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**Suitability of Pineapple (*Ananas Comosus*) Leaf as  
an Alternative Source of Raw Material for  
Production of Pulp**

**Biehitra Kumar Bachar**

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**Forestry and Wood Technology Discipline**

**Khulna University**

**Khulna**

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## **Declaration**

I, Bichitra Kumar Bachar, hereby declare that the dissertation submitted for the Degree of Master of Science (MS) in Forestry at Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh is my own original work and have not previously been submitted to any other institution.

I, hereby, give consent for my thesis, if accepted, to be available for photocopying and for inter-library loans and the title and summary to be made available to outside organizations only for research and educational purposes.

Bichitra Kumar Bachar

## **Dedication**

This thesis is dedicated to my family, more especially to my parents.

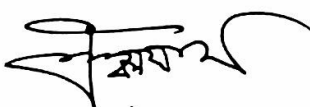
**Suitability of Pineapple (*Ananas Comosus*) Leaf as  
an Alternative Source of Raw Material for  
Production of Pulp**

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[This thesis work has been prepared and submitted to Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh for the partial fulfillment of the Degree of Master of Science (MS) in Forestry.]

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## ABSTRACT

The main objective of this study is to evaluate the potentiality of pineapple leaf as an alternative source of raw material for production of pulp by using soda pulping method. The effects of active alkali were investigated. Active alkali was added in the form of white liquor containing concentrations of 17, 19 and 21% NaOH based on oven dry raw materials. The cooking time to maximum temperature was 120 min. The dry raw materials were cooked at 120°C with a liquor-to-wood ratio (L/W) of 7:1. The cooking materials were blended for 30 minutes revolting at 25000 rpm for preparing pulp. Ten hand sheets of each treatment were made and the seven best hand sheets were selected and tested. With regard to the pulping process, the results show that with an increase in active alkali ranging from 17% to 21% the total pulp yield was decreased from 34.92% to 33.30%. The average values of burst index were 1.66, 2.55 and 3.56 (g.cm<sup>2</sup>)/(g/m<sup>2</sup>) for 17, 19 and 21% active alkali, respectively. The average tear index for 17, 19 and 21% active alkali were 12.83, 14.88 and 20.42 (g/(g/m<sup>2</sup>)) respectively. The density, breaking length and porosity at 21% active alkali gave the highest value, while the lowest average was found at 17% active alkali. The ease to pulping and physical properties of paper made from pineapple leaf indicates that it may be a suitable non-wood raw material.

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## CHAPTER ONE: INTRODUCTION

### 1.1 Background of the Study

Pulp is a crude fibrous material produced chemically or mechanically from wood or other ligno-cellulosic materials (Bierman, 1993). It is used for manufacture of paper, paperboard, rayon etc. In the 1830s, Anselme Payen found a resistant fibrous material that existed in most plant tissues (Payen, 1842). That was termed cellulose by the French Academy in 1839 and it was the turning point in the use of all fibers for production of pulp products (Hon, 1994).

Pulping refers to disintegration of bulky fibrous material to small fibres. It is the means by which the bonds are systematically ruptured within the wood structure (Smook, 1992). Pulping is done mechanically, thermo mechanically, chemically or with combinations of these treatments. Soda pulping is traditionally the most employed chemical pulping process for most of the non-wood raw materials (Khristova *et al.* 2006; Enayati *et al.*, 2009). In this method sodium hydroxide is used as cooking chemical. Lower cooking time and temperature and ease to chemical recovery are the major advantages of soda pulping (Hedjazi *et al.*, 2009). However, the Soda pulping of non-woods produces a low yield and highly colored pulp consuming a large amount of bleaching chemicals (Francis *et al.* 2006; Labid *et al.*, 2008).

The process of pulping wood fibres and forming them into a paper web was invented in 1857 (Roberts, 1996). Wood became the main raw material for paper production in the 20<sup>th</sup> century. It was quickly established as the primary source of fibre for papermaking and today provides some 90% of the fibrous raw material used in the process (Madakadze *et al.*, 1999). In 105 AD paper was first made from hemp rags and mulberry plants fibers by a Chinese named Ts'ai Lun (Lies and Booth, 1990). Before the first half of 19<sup>th</sup> centuries paper was made exclusively from non-wood fibres such as cotton, hemp, flax and grass (Roberts, 1996). Usually non-woods are characterized by a lower lignin content than wood and a higher pentosan or hemicellulose content (Hurter, 1988). Short fiber length, high content of fines and low bulk density are the most important physical features of non-wood raw materials (Oinonen and Koskivirta, 1999; Paavilainen, 2000).



