THE EFFECT OF DIFFERENT HYDRAULIC RETENTION TIME (HRT) ON BIOLOGICAL PRETREATMENT TO CHEMICAL PULPING

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A report submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering

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DECLARATION

I declare that this thesis entitled "The Effect of Different Hydraulic Retention Time on Biological Pretreatment to Chemical Pulping" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : Siti Nur Nadzmiah Binti Mohd Nor

Date : NOVEMBER 06

DEDICATION

This thesis is dedicated to my parents, Mohd Nor and Rokiah, with deepest gratitude for all their support during the many life changes I faced while working on this research. I can never say “thank you” enough. I love you both.

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ABSTRACT

Low composition of lignin and high of cellulose contains showed that banana stem wastes one of good sources for pulping purpose. These materials are cheap and can easy to get, since banana was planted widely in Malaysia for commercial used. After its harvesting, the banana stem are cut and usually left in the soil plantation to be used as organic material where actually, this crops can be used for more rational way of utilization, namely as a sources of cellulosic fibre for pulping process. Common chemical pulping process that had been used nowadays in industry frequently bring harms to the environment and also to human life as it consume and produce much of chemical reagent. Thus, the purpose of biological pretreatment using mixed culture from banana soil plantation with different Hydraulic Retention Time (HRT) in this study is to reduce the amount of chemicals that will be used and produced from the chemical pulping process and also to reduce costs, energy consumption and time needed for the pulping process. The goal of biological pretreatment is to break lignin seal and disrupt the crystallize structure of cellulose in the banana stem waste and the different HRT that was used are 9, 19.5 and 30 days where it is believed that different HRT has its own effect to the treatment process. From the experiment, the maximum amount that can be degraded is about 5.5 % of lignin. The best HRT that been analyzed is HRT equal to 19.5 days. The treated banana stem showed the positive result in chemical pulping process where percentages of lignin reduced is higher than untreated banana stem wastes.

Keyword: *Chemical Pulping, Biological Pretreatment, Hydraulic Retention Time*

ABSTRAK

Kandungan lignin yang rendah manakala kandungan selulosa yang tinggi yang terdapat dalam batang pisang terbuang menunjukkan ia adalah salah satu sumber yang baik bagi industri pemulpaan. Bahan ini adalah murah dan mudah didapati memandangkan ianya ditanam secara besar- besaran di Malaysia bagi tujuan pengkomersilan. Kebiasaannya, selepas proses pemungutan atau penuaian dilakukan, ianya akan dipotong dan dibiarkan sahaja di kebun untuk digunakan sebagai bahan organik walhal batang pisang terbuang ini boleh digunakan dalam cara yang lebih rasional iaitu sebagai sumber selulosa bagi proses pemulpaan. Proses pemulpaan kimia yang sering digunakan dalam industri pada hari ini mendatangkan ancaman kepada haiwan dan juga manusia memandangkan ia banyak menggunakan dan melepaskan bahan kimia yang berbahaya. Maka, tujuan pra rawatan biologi menggunakan kultur campuran daripada tanah kebun dengan nilai Masa Penahanan Hidraulik (HRT) yang berbeza adalah untuk mengurangkan jumlah bahan kimia yang akan digunakan dan dihasilkan sekaligus mengurangkan kos perbelanjaan,tenaga dan masa dalam proses pemulpaan kimia. Matlamat dalam prarawatan ini adalah untuk memecahkan ikatan lignin memutuskan ikatan kristal selulosa di dalam batang pisang terbuang tersebut dan nilai HRT yang berbeza yang digunakan adalah 9, 19.5, dan 30 hari dimana masing-masing akan memberikan impak yang berlainan terhadap proses pra rawatan. Berdasarkan kajian yg telah dilakukan, nilai tertinggi pengurangan lignin daripada proses prarawatan adalah bersamaan 19.5 hari. Eksperimen juga menunjukkan hasil yg positif dimana batang pisang yang dirawat menunjukkan pengurangan lignin yang lebih tinggi berbanding batang pisang yg tidak dirawat.

Keyword : *Pemulpaan kimia, pra rawatan biologi, Masa Penahanan Hidraulik*

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LIST OF SYMBOLS

HRT	-	Hydraulic Retention Time
TAPPI	-	Technical
mL	-	Mililiter
^{o}C	-	Degree Celcius
L	-	Liter

LIST OF EQUATIONS

CHAPTER 1

INTRODUCTION

1.0 Introduction

Pulping is defined as the act of processing wood (or other plant) to obtain the primary raw material for making paper, usually cellulose fibre (New Page Glossary, 2005). In the pulping process, cellulose fibres are released from the plant material, by destruction or removal of most of the hemi cellulose and lignin components. This cellulose fibre can be use for many purposes such as producing paper, textiles and also can produce ethanol if we degrade it.

