimbasan electron mikroskopik terhadap permukaan kertas, bahagian tepi pecahan dan calitan gentian. Mengsinergikan AP dan penghalusan mekanikal dapat menghasilkan pulpa dengan sifat yang berbeza-beza.

Nyahikatan gentian kepada web nipis gentian nano juga ditemui dan ini bertanggungjawab keatas pelicinan dan pengukuhan rangkaian gentian dengan meningkatkan ikatan antara gentian.

SYNERGY BETWEEN CHEMICAL AND MECHANICAL ACTIONS IN THE ALKALINE PEROXIDE PULPING OF OIL PALM EMPTY FRUIT BUNCH

ABSTRACT

The synergy between chemical and mechanical actions in an Alkaline Peroxide Pulping (APP) system was applied for producing pulp and paper from oil palm Empty Fruit Bunch (EFB). In the APP, both pulping and brightening process occurring as one process. This process was found appropriately undertaken for 40 minutes at 70°C. Softening and brightening of EFB was found most effectively done by synergizing the strength of alkaline peroxide with mechanical fibrillation from two different Andritz Sprout Bauer refiner blade patterns. Variation of the AP strength was done by increasing the alkali-to-peroxide ratio from 2:2.5%, 4:5% to a maximum of 8:10%. Apart from that, AP strength was also increased by applying AP impregnation in multiple stages. Applying these variations on EFB and subjecting the AP-treated EFB to subsequent refining indicated that refining effect could be intensified by plate D2A505. The effect was so tremendous that variation in chemical strength was to a certain extent masked/ruled out. The effect of increasing AP chemical strength was clearly delineated by refining with plate 12716, which depended more on chemical strength to produce adequate fibrillation. These were assessed by scanning electron microscopic analyses of paper surface, burst edge and fibre smear. Synergising the AP and mechanical refining could produce a range of pulp rendering varying properties. Delamination of fibres into thin webs of nano-fibrils were also encountered and these were responsible for smoothing and strengthening of fibre networks by enhancing the inter fibre bonding.

CHAPTER 1

INTRODUCTION

1.1 Fibre, Pulping and This Study

Fibres, known for their cellulose predominance, are extracted from trees and processed into a web that can be made into sheet of paper, tissue or cardboard, depending on the amount and thickness of fibre layers. Fibres can also be molded into pulp-based products like packaging materials such as egg trays, cushions of electronic devices and fragile. While virgin wood fibre is primarily extracted from hardwood trees and softwood trees in the North American countries, China and India dominate the world non-wood pulp production. Whether of non-wood or wood origin, fibres can also be recycled from the used paper materials to complement the virgin fibres demands for paper and pulp-based products manufacturing.

Pulping is the process of extracting fibre from lignocellulosic materials , commonly wood and non-wood. It dates back from the time of Tshai Lun (105 AD) who introduced the use of chemical in the treatment of mulberry bark, which then led to the yield of papermaking fibres. The technique travelled from central Asia to Arab countries where paper mills were first built to cater for the domestic demand and export to European countries. By the 18^{th} century, papermaking process was mechanised and other pulping techniques emerged to suit the demand for mass production of paper, particularly in the time of industrial revolution. Such progress led to the present classification of pulping into three main groups: chemical, mechanical and hybrid pulping techniques.

Chemical pulping (CP) can be exemplified by Soda & Kraft pulping, which generate high pulp quality. These are also characterized as high power processes for

using high chemical, temperature and energy for pulping and subsequent bleaching of the low brightness pulp. In contrast to chemical pulping, mechanical pulping are chemical free systems and it follows that the generated pulp is of lower quality. In between the polarity are the hybrid systems, which employ a moderate amount of chemical and mechanical power for generation of wide pulp quality range.

The pulping industry is recognized as one of the most polluting sectors and since then, solution was being sought after to sustain the industry and in turn, cope with the increasing paper demand. In June1989, Andritz Sprout-Bauer came up with a so-called phase 1 of the solution to the polluting industry. Being an improvement to the Chemi-Thermo-Mechanical Pulping (CTMP) process (Cort & Bohn, 1991), the technique, known as Alkaline Peroxide Mechanical Pulping™ offers wide pulp quality range. The method is so flexible that process conditions can be adjusted to the targeted pulp properties. As a result, APMP pulp grade can be compatible to CP and at the same time environmentally friendly. The eco-friendliness of the system lies in the integration of both pulping and bleaching in a single process and this eliminates the need for a separate bleaching plant. APMP also emits low effluent volume, besides being sulfur and chlorine free. This is especially found for non-wood APMP, known for its low chemical requirement. For the basic features, the APMP™ was ever since saluted as solution to the pulping industry.

In wood pulping, this method suit excellently with some hardwoods, especially Aspen (Pan and Gordon, 2000). Recent development in APMP™ known as P-RC APMP™ had overcome the difficulties in the application of the conventional APMP™ to darker and denser hardwoods such as maple, birch and beech (Blodgett, Genco & Cole, 1997). However, to date, the availability of forest woods to fulfill the needs in papermaking resource, construction usage, and other

applications are declining due to limited and competing use of the land. Besides that, cutting trees, which is an elimination of forest fauna habitat, would cause loss of land fertility and instability in the ecosystem and ultimately, global warming. For this, non-wood has always enticed research pertinent to alternative fibre source. Species, such as kenaf, straw (Xu, 2001a), jute (Xu, 2001b) and baggase (Xu, 2001c) has been demonstrated successful in the extraction fibre via APMP systems.

When adjusted to the needs of the tropical lignocellulosic such as the oil palm biomass, only the principal concepts of APMP^{TM} were adopted. While all others gadgetries for the associated treatment system differed significantly, the use of alkaline peroxide, and the related synergistic effect of mechanical actions from the native APMP^{TM} were applied in variable ways. Considering the vast differences and the minimal commonalities, the system adopted in this study is named alkaline peroxide pulping, denoted as APP.