The worldwide consumption of paper and board products increases continuously due to population growth, better literacy, development of communication and industrialization in developing countries. World demand for paper was 300 million tons in 1996/97 (Hurter, 1997) and is estimated to rise over 490 million tons by the year 2020 (John, 2006). The conventional paper is mainly derived from wood. Now a days the paper industry is mainly depending upon forest resources, as a result deforestation take place to meet the availability of raw material for paper making industry. The deforestation causes environmental pollutions and global warming. In many countries like China, India, Thailand, The Philippines etc. wood is not available in sufficient quantities for the rising demand of pulp and paper but the availability of agro-residues is high. In recent year, people have placed a high emphasis on forest preservation and rational use of forestry and agriculture residues (Shiyu Fu Li *et al.* 2010). As this issue becomes a critical one, alternative fibers from non-wood sources will provide a good solution to limit the shortage of conventional raw materials for pulping and the destruction of the environment .Studies have shown that the production process of paper from non-wood fibre is significantly less expensive than wood fibre (Weston, 1996).

Bangladesh is an extensively populated country (1015 person living per square kilometer) with an average growth rate of 2.8 % per year (BSS, 2012). The high population growth rate is creating depression on all forms of daily products. Huge amount of necessary daily products such as furniture, construction timber, pulp and paper, fuel wood etc. come from the woody species and the demands for woody products is increased day by day within their limited supply or sources (Azam, 2001). In this situation, the shortage of fibrous materials for pulp and paper industries can be mitigated by non-wood species. In Bangladesh the non-wood species and agro residues are large enough and their potentiality is suitable for paper making like straw, jute, dhoincha, golpata frond, bagasse, corn stalk, cotton stalk etc. Pineapple is one of the prominent species of Bangladesh covering an average area of about 40 thousand acres (BBS, 2011).Crown leaf of pineapple contains approximately 75% holo-cellulose which is suitable for pulp products (Zawawi *et al.*, 2014). Crown leaf of pineapple may be a potential non-wood material for paper making because of its availability, chemical constituents and other properties.

## 1.2 Objectives of the Study

Pineapple (*Ananas Comosus*) is the common tropical plant which consists of coalesced berries. Waste pineapple leaf is a very good source of cellulose. It contains 65.0 % cellulose and 11.5% lignin with some extractives such as gum and resin (Zawawi *et al.*, 2014). Among all the fruits produced in Bangladesh, pineapple ranks 4th in terms of total cropping area and production. Pineapple crop is normally cultivated in an average area of about 40 thousand acres (BBS, 2014). Pineapple Leaf is one of the materials which do not have immediate beneficial applications in Bangladesh. A huge mass residue is produced from pineapple plantation, all of which goes waste due to non-availability of suitable technology for its commercial utilization. In order to add value to pineapple plantation, the waste leaf could be processed into valuable products such as pulp and paper which can be an alternative source of raw material. The specific objectives of the study are-

- To prepare pulp from pineapple leaf by soda pulping method.
- To assess the quality of pulp by evaluating the hand sheets.

## CHAPTER TWO: LITERATURE REVIEW

### 2.1 Pulp and Pulping

Pulp can be defined as a crude fibrous material produced chemically or mechanically from fibrous cellulosic raw materials for subsequent manufacture of paper, paperboard, rayon etc. Basically pulp consists of wood or other ligno-cellulosic materials that have been broken down physically or chemically such that discrete fibers are liberated and can be dispersed in water and reformed into a web (Bierman, 1993). The paper industry is the largest consumer of pulp.

Pulping refers to disintegration of bulky fibrous material to small fibres. It is the process by which wood or other fibrous raw materials are reduced to a fibrous mass. Basically, it is the means by which the bonds are systematically ruptured within the wood structure (Smook, 1992). Pulping is done mechanically, thermo mechanically, chemically or with combinations of these treatments.