Almost all pulping processes are generally classified as chemical pulping and mechanical pulping. In paper and pulp industry, using chemical pulping is more expensive to produce paper than mechanical pulping, but it has better strength and brightness properties. Chemical pulping is defined as the process by which wood or non wood is broken down into pulp with the use of chemicals which remove lignin and other wood constituents from the wood fibre (Pulp and Paper Technology, 2006). The use of the chemical in this process is not environmental friendly and can bring harm to human life (Scott, 2001). Thus, in this study, biological pretreatment will be applied to chemical pulping process, in order to reduce the consumption of chemical and energy and have less impact to the environment.

Biological pretreatment or bio pulping can be defined as the pretreatment of wood or non wood chips with a lignin-degrading fungus prior to pulping. (Scott, 2001) The biotreatment process is designed to produce a uniform treatment. Thus, the uniformity of the chips being sent to the digesters can potentially improve, since random degradation by other organisms is eliminated through the use of biopulping. In this study, the organisms that will be used are mixed culture which can degrade lignin from the raw materials.

The aims of this study are to study what is the optimum hydraulic retention time for pretreatment of banana stem waste. Hydraulic retention time in biotechnology is the average time a particle or volume element of the culture resides in a bioreactor (or other device) through which a liquid medium continuously flows. Hydraulic retention time of the liquid is the reciprocal of dilution rate (Wikipedia, 2006).

In this study, banana stem wastes will be used as the raw material because of besides it's easy to get, and a very good source of cellulose fibre. Banana stem wastes are extremely cheap and often free so this will decrease the cost of producing the paper.

There are two types of operations in chemical pulping process, that are batch and continuous. In this study, semi continuous operations will be used because there are lots advantages compared to continuous process. Some of the advantages are do not require much control, can be accomplished with unskilled labor and it also has greater flexibility compared to continuous operation (Hisa, 2005).

1.1 Problem Statement.

The use of forest sourced fibre to produce paper has increased greatly over the last hundred years. This has placed great demands on the world's available forest resources and it is now widely recognized that alternatives must be found. Recycling has been embraced in many countries as one way to reduce the amount of deforestation by the re-use of paper. Although recycling can assist in the reduction of the amount of forests being harvested, it cannot stop it (Papyrus Australia, 2006). The costs of collection and reproduction in addition to the continuous deterioration in quality of recycled fibre means that it can only be recycled a handful of times and then only into inferior products.

Current paper production technologies are faced with considerable environmental challenges. Consumer environmental awareness and the imposition of increasingly rigorous environmental standards dictate that current pulp and paper producers will need to make further significant investments aimed at reducing:

- The amount of water used during production.
- The amount of energy consumed, and therefore the amount of green house gases generated
- The amount of chemical additives in the production process
- The amount of harmful chemicals in the effluents which are released back into the environment.

Using biological pretreatment before chemical pulping process can reduce the impact of chemical pollution from chemical pulping by reducing the consumption of chemical reagent. Biological pretreatment also has a high interest in the industry due to its potential to save energy and costs. The usage of banana stem waste as the raw material also is one advantages as besides providing the cellulose fibre, it also can reduce the forest issue.

1.2 Objective

The aim of this study is:

i. To study the effect of hydraulic retention time (HRT) on biological pretreatment to chemical pulping process.

1.3 Scope of Study

To achieve the objective of this research, there are three scopes that have been identified:

i. To study the effects of biological pretreatment to the chemical pulping process.
ii. To study the lignin biodegradation of banana stem wastes.
iii. To analyze lignin, cellulose and glucose composition

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biological pretreatment has the potential to improve the quality of pulp, properties of paper and to reduce energy costs and environmental impact relative to traditional pulping operations. It has been suggested that energy savings alone could make the process economically viable. Other benefits include improved burst strength and tear indices of the product and reduced pitch deposition during the production process (Breen and Singleton, 1999).

It is hypothesize that the biological pretreatment actions of the fungi cause a swelling and softening of wood cell walls as a result of the modification and depolymerization of the lignin. This action should result in better liquor penetration thus improving the chemical pulping process (Scott, 2001)

2.2 Material for Pulping

Almost all pulp and paper fibre resources are plant materials obtained from trees or agricultural crops. These resources encompass plant materials harvested directly from the land (wood, straw, bamboo, etc.), plant material byproducts or residuals from other manufacturing processes (wood chips from sawmills, bagasse fibre from sugarcane processing, cotton linter, etc.), and fibres recovered from recycled paper or paperboard (Ince, 2004). Figure 2.1 show that wood is the main raw material that used for the pulping process with 40%, follow by 32% of agro residue such as wheat straw, hemp, sugarcane and about 28% from wastepaper.