Specifically in this study, APP was attempted on the most abundant OPB (Law & Jiang, 2001) wastes in the palm oil milling activities. The oil palm empty fruit bunches, EFB, constitutes 20-22% (Ramli et al., 2002) of FFB (fresh fruit bunch). Besides a positive response to Green World Campaign, the effort is also to uncover the possible outcome of applying variable synergies of alkaline peroxide and mechanical fibrillation effects to liberate fibres, beyond the basic APMP.

In this study, a number of processing parameters were studied by looking at their effects of the fibre, fibre web properties and the quality of pulping effluent. In this regard, several selected environmental assessment (EA) parameters such as COD, TDS, turbidity and residual peroxide were deemed as relevant to the experimented APP system. To facilitate addressing, as a group, these EA parameters

will be referred to as CTTRP. The section that follows lists the aims of the designed study.

1.2 Objectives

1. To examine the effect of AP treatment duration on fibre web (paper) properties and on a selected set of environmental assessment parameters (CTTRP).
2. To examine the effect of impregnation stages on paper properties and CTTRP.
3. To examine the effect of refiner plate pattern on paper properties and paper morphology.

CHAPTER 2

LITERATURE REVIEW

2.1 EFB as Magnet to Pulp and Paper Industry

2.1.1 Oil Palm Plantation in Malaysia

The oil palm, *Elaeis guineensis,* is native to West Africa, but now it is planted in most of the tropical countries all over the world. It has become the most important industrial crops especially in Malaysia and Indonesia (Shuit et al., 2008) (Tanaka et al., 2004) (Sreekala et al., 1997). Malaysia was the first country to embark on large-scale planting and processing the plant (Hai, 2002), and now, Malaysia produced about 47% of world's palm oil (Sumathi et al., 2008).

The global demand of edible oil has increased from year to year as the increase of world's population. To date, palm oil is the biggest source for edible oil and fat production. This has triggered the growth of oil palm plantation, especially in Malaysia as one of the world's largest palm oil producer. Table 2.1 showed the increase of total oil palm planted areas together with oil palm Fresh Fruit Bunch (FFB) and Crude Palm Oil (CPO) average production from each state in Malaysia, including Sabah, Sarawak and Peninsular area. The largest planted area expansion occurred in 2008, which was mainly in Sabah and Sarawak.

With the growth of the oil palm plantation, it increases the generation of biomass residue, like Empty Fruit Bunch (EFB), palm kernel, fronds, and trunks. EFB can be obtained after fruits removal in the making of crude palm oil (CPO). In Malaysia only, there are almost 4.5 million hectares of palm oil planted area. This planting area could produce more than 90 million tonnes of oil palm FFB in 2008.

Each tonne of FFB generates 20-22% EFB (Ramli et al., 2002), which equal to 18.9 million tonnes annually. This large quantity of biomass need to be treated properly and utilized, rather than being burned in incinerators or left in plantation floor of palm oil mills, creating problems to the environment and also difficulties in replanting (Law & Jiang, 2001) (Sreckala et al., 1997).

Table 2.1 Palm Oil Productions in Malaysia (2004-2008)

Year	2004	2005	2006	2007	2008
Total Planted Areas (hectares)	3,875,327	4,051,374	4,165,215	4,304,913	4,487,957
Average FFB Production (tonnes/hectare)	18.6	18.88	19.60	19.03	20.18
Average CPO Production (tonnes/hectare)	3.73	3.80	3.93	3.83	4.08

Source: MPOB, 2010

2.1.2 EFB as Lignocellulosic Biomass for Pulp and Papermaking Raw Material

To prevent its accumulation, there are many attempts that has been applied to EFB to convert it into various value-added products, such as in the production of panel products (Ahmad et al., 2005), ash glaze (Mohamad, 2005), animal feed (Shuit et al., 2009), briquette as biofuel feed (Shuit et al., 2009), fillers for polymer (Abu Bakar and Hassan, 2005), and pulp. However, most of this oil palm biomass remains unused.

EFB is a fibrous material, which is also called as lignocellulosic material because it is mainly composed of holocellulose, lignin, and extractives. Table 2.2 shows the detailed chemical compositions of this biomass from some referred literature. The high content of the cellulose and hemicellulose of EFB have extent the

list of non-woody materials that the researchers tend to use in papermaking technology nowadays.

Table 2.2 Chemical constituents of EFB

Constituent	**(Law et al., 2007)**	**(Ferrer et al., 2011)**	**(Shahriarinour et al., 2011)**
Extractives	3.7±0.3	-	4.1
Acid insoluble lignin	18.8±0.3	24.45	21.2
Ash-free acid insoluble lignin	17.8±0.2	-	-
Ash	1.3±0.2	-	3.5
Hot water soluble	7.5±0.8	-	5.6
1% NaOH soluble	14.5±2.7	-	-
Holocellulose	82.4±1.4	66.97	65.5
Cellulose	62.9±2.0	-	-
α-cellulose	-	47.91	-
Hemicellulose	28.0	-	-
Arabinose	2.5±1.1	-	-
Xylose	33.1±2.6	-	-
Mannose	1.3±0.01	-	-
Galactose	1.0±0.0	-	-
Glucose	66.4±3.7	-	-

Therefore, as a major oil palm biomass generator, Malaysia has a potential in utilizing those oil palm residue such as EFB efficiently and effectively in pulp and papermaking. Its renewable potential makes EFB even more important and attracting in pulp and paper industry.