#### 2.1.1 Mechanical Pulping

Mechanical pulping is the pulping process in which it is possible to disintegrate the wood into fibrous state without the use of chemicals (Troup, 1907). The first and one of the most common mechanical pulping methods is the stone ground wood process (SGW). This process involves grinding of wood bolts (small logs) into pulp against a rough revolving grinding stone (Troup, 1907). The wood fibers are torn out of the wood, abraded and removed from the stone surface with water. If the wood is steamed prior to grinding it is known as pressure ground wood pulp (PGW). A modern process, called refiner mechanical pulp (RMP) utilizes chips rather than logs. The wood chips are disintegrated into fibers between large rotating metal disks of a device called a refiner. If the chips are steamed while being refined the pulp is called thermo-mechanical pulp (TMP). Steam treatment significantly reduces the energy use and modifies resultant pulp properties.

Mechanical pulping has the advantages of converting up to 95% of the dry weight of the wood into pulp as it contains all the lignin of original wood (Smook, 1992). It requires a large energy input. The paper from mechanical pulp is highly opaque, relatively weak and discolors easily with exposure to light. Newsprint is a major product of mechanical pulp. Generally long-fibered softwood (conifer) species are preferred for producing mechanical



pulps. The smaller, thinner fibers from hardwoods are more severely damaged by the mechanical action and consequently yield a weaker paper.

### **2.1.2 Semi-chemical Pulping**

Semi-chemical pulping is a two-stage pulping process involving chemical treatment to remove part of the fiber bonding material (i.e. lignin) and mechanical refining to complete the pulping action. At first wood chips are given a mild cooking with a conventional pulping agent. Generally acid sulfite, neutral sulfite, cold soda and sulfate liquors are used as pulping agents. Then the softened chips are subject to disintegrate in a suitable refiner.

In semi-chemical pulping, yields are somewhat lower than mechanical pulping (over 90% yield for mechanical pulps and over 80% for semi-chemical pulp) depending on the degree of cooking (Smook, 1992). The semi-chemical pulping process is used to produce newsprint-grade products (Troup, 1907). The neutral sulphite process is the widely used semi-chemical process which is applied mainly to hardwood chips. Unbleached neutral sulphite semi-chemical pulps are used for the production of corrugating medium. Bleached neutral sulphite semi-chemical pulps have high strength properties and are used for printing, writing and other fine paper products.

### **2.1.3 Chemical Pulping**

Chemical pulping involves treatment of wood chips with chemicals to remove the lignin and other extraneous compounds and finally separation of fibers (Troup, 1907). Usually wood chips are cooked with suitable chemicals in aqueous solution at elevated temperatures and pressures in a heated digester vessel for an extended period (up to several hours or more) followed by mechanical refining. Chemical processes may yield only half the fiber that can be recovered by the use of mechanical pulping techniques.

The fiber quality of chemical pulp is usually better and more uniform with less lignin or other wood constituents and proportionately more cellulose fiber and more intact fibers. The paper made from chemical pulp is superior in quality (i.e. strength, durability, brightness etc.) than mechanical pulping. The principal chemical pulping methods are briefly discussed in below.

### **2.1.3.1 Sulfit Process**

In the sulfite process, an aqueous solution of sulphur dioxide and calcium, sodium, magnesium or ammonium bisulfite are used to attack and dissolve the lignin (Troup, 1907). The digestion of raw materials is happened in a digester at high temperature and pressure. Although calcium is the cheapest chemical used in sulfite pulping, calcium-based pulping is seldom used. Because calcium based chemicals forms insoluble compounds that cannot be reclaimed economically. Magnesium and sodium based chemicals are recoverable and ammonium based chemicals are less expensive and can be burned without harmful environmental effects. So these chemicals are frequently used in sulfite pulping process. Sulfite pulping processes are suitable only for species with low extractive contents (i.e., tannins, polyphenols, pigments, resins, fats etc.) because of the interference of these substances with the sulfite pulping chemicals. Sulfite pulps are lighter in color but weaker than kraft pulps. It can be bleached more easily to produce very bright pulps for writing and printing paper.