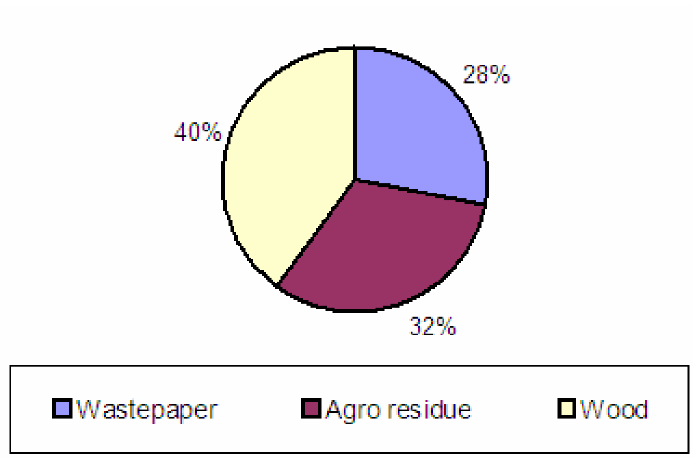

Figure 2.1: Share of paper production based on raw material (Efficient Water use in Agro Based Industries, (2002))

All this while, wood has been the primary fiber used to manufacture paper. The coniferous woods or softwoods are the most preferred species. Although hardwoods are now increasingly being used, they are not preferred because they do not, as do many softwoods, give a uniform pulping. The chemical composition of a hardwood sometimes renders it less suitable for pulping, and sometimes its structure is so dense that pulping liquors cannot penetrate easily. Hardwoods have been considered less suitable for pulping than softwoods as they possess shorter fibre and produce less uniform pulp. Fibre length has for a long time been considered of primary importance for the quality of paper pulps (Banglapedia, 2006).

However, either hardwoods or softwoods both are come from forest. The plundering forests by the timber industry have severe ecological consequences for the nation and the world: loss of wildlife and habitat; degradation of riparian ecosystem;

increase global warming; pollution of air and water; and disruption of local communities and economies. With global fiber demand expected to increase yet another 32% by the year 2010, experts are wondering just where the material will come from. While we must focus on paper-use reduction strategies to limit paper production, the reality is, paper will continue to need fiber. Reducing paper consumption levels through reduction, reuse and recycling strategies is crucial to preserving our forests. However, we have yet to succeed in adequately protecting domestic forests. It is critical that we stimulate public demand for tree free fiber papers and support the development of a non-wood pulping industry in order to slow the destruction of our global forests being logged for wood-based paper production (Hurwitz, 2000).

Paper made without trees is not a new concept. In fact, it is as ancient as paper itself: throughout history, paper was made exclusively from non-wood plant fibers (Hurwitz, 2000). Non-wood fibers have a long history as a raw material for papermaking. Hemp, ramie, cotton and rag fibers have been used for almost 2,000 years and wood only started to replace them when paper usage began accelerating about 200 years ago and textile fibers out-priced themselves (Central Pollution Control Board, 2006). Numerous agri-fibers are ideally suited for paper production, including kenaf, hemp, agricultural residues (such as cereal straw, sugarcane bagasse, cotton Linters, corn stover, etc.), and reclaimed fabrics and even recovered currency. Most of these fibers yield more pulp per acre than forests or tree farms, and require fewer pesticides and herbicides (Hurwitz, 2000).

Non wood fibres are an excellent raw material for printing papers, providing up to 50% of the fibre furnish, and can also be used for tissue and board production (Central Pollution Control Board, 2006). Moreover, due to their inherently light color, agri-fibers can be effectively brightened using totally chlorine-free (TCF) bleaching processes, eliminating the production of highly toxic chlorine by-products such as dioxin. Annual crops like hemp and kenaf also provide a means of adding strength to recycled fibers without using wood to produce recycled paper and paper products (Hurwitz, 2000).