2.2 Formation of Paper

Paper is a composite material that needs a high degree of fibre bonding in the sheet formation. Paper properties depend on the chemical and physical nature of the fibres when they form the sheet of paper (Karademür et al., 2004). Fibre morphology and chemical constituent are very important to predict the pulp behavior in papermaking.

2.2.1 Fibre chemistry

The cell walls of most plants fibres (except cotton) are composed of cellulose, hemicellulose, lignin, waxes, and some water-soluble compounds that are in tight association to each other (Evans, 1994). Cell wall thickness plays important role in making the differences (Foelkel, 2007). The major components of fibre cell walls are cellulose, hemicellulose, lignin, and extractives.

2.2.1(a) Cellulose

Cellulose is the most abundant natural polymer in the world. It is a carbohydrate and is composed of only glucose. This substance determines the character of the fibre and it is a very important parameter in selecting raw material for papermaking (Smook, 1992). Cellulose is resistant to strong alkali (17.5 wt%) but it is easily hydrolyzed by acids to water-soluble sugars (Mohanty et al., 2005).

The amount of cellulose, in lignocellulosic systems, can vary depending on the species and the age of the plant. The hydroxyl group of this linear chain forms intermolecular and intramolecular hydrogen bonds with the macromolecule itself and with other cellulose macromolecules or polar molecules (Mohanty et al., 2005). Bundles of cellulose molecules known as microfibrils, gives the wood fibres their strength and rigidity. Long chain cellulose is called alpha cellulose. This chain has a Degree of Polimerization (DP) over 10000 in native wood (Smook, 1992). Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose materials. Therefore, all natural fibres are hydrophilic in nature. Although the chemical structure of cellulose from different

natural fibres is the same, the degree of polymerization (DP) varies. The mechanical properties of a fibre are significantly dependent on the DP (Mohanty et al., 2005).

2.2.1(b) Hemicellulose

The shorter chain, known as hemicellulose can be categorized as beta cellulose (DP between 90 to 15) and gamma cellulose (DP less than 15) (Smook, 1992). Cellulose in lignocellulosic materials is physically linked with hemicellulose (Shahriarinour et al., 2011). Hemicelluloses form the supportive matrix for cellulose microfibrils. Hemicellulose is very hydrophilic and soluble in alkali and easily hydrolyzed in acids (Mohanty et al., 2005). Hemicelluloses are polymers of five different sugars:

- Hexoses : Glucose, Mannose, Galactose
- Pentoses : Xylose, Arabinose.

During pulping, the amounts, locations and structures of hemicelluloses in fibre usually change, and they are the least resistant to biodegradation, microabsorption, and thermal degradation (Smook, 1992; Law and Jiang, 2001).

Among the hemicellulose, xylans are one of the most abundant biopolymers after cellulose and may constitute more than 30% of a cell wall in dry weight (Evans, 1994). Xylose is the highest sugar content in EFB among the hemicellulose's sugar. Xylans are also varying in structure, according to their botanical origin. In the plant wall, xylans interact with other structural component by covalent and non-covalent bond. Covalent bond of xylans interconnect xylans, lignin, and some phenolic acids, while non-covalent bonds, which essentially involved hydrogen bonding, interconnect xylans with other polysaccharides, in particular with cellulose

microfibrils. Xylans are present in various proportions in the cell walls and usually are constituent of secondary walls. Nevertheless, they are also present to some extent in the primary walls (Evans, 1994).

Xylans presence in the pulp fibre also gives a distinct impact on recycling behavior. The pulp loss of strength during recycling can be reduced especially in non-wood pulps with high xylans content, because higher levels of xylans promote bonding strength loss resistance during recycling (Tschirner, 2007).

2.2.1(c) Lignin

Lignin is an amorphous and highly polymerized substance, which forms the middle lamella. Lignin chemistry is extremely complex. Lignin as another primary component of plant biomass, it contains many oxygen functional groups; phenolic compounds, hydroxyl, carboxyl, carbonyl groups, ether and ester bonds (Wahyudiyono et al., 2008). During the biological synthesis of plant cell walls, polysaccharides such as cellulose and hemicellulose are produced, and simultaneously lignin fills the spaces between the polysaccharide fibres, cementing them together. This lignification process causes a stiffening of cell walls, and the carbohydrate is protected from chemical and physical damage.

Lignin is a biochemical polymer that functions as a structural support material in plants. Lignin is a high molecular-weight phenolic compound, generally resistant to microbial degradation. The exact chemical nature of lignin still remains obscure (Mohanty et.al. 2005). Lignin is believed to be linked with portions of carbohydrates through two types of linkages; alkali sensitive and the other, alkali resistant. The alkali-sensitive linkage forms an ester-type combination between lignin hydroxyls and carboxyls of hemicellulose uronic acid. The ether-type linkage

occurs through the lignin hydroxyls combining with the hydroxyls of cellulose. The lignin, being polyfunctional, exists in combination with more than one neighboring chain molecule of cellulose and/or hemicellulose, making a cross-linked structure. (Mohanty et al., 2005). It is believed that the structural units of a lignin molecule are derivatives of 4-hydroxy-3-methoxy phenylpropane.

Lignin is amorphous and hydrophobic in nature. It is a thermoplastic polymer, exhibiting a glass transition temperature of around 90°C and melting temperature at which the polymer starts to flow of around 170°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol (Mohanty et al., 2005).

Generally, the best balance of papermaking properties occurs when most of the lignin is removed from the fibres while retaining substantial amounts of hemicellulose (Smook,1992). Lignin is insoluble in many solvent and its degradation can only be done by physical and chemical treatment (Ibrahim et al, 2008).