### **2.1.3.2 Soda Process**

The soda pulping is a principal pulping method of alkaline process. In soda process only sodium hydroxide is used as cooking chemical. The use of soda process is restricted to pulping of non-wood materials. The Soda pulping of non-woods produces a low yield and highly colored pulp consuming a large amount of bleaching chemicals (Francis *et al.* 2006; Labid *et al.* 2008). Some drawbacks of Soda pulping could be overcome by the using of suitable pulping additives such as anthraquinone (AQ). The addition of AQ in soda cooking accelerate the delignification, reduce alkali consumption, increase yield and viscosity and gave pulps with properties superior to those of soda pulping.

### **2.1.3.3 Kraft Process**

The kraft process dominates the pulp and paper industry. Kraft pulping involves cooking the wood chips with a sodium hydroxide and sodium sulfide solution (Smook, 1992). The highly alkaline chemical and wood mixture is cooked with steam under pressure for between 1 and 3 hours. Most of the lignin and some of the hemicellulose is dissolved leaving the remaining cellulose fibers separated. Both softwood and hardwoods can be pulped by the kraft process. The strength of kraft pulp is very high. Unbleached pulps characterized by a dark brown color are generally used for packaging products. Bleached pulps are made into white papers. In this process, the used chemicals can be recovered with only a relatively small loss in volume.

In recovery plant, the lignin and other organic wastes are burned to produce energy needed in the pulping process. In addition, valuable extractives (i.e., turpentine, tall oil, resin etc) are separated for commodity chemicals.

## 2.2 Paper and Paper Board

Paper is essentially a sheet of cellulose fibres with a number of added constituents to affect the quality of the sheet for the intended end use (Troup, 1992). It is a major product of the forestry industry and is made by pulping wood and other plant materials. Virtually all writing and printing are done on paper. It provides the means of recording, storage and dissemination of information. It is the most widely used wrapping and packaging material and is also important for structural applications.

The difference between paper and paper board is based on product thickness. Usually all sheets above 0.3 mm thicknesses are classed as paper board (Smook, 1998). According to the Confederation of European Paper Industries (CEPI), paper is usually called board when it is heavier than 220 g/m<sup>2</sup>.

### 2.2.1 Types of Paper and Paper Board

Type	Description	Uses	GSM
Tracing paper	Transparent, hard and strong. It is good for tracing fine details as it is translucent. Tracing papers strength enables you to scrape off mistakes using a craft knife.	Used for working drawings	60/90 gsm
Layout paper	Thin transparent paper with a smooth surface. Used for sketching and developing ideas. It is translucent so ideas can be traced and altered. However layout paper is looked at as a cheaper medium.	It is often used in preparation of final ideas and is used for tracing usually.	50 gsm

Cartridge paper	It is more expensive than copier paper. It is creamy white paper, slight texture usually.	General used for drawing but can be used with paint as it has a good quality surface for pens, pencils and markers	120-150 gsm
Photocopier paper	Fairly cheap when bought in bulk and is available in a range of colours.	General used for drawing but can be used with paint as it has a good quality surface for pens, pencils and markers. It can also be used with watercolours, pastels, crayons, inks and gouache.	80 gsm
Corrugated card	Contains two or more layers of card with interlacing fluted inner section. The fluted inner section adds strength to the card without a huge increase within its weight.	It is mainly used for packing items that need protecting during shipping.	250+ gsm
Bleed proof paper	Bleed proof paper is similar to cartridge paper but it is particularly good at separating water based paints and pens. So they don't run into areas where you don't want them.	It is mainly used in for important presentations where quality is needed.	120-150 gsm
White board	White board is a strong and medium board. It is bleached so it provides a good surface for printing.	It is mainly used for good quality packaging and book covers.	200 - 400 gsm

Duplex board	Duplex board is a cheaper version of white board; it also provides different textures for printing.	It is mainly used in food packaging as recycled materials cannot be used for this purpose.	230 - 420 gsm
Ink jet card	Ink jet card is treated so that it can go through all types of inkjet printers.	It is used for high quality print finishes on inkjet printers only.	120 - 280 gsm
Cardboard	Cardboard is a cheap, recyclable, stiff board which has a good surface to print.	It is mainly used for packaging, boxes and cartons.	125 - 300 gsm
Grid paper	A ready printed grid sheet with vertical and horizontal lines on it.	Mainly used for working drawings.	80 - 100 gsm