In this study, banana stem wastes will be used as the raw material. Banana fibre paper is believed to be an alternative to the conventional recycled and virgin wood paper as it has great advantages in processing and in producing unique paper products. Banana fibres have emerged as the most popular raw material, as they are produced from banana growing. Furthermore, paper manufactured from banana fibers demonstrates higher quality of pulp. Banana paper is produced using the fiber inside the pseudostem of banana plant (Nurul Huda, 2004). These pseudostems is usually considered waste in the banana industry and are a particularly beneficial raw material for papermaking as they are a co-product of agricultural production, require no additional land, and are currently available in large quantities at low prices (Hurwitz, 2000). Harvesting banana for use in papermaking helps farmers avoid polluting the air and violating regional burning phase-downs or paying for disposal. Therefore, it makes sense to turn such waste into a useful product like paper.

Banana fibre has great advantages over paper from wood pulp. One of the advantages is its strength. Studies have shown that banana paper is 300 times stronger than normal paper. The unit to measure the strength of paper is BF or bursting force. Ordinary paper from wood pulp has a BF in the range of 15 to 20 units; while banana paper has strength as high as 44 BF (Nurul Huda, 2004).Another advantage bananas stem wastes as the raw material is low lignin composition and high cellulose composition. Because they contain less lignin, fewer chemicals and less time and energy are needed to pulp it.

As shown in Table 2.1, there is only about 12.25 wt% dry of lignin in banana stem. This lignin is undesirable product while cellulose is the desirable product of pulping process.

Table 2.1Chemical composition of Banana stem (Belgacem, 2003)

Name	Banana stem
Chemical composition	(wt% dry)
Ashes	14.6
Diethyl ether	0.4
Ethanol/ toluene	2.3
Water	5.4
Holocellulose	65.2
Lignin	12.7
Cellulose	40.2

Currently, most of the producers of banana paper are small in size. They produce products like gift wrapper, card and wallpaper. In Malaysia, the banana fiber paper industry is yet to be developed. Countries planning to develop banana paper on a larger scale include Australia, Japan and India. However, they are all in the early stages of commercialization. Since banana in grown extensively in Malaysia, banana paper industry can potentially be commercially viable (Nurul Huda, 2004).

Shifting towards agricultural fiber sources offers a tremendous opportunity to diversify the paper industry's reliance on trees and forests for paper fibers while reducing the pollution associated with wood-based pulping processes, and providing an economically feasible means of disposing of agricultural residues other than burning. It also stimulates new economic activity in rural communities. Of course, by substituting non-wood fibers for wood, we can also significantly reduce the number of trees clear-cut for paper, thereby helping to preserve our forest heritage for generations to come (Hurwitz, 2000).

2.3 Biological Pretreatment

Biological pretreatment in pulping or biopulping is the process of using genetically modified fungus to metabolize the lignin in wood, rendering it soft and ready for paper production (Rademacher, 2005). The fungal treatment wills not appreciably effecting cooking liquor consumption. Environmentally, BOD and COD (Biological and Chemical Oxygen Demand) remained essentially unaffected, while the effluent toxicity was substantially lowered with the treatment (Scott, 2001). Thus, the fungal pretreatment was shown to be advantageous for chemical pulping. Additional benefits from pretreating wood with fungi for biological processing include the reduction of wood extractives such as tringlycerides, fatty acids, and resin acids (Blanchette et al., 1992; Brush et al., 1994; Farrell et al., 1993; Fisher et al., 1994). These components, commonly called pitch, cause major problem during pulping and papermaking processes by increasing the frequency and length of machine shutdowns, increasing break in the paper roll, and decreasing paper strength (Allen, 1980 and Smook 1992). The goal of biological pretreatment is to break lignin seal and disrupt the crystallize structure of cellulose was shown in Figure 2.2.

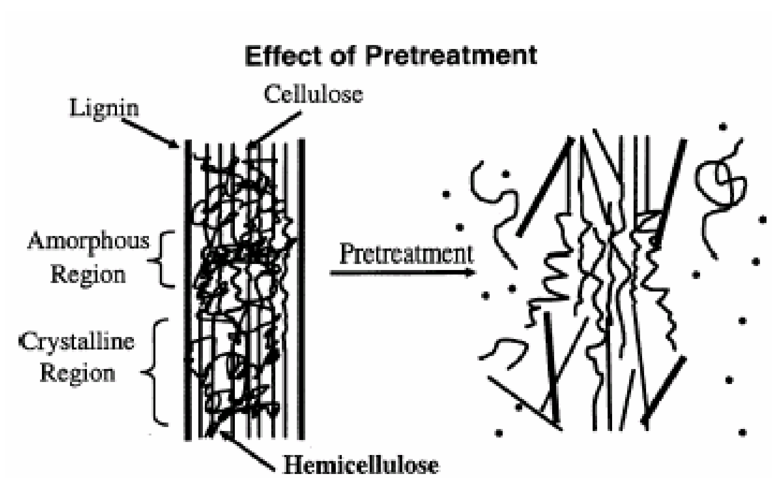

Figure 2.2: Schematic of goals of pretreatment on lignocellulosic material (Hsu et al., 1980)