2.2.1(d) Extractives

Extractives content vary depending on the plant source. Examples for extractives are resin acids, fatty acids, turpenoid compounds and alcohols. Most of them are soluble in water or organic solvents and collectible (Smook, 1992). Extractives are found on the primary wall of fibres. Removal of extractives would promote the external fibrillation of fibres.

2.2.2 Fibre Structure in Plants

Plant fibres are like microscopic tubes (Fig. 2.1), i.e., cell walls surrounding the center lumen. The lumen contributes to the water uptake behaviour of the plant

fibres. The cell wall is built of several layers: the primary cell wall, which is the first layer deposited during cell growth, and the secondary cell wall (S), which again consists of three layers (S1, S2, and S3). The cell walls are formed by oriented reinforcing semicrystalline cellulose microfibrils embedded in a hemicelluloses/lignin matrix of varying composition. Such microfibrils are made up of 30 to 100 cellulose molecules in extended chain conformation, and provide mechanical strength to the fibre. The amorphous matrix phase in a cell wall is very complex and consists of hemicellulose, lignin and in some cases, pectin. The hemicellulose molecules are hydrogen bonded to cellulose and act as a cementing matrix between the cellulose microfibrils, forming the cellulose/hemicellulose network, which is thought to be the main structural component of the fibre cell. The hydrophobic lignin network affects the properties of the other network in a way that it acts as a coupling agent and increases the stiffness of the cellulose/hemicellulose composite. The cell walls differ in their composition, the ratio between cellulose and lignin/hemicellulose, and in the orientation of the cellulose microfibrils.

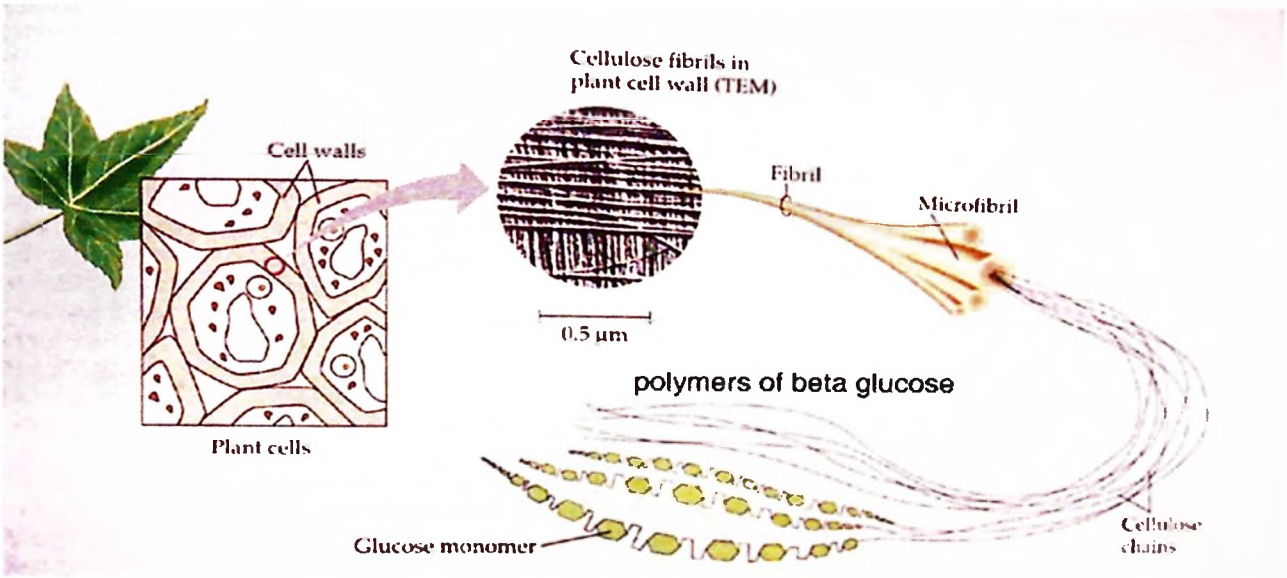

Figure 2.1. Plant cell walls (Source: http://academic.brooklyn.cuny.edu/biology/bio4fv/page/cellulose-fibres.jpg).

Fig 2.1 generally describes fibre structure in most plants. The position of the cellulose and other polysaccharides are shown in Fig. 2.2.