## 2.3 Raw Materials

Pulp is manufactured from raw materials containing cellulose fibers generally wood, recycled paper and agricultural residues. Historically the first paper was made from non-wood material by Tsai Lun in China around 100 A.D (Lines and Booth, 1990). Wood as a papermaking fiber is a relative newcomer. In 20th century, wood has been dominant to be the main source for pulp and paper material due to its availability, low cost and good paper properties (Madakadze *et al.*, 1999).

### 2.3.1 Non-wood Fibers

On a global scale, non-wood fibres are a minor raw material for production of paper and paperboard. Non-wood raw materials account for less than 10% of the total pulp and paper production worldwide (El-Sakhawy *et al.*, 1996). In many countries, wood is not available in sufficient quantities to meet the rising demand for pulp and paper. The production of non-wood pulp mainly takes place in countries with a shortage of wood. The region that has invested the most time and resources into the pulping of non-woods is Asia and the Pacific. In particular, China and India are leaders in the utilization of non-woods for paper making.

China accounts for more than two thirds of the non-wood pulp produced (Hammett *et al.*, 2001). In China and India more than 70% of raw materials used by pulp industries come from non-woody plants. In North America, Latin America, Europe, the Russian republics and Africa the use of non-wood fibre sources has been relatively limited.

According to their origin, non-wood fibers are divided into three main types: (1) agricultural by-products; (2) industrial crops; and (3) naturally growing plants (Rowell and Cook, 1998; Svenningsen *et al.*, 1999). Agricultural by products are the secondary products of the principal crops (usually cereals and grains) and are characterized by low raw material price and moderate quality such as rice straw and wheat straw (Navaee-Ardeh *et al.*, 2003; Deniz *et al.*, 2004). Industrial crops, such as hemp, sugarcane and kenaf can produce high quality pulps with high expense cost of raw materials (Kaldor *et al.*, 1990; Zomers *et al.*, 1995). Naturally growing plants are also used for the production of high quality pulps. This includes bamboo and some grass fibers such as elephant grass, reed and sabai grass (Walsh, 1998, Poudyal, 1999; Shatalov and Pereira, 2002; Salmela *et al.*, 2008).

There is a growing interest in the use of non-wood fibers as a raw material for pulp and paper. The non-wood plants can be used as an effective substitute for the eternally decreasing forest wood resources (El-Sakhawy *et al.*, 1995; 1996; Jimenez *et al.*, 2007). The benefits of non-wood plants as a fiber resource are their fast annual growth and the smaller amount of lignin that binds the fibers together. Another advantage is that the non-wood plants high-quality bleached pulp can be produced at low temperatures with lower chemical charges. These allow the production of high quality pulp by a less polluting process than hardwood pulps (Johnson, 1999) and the reduced energy requirements (Rezayati-Charani *et al.*, 2006). Moreover, non-food applications can give additional income to the farmer from food crops or cattle production (Rousu *et al.*, 2002; Kissinger *et al.*, 2007; Rodríguez *et al.*, 2007).

### **2.3.2 Properties of Non-wood Fibers**

There is considerable variability within non-wood plant fibers in their physical and chemical characteristics compared to wood fibers (Gumuuskaya and Usta, 2002; Rezayati-Charani *et al.*, 2006). They varies widely depending on the type of plant and the soil and growing conditions (Bicho *et al.*, 1999; Jacobs *et al.*, 1999).

Short fiber length, high content of fines and low bulk density are the most important physical features of non-wood raw materials (Oinonen and Koskivirta, 1999; Paavilainen, 2000). The large amount of fines and the short fiber length (< 2 mm) affect the drainage properties of

pulp. The low bulk density affects the logistics of non-wood raw materials. Table shows the physical properties of some non-wood fibers.