2.3.1 Lignin Biodegradation as Biological Pretreatment

Lignin degradation and or modification by fungi are the key step in lignocelluloses decay (Martinez et al., 2005). Lignocellulose is the predominant component of woody plant and dead plant materials, and the most abundant biomass on earth. Lignocellulosics materials are comprised of lignin, hemicellulose and cellulose and are thus sometimes called cellulosics materials. One of the primary functions of lignin is to provide structural support for the plant. Thus, in general, trees have the higher lignin contents then grasses (Hisa, 2005).

Unfortunately, lignin which contains no sugar encloses the cellulose and hemicellulose molecules, making them difficult to reach. Lignin or sometimes called *"lignen"* is a chemical compound that is most commonly derived from wood. It is the second most abundant organic compound on earth after cellulose. Lignin makes up about one-quarter to one-third of the dry mass of wood (Wikipedia, 2006). Lignin is highly resistant towards chemical and biological degradation, and confers mechanical resistance to wood. The highest concentration of this recalcitrant polymer is found in the middle lamella, where it acts as a cement between wood fibers, but it is also present in the layers of the cell wall (especially the secondary cell-wall), forming, together with hemicelluloses, an amorphous matrix in which the cellulose fibrils are embedded and protected against biodegradation (Fengel and Wegener, 1984). Lignin plays a crucial part in conducting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water. Lignin makes it possible to form vessels which conduct water efficiently. Lignin is difficult to degrade and is therefore an efficient physical barrier against pathogens which would invade plant tissues. For example an infection by a fungus causes the plant to deposit more lignin near the infection site (Wikipedia, 2006). Chemically, lignin is made up of thousands of rings of carbon atoms joined together in a long chain. The way in which they are linked up varies along the chain.

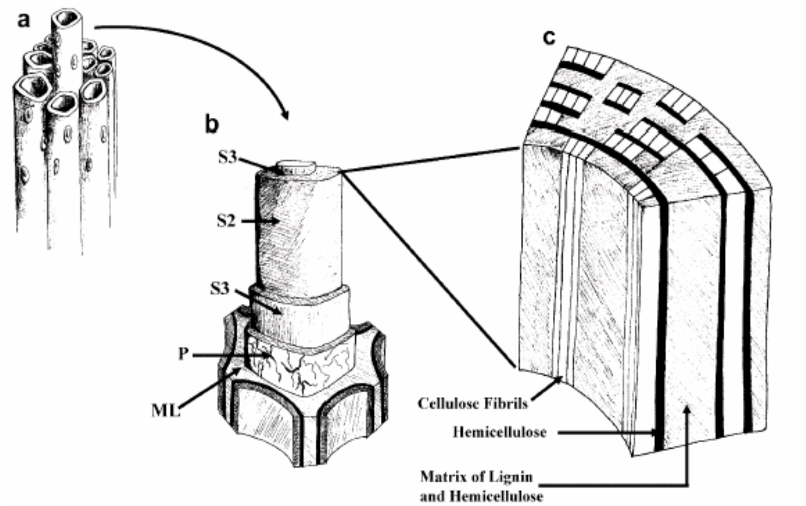

Figure 2.3 Configuration of wood tissues. **A** Adjacent cells, **B** Cell wall layers. **S1, S2, S3** Secondary cell wall layers, **P** primary wall, **ML** middle lamella. **C** Distibution of lignin, hemicellulose and cellulose in the secondary wall (Kirk and Cullen, 1998).

From Figure 2.3, the configuration of wood tissue shows the distribution of lignin, cellulose and hemicellulose in secondary wall layers. The secondary wall layer is covered by primary wall and also the middle lamella. As stated before, the middle lamella provides strong protection to wood fibre which causes the difficulties to degrade the undesirable lignin.

Cellulose $(C_6H_{10}O_5)_n$ is a long-chain polymeric polysaccharide carbohydrate, of beta-glucose. It forms the primary structural component of green plants. The primary cell wall of green plants is made primarily of cellulose; the secondary wall contains cellulose with variable amounts of lignin (Wikipedia, 2006). It is a common material in plant cell walls and was first noted as such in 1838. In combination with lignin and hemicellulose, it is found in all plant material. Cellulose is the most abundant form of living terrestrial biomass (Crawford, 1981).