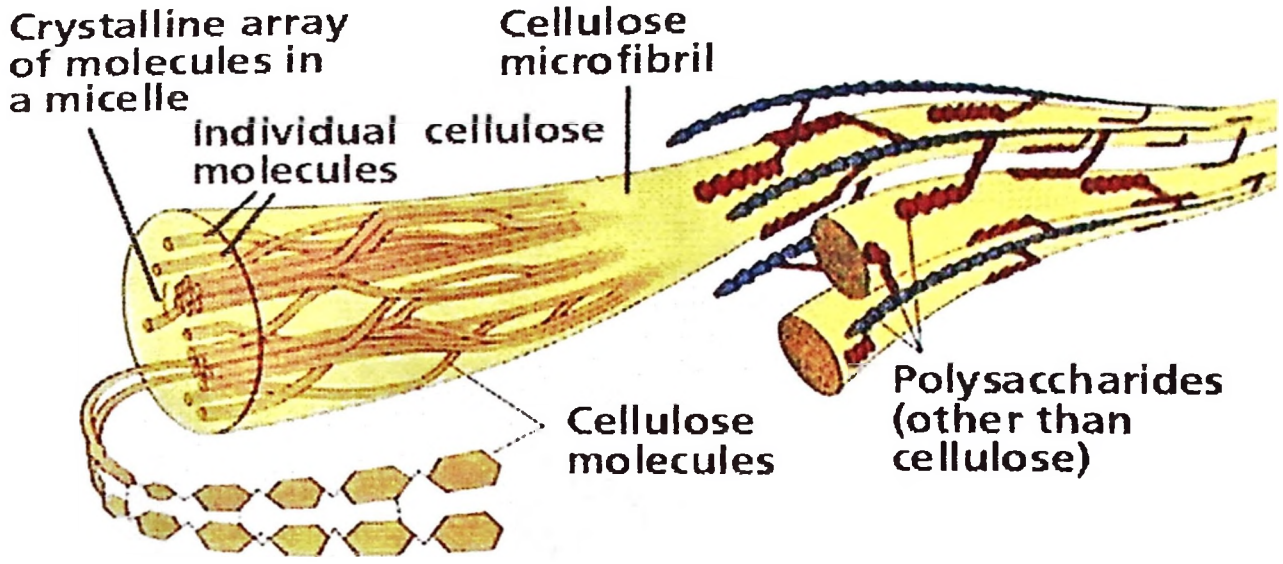

Figure 2.2. Cellulose molecules and other polysaccharides in a fibril (Source: http://www2.estrellamountain.edu/faculty/farabee/biobk/cellulose.gif).

Cellulose is indigestible by human body. The cellulose molecule is shown in Fig. 2.3.

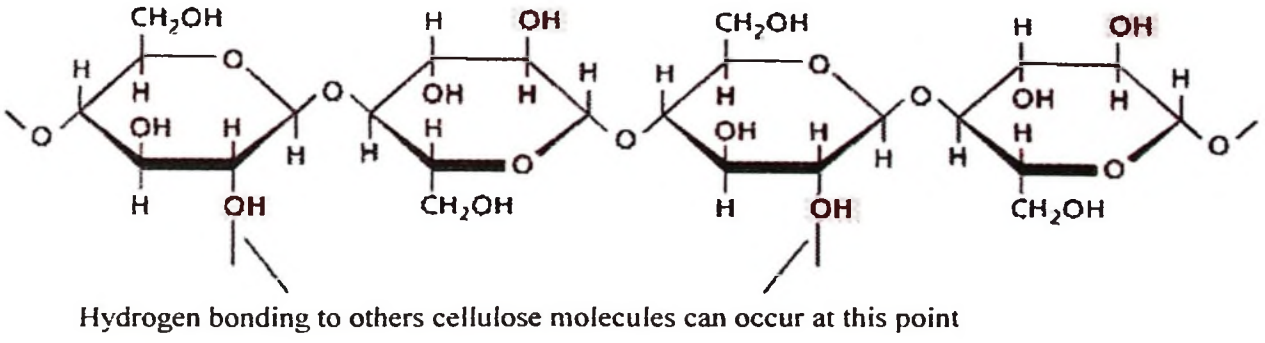

Figure 2.3. Cellulose molecule (Source: http://www2.estrellamountain.edu/faculty/farabee/BIOBK/cellulo.gif).

2.2.3 Pulp quality parameters

According to Foelkel (2007), papermaking behavior of the pulp depends on the anatomical and chemical properties of the fibres, fibre debris, fines, and vessel elements, which are parts of the pulp itself. Drainage or Canadian Standard Freenesss (CSF) is depends on the number of fines, fibre population, water retention (fibre swelling), flexibility of fibre, and ability to form a web. Sheet behavior depends on fibre strength, fibre length, fibre bonding, contaminants (shives, sand, etc.), and individual fibre strength.

2.2.3(a) Population of fibre

Fibre population means number of fibre per gram pulp, in other words, it is related to the weight of individual fibre. This depends on the fibre coarseness, which depends on the fibre wall thickness, lumen diameter, fibre length, fines, etc. (Foelkel, 2007). Lower fibre population will results in better drainage, more porous pulp, more permeable and absorbent.

2.2.3(b) Individual fibre strength

Zero spans are very useful in predicting this pulp quality (Foelkel, 2007). This is known as a fast and economical method for assessing the individual fibre strength from various types of papermaking pulp. however, there are uncertainities regarding this concepts, because the zero span is indicated to both increase and decrease with the degree of refining. The results are affected by several parameters, such as fibre bonding, amount of fibres in ruptured area, fibre length distribution, etc. (Somboon & Paulapuro, 2009).

2.2.3(c) Fibre collapsibility

Fibre with better collapsibility will make the paper sheet denser and causes the fibre walls closer to each other, improving fibre bonding and strength properties that depends on it, like tensile, burst and folding (Foelkel, 2007).

2.2.3(d) Fibre swelling

This property is highly affected by pulping and bleaching process. It is also affected by hemicellulose content in the pulp (Foelkel, 2007).

2.2.3(e) Fibre deformation

Fibre deformations during papermaking may reduce individual fibre strength, but they give benefit in promoting bulk. Fibre deformation includes curl index, fibre kinks, fibre latency, and fibre microfractures in the cell wall, which affect the individual fibre strengths but improve paper sheet porosity, bulk, smoothness and water absorption (Foelkel, 2007).

2.2.3(f) Fibre bonding

Bonding ability depends on fibrillation, fibre collapsibility, hemicellulose content, fibre population, draiability, and fines content. Low hemicellulose and high coarseness will result in low bonding ability (Foelkel, 2007).

2.2.3(g) Fines content

Fines are important for fibre bonding. Pulp without fines has poor bonding ability and low strength, while pulp with excess fines creates high density of paper.

Fines are seen as filler in the pulp supply. Fines are not fibres, they are debris or "weak parenchyma cells". But when they are created in great extent during refining, the fines dramatically affect drainability in the wet end section (Foelkel, 2007).

2.2.4 Bonding in paper

The bonds between fibres occur due to multiple hydrogen bonds within bonded areas in between the contacting part of fibres (Roberts, 1996). To accommodate the hydrogen bond which its length is only in few nanometers, the surface of the fibres must be close enough to contact to each other (Roberts, 1996).