Table-2.1. Physical properties of Some Common Non-wood fiber

Fiber source common name	Scientific name	Fiber length mm	Fiber diameter microns
<b>Straw and stalk fibers</b>			
Cereal Straw		1.5	23
Wheat Straw	<i>Triticum aestivum</i>	1.0-1.5	13
Corn Straw	<i>Zea mays</i>	1.0-1.5	18
Rye Straw	<i>Secale cereale</i>	1.5	13
Oat Straw	<i>Avena sativa</i>	1.5	13
Barley Straw	<i>Hordeum vulgare</i>	1.5	13
Rice Straw	<i>Oryza sativa</i>	0.5-1.4	8-10
Sorghum Straw	<i>Andropogon bicolor</i>	1.0-1.7	20-47
Cotton Straw	<i>Gossypium hirsutum</i>	0.6-0.9	2-30
<b>Reed and grass fibers</b>			
Common Reed	<i>Phragmites communis</i>	1.5-2.5	20
Giant Reed	<i>Arundo donax</i>	1.2	15
Papyrus	<i>Cyperus papyrus</i>	1.5	12
Reed canary grass	<i>Phalaris arundinacea</i>	1.0	20
Elephant grass	<i>Miscanthus sinensis</i>	1.2	20
Esparto	<i>Stipa tenacissima</i>	1.1-1.5	9-12
Sabai	<i>Eulaliopsis binata</i>	2.1	9
Switch grass	<i>Panicum virgatum</i>	1.4	13
<b>Cane fiber</b>			
Bagasse/sugarcane	<i>Saccharum officinarum</i>	1.0-1.7	20
Bamboo		2.7-4	15
<b>Bast fibers</b>			
Flax	<i>Linum usitatissimum</i>	25-30	20-22
Hemp	<i>Cannabis sativa</i>	20	22
Sun hemp	<i>Crotalaria juncea</i>	2.5-3.7	25
Kenaf	<i>Hibiscus cannabinus</i>	2.6	20



Jute	<i>Corchorus capsularis</i>	2.0-2.5	20
<b>Core fibers</b>			
Kenaf	<i>Hibiscus cannabinus</i>	0.6	30
<b>Leaf fibers</b>			
Abaca	<i>Musa textilis</i>	6.0	20-24
Sisal	<i>Agave sisalana</i>	3.0-3.5	17-20
<b>Seed hull fibers</b>			
Cotton staple	<i>Cossypium hirsutum</i>	20-30	20
Cotton linters	<i>Cossypium hirsutum</i>	0.6-3.0	20
EFB	<i>Elaeis guineensis</i>	1.0	20
<b>Tree based fibers</b>			
softwood		2.7-5.0	32-43
hardwood		0.7-3.0	20-40
Eucaluptus		0.7-1.3	20-30

[Isenberg, (1967) and Hurter]

All non-woods are characterized by a lower lignin content than wood and a higher pentosan or hemicellulose content. They also have higher silicon and nutrient contents than wood (Hurter, 1988).

Table-2.2. Chemical Composition of Some Common Non-wood fiber

Fiber source	Cellulose	Lignin	Pentosans	Ash	Silica	Pulp yield
<b>Straw and stalk fibers</b>						
Wheat Straw	29-51	16--21	26-32	4.5-9	3-7	39-62
Rye Straw	33-50	14-19	27-30	2-5	0.5-4	
Oat Straw	31-48	14-19	27-38	6-8	4-6.5	
Barley Straw	31-45	14-15	24-29	5-7	3-6	
Rice Straw	28-48	12-16	23-28	15-20	9-14	
Cotton Straw	80-90	3-3.5		1-1.2	<1	
<b>Reed and grass fibers</b>						
Common Reed	40-46	22-24	20	3-4	2	45
Esparto	33-38	17-19	27-32	6-8	2-3	
Sabai		22	24	6		