2.2.4(a) External fibrillation

In external fibrillation, outer layers of fibre bonds are removed, exposing fibrils of the secondary wall, thus create interfibre bonding. Fig. 2.4 illustrates the external fibrillation, fibre shortening and fines generation.

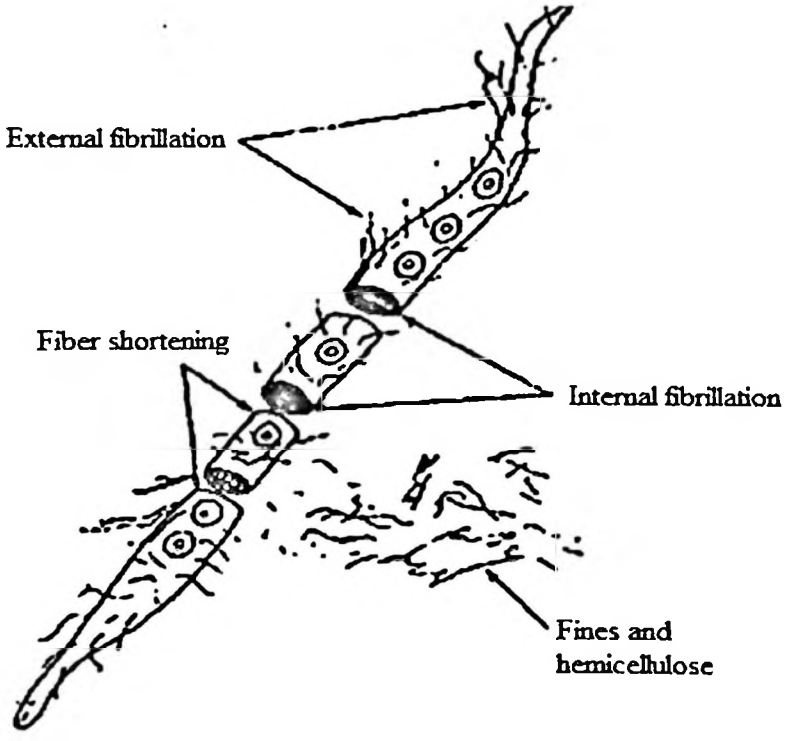

Figure 2.4. External fibrillation on fibre (Source: Anonymous, 2012).

2.2.4(b) Internal fibrillation

Fig. 2.5 illustrates the mechanism of internal fibrillation due to fibre swelling caused by refining/beating after delignification. In a study by Ashaari et al. (2010), the sodium hydroxide (NaOH) treatment is very helpful in the swelling of the cell wall and in producing fibre with small lumen size known as closed lumen.

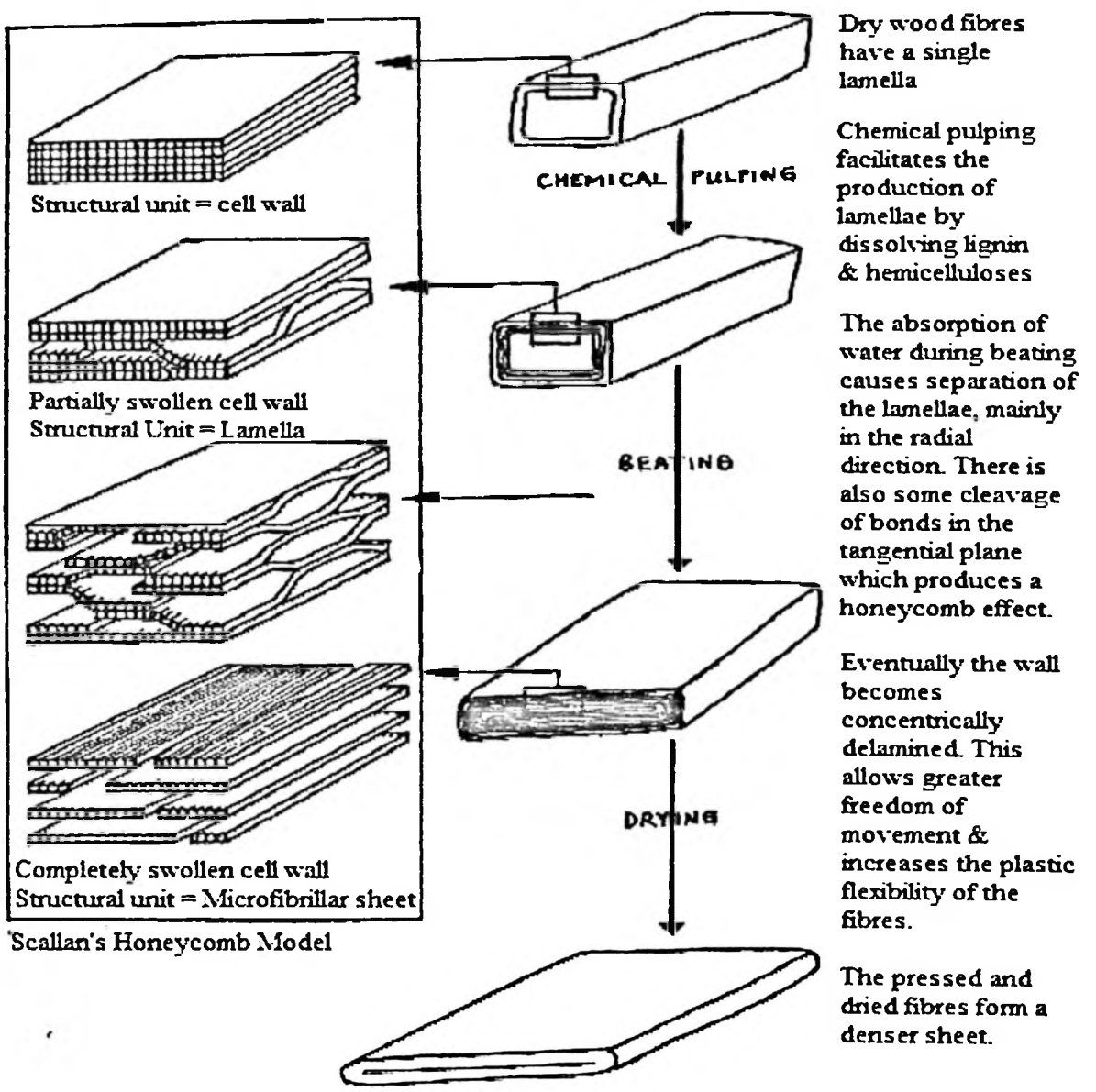

Figure 2.5. The mechanism of internal fibrillation by chemical pulping and beating. (Source: Anonymous, 2012).

During chemical pulping, lignin and some hemicellulose are dissolved in the pulping liquor, which made the water absorption easier. Beating or refining would stimulate the water absorption and cause the fibre to swell. The fibre walls become delaminated and the flexibility increases, and when it is made into handsheet, the internal fibrillations occur and a denser sheet is formed.

It is known that internal fibrillation separates bundles of fibrils located in the interior of the cell wall of fibres without causing generation of fines. Water is then able to reach the new surfaces producing swelling and separating individual interior fibrils (hydration). Because of the internal fibrillation, the fibres become plasticized and more deformable, improving fibre to fibre contact area during pressing and dewatering (Anonymous, 2012).

All this is very much influenced by the technique of extracting the fibre called pulping.

2.3 Pulp and Papermaking

2.3.1 Development in Pulp and Papermaking Process

It is widely known that papermaking was initiated in China in the 2nd century B.C during the former Han Dynasty, which was at least 200 years earlier than what was recorded in the official history. This includes the invention of craft papermaking by Tshai Lun in 105 A.D. The early paper was made from hemp or ramie fibres, which was taken from rags or fishing net. Meanwhile, 200 years later, the papermaking invention by Tshai Lun was using new materials of tree bark and hemp ends. This invention is the real technical innovation, which determined the rise of Chinese cultural society onwards. This new pulping technique spread gradually to

the neighboring countries for over 300 years including Korea and Japan in the beginning of 7th century (Enami et al, 2010).

Afterwards, it was not the sophisticated papermaking craft that has been spread to the westward by Chinese craftsmen in 751 during the battle of Tang Empire and Arabs. It was the primitive papermaking craft using cloth rags that had been kept by the Arabs for over 400 years. This papermaking was then accepted by European countries in Spain in 12th century and the Italy in13th century. Due to the deficit in rags and the increasing demand of paper, in early 18th century, the European started to produce paper by making use of plant fibres as the printing technique started developing since the year 1450 (Enami et al, 2010). This was a sign of the end of handmade paper and the beginning of mechanization of papermaking.

The researches in papermaking have been developing through centuries in order not only to fulfill the increasing demand, but also to face the challenges and the desire to improve the pulp and paper quality, the effectiveness of the process, the efficiency in raw material, chemical and energy usage.

In general, there are three classification of pulping techniques. Mechanical pulping can involves mechanical action with elevated pressure or mechanical action with both elevated pressure and temperature. While chemical pulping involves in cooking of wood chips in aqueous solution, containing appropriate chemicals at elevated pressure and temperature. Semichemical (hybrid) pulping is a combination between chemical and mechanical pulping method (Smook, 1992).

Those three types of pulping methods would also produced different range of pulp and paper properties, as well as different range of yield. The highest pulp yield can be obtained from mechanical pulping, which is 85-95% (Smook, 1992). The yield of pulp produced by chemical pulping is usually very low, which is around

40-50% (Anonymous, 2011; Smook, 1992). Meanwhile, pulp from a hybrid process would yield about 55-85% of oven dry raw material (Biermann, 1996; Smook, 1992).

2.3.2 Mechanical Pulping

The main processes for mechanical pulps are Stone Groundwood (SGW), Pressure Groundwood (PGW) Thermomechanical Pulping (TMP) or Refiner Mechanical Pulping (RMP) (Bajpai, 2012; Smook, 1992). Groundwood process is one of the major and the oldest method in the production of mechanical pulps. The process is simple but it needs special care to produce a good quality pulp. In SGW, debarked shorts logs (roundwood) are fed whole against a wetted, roughened grinding stone which is revolving with pheriperal speeds of 1000-1200 m/min (Smook, 1992; US Congress, 1989). Fibres are washed away from stone surface with water. The grinding process usually is automatic and continuous. Oversize particles are removed from the slurry of fibre and fibre fragments by screening and prepared for the paper machine (Smook, 1992).

Compared to chemical pulp, groundwood pulp is lower in strength and turn yellow with time (Fernando et al., 2007; Koivo, 2002; McDonald et al., 2004). Individual fibres, broken fibres, fines and bundle of fibres are common composition in groundwood pulp (Riegel, 2007). A very harsh mechanical actions in SGW generates large portions of fines with shorts fibre compared to TMP (Fernando, 2011). In order to achieve high yield with acceptable properties in mechanical pulping, the main part of lignin is maintained, so that the groundwood pulp is often cooked to soften it (Bajpai, 2012). Nevertheless, groundwood pulp is economical since all the wood is used and it provides smoothers papers (Bajpai, 2012; Fernando et al., 2007; Koivo, 2002; McDonald et al., 2004).