Switch grass	43	34-36	22-24	1.5-2		
<b>Cane fiber</b>						
Bagasse/sugarcane	32-48	19-24	27-32	1.5-5	0.7-3	45-65
Bamboo	26-43	21-31	15-26	1.7-5	0.7	38--45
<b>Bast fibers</b>						
Flax	43-47	21-23	24--26	5		
Hemp	57-77	9-13	14-17	0.8		
Jute bast	45-63	21-26	18-21	0.5-2		
Kenaf bast	44-57	15-19	22-23	2-5		
<b>Core fibers</b>						
Jute	41-48	21-24	18-22	0.8	<1	42
Kenaf	37-49	15-21	18-24	2-4	4	46
<b>Leaf fibers</b>						
Abaca	56-63	7-9	15-17	3	<1	
Sisal	47-62	7-9	21-24	0.6-1	<1	
<b>Seed hull fibers</b>						
Cotton staple	85-90	3-3.3		1-1.5	<1	
Cotton linters	85-90	3-3.5		1-1.2	<1	
<b>Tree based fibers</b>						
softwood	40-45	26-34	7-29	<1	<1	
hardwood	38-49	23-30	19-26	<1	<1	

[Hurter and Parham and Kausfinen (1974)]

### 2.3.3 Pulping of Non-wood Fibers

Most of the non-wood materials can be pulped with simple chemical systems such as caustic soda as they have considerably less lignin than the wood materials. Traditionally, non-wood material is cooked with hybrid chemi-mechanical and alkali-based chemicals (Goyal *et al.*, 1992; Jahan *et al.*, 2007). The alkali charge required for a non-wood fibrous raw material is normally lower than what is required for wood based raw materials to achieve the same degree of delignification.

### 2.3.4 Non-wood fibers in Bangladesh

The main raw materials in Bangladesh are bamboo, mixed tropical hardwood (i.e. gamar, shimul, kadam, pitraj, etc) and few non-wood plants. Shortage of fibrous raw materials (wood, bamboo) are the regular problem of major pulp and paper industries in Bangladesh because of many unavoidable reasons including high population, less land, climate, soil property, knowledge etc. Non-wood plays a vital role in pulp and paper sector in Bangladesh. Non-wood fibers available in Bangladesh and potentially suitable for paper making are straw, jute, golpata fronds, dhanicha, bagasse, corn stalks, cotton stalks and kash. Production, Yields per hectare, and Pulp Yield per hectare of Non-woods in Bangladesh are given in following table.

Table-2.3. Production, yields per hectare and pulp yield per hectare of non-woods in Bangladesh

Plant	Production (thousands of tons)	Annual fiber yield (tons/hectare)	Annual pulp yield (tons/hectare)
Rice straw	34,020	3	12
Wheat straw	25.8	4	1.9
Jute	963	15	7
Golpata fronds	60	n.a.	n.a.
Dhanicha	50	15--18	7-9
Bagasse	700	9	4.2
Corn stalks	128	8-10	3.2-4.3
Cotton stalks	36	8-10	3.5-4.3

[Jahan (2003b)]

### 2.4 Pineapple

The genus *Ananas* belongs to the family *Bromeliaceae*, a large family of 56 genera and approximately 2794 species (Bartholomew *et al.* 2003). The pineapple is the leading edible member of *Bromeliaceae* contributing to over 20 % of the world production of tropical fruits (Coveca, 2002). It is the second harvestable fruits (i.e. banana is in first position). Nearly 70% of the pineapple is consumed as fresh fruit in producing countries.

### 2.4.1 General Description

Pineapple is a perennial, herbaceous monocot of the family Bromeliaceae (Py, 1969, Bartholomew *et al.* 2003). The adult plant is approximately 1–2 m high and wide. The stem is a distinct central cylinder, erect and club-shaped approximately 25-50cm long, 2-5cm wide at the base, 5-8cm wide at the top and contains nodes and internodes. The fruit has a cylindrical shape with flat berries of 2.5 cm of diameter. The top of the fruit is covered with phylotaxia leaves. A mature pineapple plant has approximately 68-82 leaves spirally organized in the form of a dense compact rosette. The older leaves are located at the base of the plant and younger ones in the centre. The leaves are usually sword shaped. The margins may or may not contain spines. Both surfaces of the leaf are covered with hairs but that are prominent in lower surface. The leaves are semi rigid. Pineapple flowers are hermaphroditic and trimerous, with three sepals, three petals, six stamens in two whorls, and one tricarpellary pistil. The root system is primarily adventitious and may spread up to 1-2 m laterally and 0.85 m in depth under optimal conditions (Py, 1969, Bartholomew *et al.* 2003, Collins, 1949).