A more recent development is known as refiner mechanical pulp (RMP) involves defibreization of wood chips using a device called refiner. This process yield a stronger paper compared to groundwood pulp. When a pressurized steam pretreatment to the wood chips is applied, the product is called thermomechanical pulp (TMP). This is a common pulping method in producing pulps from softwood species (Smook, 1992).

2.3.3 Chemical Pulping

The most used pulping technique in world pulp production is chemical pulping. There are several chemical pulping processes and all of them are intended to remove lignin from biomass as much as possible. During chemical pulping, lignin was degraded and dissolved into spent liquor due to high temperature and high pressure (Ibrahim et al, 2008). In chemical pulping of EFB, lignin was degraded into 8 compunds; vanillin, hydroxybenzaldehyde, syringaldehyde, vanillic acid, 4-hydroxybenzoic acid, syringic acid, p-coumaric acid and ferullic acid (Ibrahim et al, 2008). Examples for chemical pulping techniques are kraft, soda and sulfite pulping.

2.3.4 Semichemical Pulping

Among semichemical processes in 1990's, the neutral sulfite process is the most widely used. This pulping process is called as Neutral Sulfite Semichemical (NSSC), which utilized cooking liquor made of sodium sulfite buffered with sodium carbonate for neutralization of organic acids form during wood chips cooking (Smook, 1992).

The other hybrid process is known as Cold Caustic Soda (CCS) process, is one of earliest chemical mechanical pulping (CMP) process for hardwood. This

method used cold caustic in the pretreatment of raw material (hardwood chips) before refining. Later, a pressurized refining process was introduced, which is referred as CTMP (Chemi-Thermo-Mechanical Pulping) process. For some CTMP system, there is a need for post bleaching to improve the properties of pulp, especially the brightness. This system was then often called BCTMP.

Due to the concern in environmental impact cause by pulp mills effluent, there were many research have been done in order to minimize the toxicity of the spent liquor, such as by chemical recovery or extraction of some organic compound from spent liquor such as lignin (Ibrahim et al, 2008) and hemicellulose (Ribe et al, 2010) for other uses. But the most attractive is the invention of a new CMP technology called APMP. This method will be focused separately in Subchapter 2.4 as it is closely related to the APP method.

2.4 Alkaline Peroxide Pulping (APP)

Alkaline Peroxide Pulping (APP) is a simple pulping method derived from the concept of Alkaline Peroxide Mechanical Pulping (APMP^{TM}). APMP^{TM} has been proven as the most attractive pulping method since its invention in 1989. Now, it has been used widely all over the world (Zhang et al., 2011).

In early studies, this method suit excellently with some hardwoods especially Aspen (Pan and Gordon, 2000). There are also several studies that have been carried out on APMP^{TM} involving softwoods and non-woods. Some of them also showed very good responds to alkaline peroxide treatment. In the work of Xu, kenaf, straw (Xu, 2001a), jute (Xu, 2001b) and bagasse (Xu, 2001c), were amongst the non-wood raw materials researched for their APMP success. It was found that alkaline peroxide treatment in general gives better optical properties and higher pulp yield at

similar strength compared to other conventional chemical pulping, such as kraft and cold soda pulping (Xu, 2001d). The application of APMP™ on baggase would consume less energy and better bleachability compared to the application of kraft pulping, and at medium chemical level, the resulting pulp strength was similar to Aspen (Xu & Rao, 2001).

Generally, integration of pulping and bleaching processes into a single APMP process, particularly, offers reduction in refining energy up to 35% while eliminating the installation cost by 50%, in comparison to chemical pulping or chemithermomechanical pulping with bleaching process (Xu & Rao, 2001; Burkhart, 2001).

The mechanism of APMP system includes chemical impregnation in single or multiple stages and then followed by refining process, washing, and a final stage of refining respectively. For the first stage, the chips are presteamed prior to any mechanical compression, so that the chips will compress without shattering, which means fewer fines would be generated from the process. After steaming, the chips are compressed so that some of the water-soluble organic components are squeeze out of the wood and then the chemicals are added for pulping and bleaching purposes. The second stage of impregnation is count on a high-compression screw to squeeze out the first stage chemicals and reaction products from the chips as much as possible. This is a kind of washing that helps to improve the bleaching reactions to occur in the second impregnation zone (Cort & Bohn, 1991).

The major difference between APP and APMP ™ is that the APP technique has eliminated the use of impressifiner (Figure 2.6), which is the "heart" of the APMP™ technology. Impressifiner in original is a type of a screw feeder that gives mechanical compression to the raw materials. Compression would create cracks in

raw materials and squeeze out fluid contents (Blodgette, Genco & Cole, 1997). This increases the penetration ability of the said raw material upon decompression. Therefore, as the fluids squeezed out (most of them are probably moisture and air), the pulping liquor can be absorbed due to the re-expansion of material at decompression stage (Cort & Bohn, 1991).

Nowadays, there are several pulp and paper mills operating under APMP technique. The raw materials that they have been using are aspen, eucalyptus and spruce. But some difficulties were found in the application of this method to the darker and denser hardwoods such as maple, birch and beech (Blodgett, Genco & Cole, 1997). A more recent development in APMP from Andritz Inc., an international technology group, headquartered in Graz, Austria has lead to the application of chemical refining process after impregnation process, known as P-RC APMP (Pre-conditioned Refiner Chemical APMP). Several benefits of P-RC APMP^{TM} technology over other pulping techniques:

- High process yield
- Low specific energy consumption
- High efficiency, because of low chemical consumption
- Superior pulp quality
    - Excellent optical properties, including brightness, light scattering, opacity
    - High tensile strength
- Low operating costs
- The pulping effluent gives minimum level of COD and BOD
- One of the sulphur-free process, which leads to improve bio-degradability of pulp mill effluent