**Fig2.1:** (a) General features of pineapple plant (b) Structure of pineapple plant.



#### 2.4.2 Taxonomy

According to Py *et al.* (1969) the taxonomical location of the pineapple is:

Kingdom:	Vegetal
Phyllum:	Pteridofitae
Class:	Angiosperm
Subclass:	Monocotyledoneal
Order:	Farinosae
Family:	Bromeliaceae
Genus:	Ananas
Species:	comosus

#### 2.4.3 Origin and Distribution

The pineapple was originated in Brazil/Paraguay in the Parana-Paraguay River drainage basin area in South America (Collins, 1949). It was domesticated in that area by the Tupi-Guarani Indians before the arrival of Columbus (Bertoni, 1919). Worldwide production started by 1500 when pineapple was propagated in Europe and the tropical and warm subtropical areas of the world including Africa, Asia, the South Pacific and Australia. Pineapple is currently grown over a wide range of latitudes from approximately 30 N to 30 S (Hayes, 1960; Purseglove, 1972; Medina & Garcia 2005). Thailand, Philippines, Brazil and China are the main pineapple producers in the world delivering nearly 50 % of the total output (FAO, 2004). Other important countries including India, Nigeria, Kenya, Indonesia, México and Costa Rica produce a considerable amount of pineapple every year.

#### 2.4.4 Soils and Climatic Requirements

Pineapple is grown in a wide range of soil types including very poor soils. However the sandy and loamy soils with a lot of organic matter and proper drainage capacity are suitable for better growth of pineapple. It prefers soils with a pH range of 5.0 to 6.0 (Joy PP, 2010). Pineapple grows well in warm and humid climate. The optimum temperature for normal growth is 15 C to 30 C. Pineapple is fairly resistant to drought but for high yields a medium to high evenly distributed annual rainfall of at least 1000-1500mm is required. Medium altitudes of 1100m above the sea level are best for pineapple cultivation (Joy PP, 2010).

#### **2.4.5 Harvesting**

Naturally pineapple harvesting is occurred during May-August (Joy PP, 2010). Pineapples will mature by about 15-24 months depending on the planting material used. The fruit should be harvested when 1/3 to 2/3 or more of the peel (called a shell) color has turned from green to yellow. Harvesting is done with a clean cut retaining 5-7m of stalk with the fruit by a sharp knife.

#### **2.4.6 Uses of Pineapple and By-products**

Mainly pineapple is cultivated for its fruit that is consumed fresh or as canned fruit and juice. The fruit is a rich source of vitamins C and B<sub>1</sub>. It contains significant amounts of manganese. Pineapple is the only source of a complex proteolytic enzyme named bromelain which is used in the pharmaceutical market for medicinal purposes and as a meat-tenderising agent (Gailhofer *et al.* 1998, Hale *et al.* 2005). Pineapple is used as an ingredient in a variety of foods including pizzas, sweets, cakes, punches, ice creams etc (Purseglove 1972, Bartholomew *et al.* 2003). Alcoholic beverages can also be made from juice (Stanley and Ishizaki 1979).

Parts of the plant may be used as silage and hay for livestock. Hearts and peels from the canning operation and centrifuged solids from juice production can be dried and mixed with molasses to produce a meal for animal feed.

The stems and leaves of the pineapple plants are a good source of fibre. Pineapple leaf fibre is potentially used in paper and low density polyethylene composites industries (Fujishige 1978). This fibre is also used in making threads for textile fabrics from several decades. At present the Philippines small cottage industries make high quality clothes from pineapple fibre (Purseglove 1972, Collins 1960).

#### **2.4.7 Chemical Composition of Pineapple Leaf**

The chemical composition of pineapple (*Ananas comosus*) leaf has a high potential as alternative fibers for pulp and paper making. The quality of fiber produced from non-wood materials depends on the contents of cellulose, hemicellulose and holocellulose. Pineapple leaf contains high holocellulose content (85.7%). Higher content of holocellulose inside the material will provide better quality paper. Cellulose is the component that makes the fiber stronger and eventually increasing the quality of the paper produced (Enayati *et al.*, 2009;

Khalil et al., 2006). Pineapple leaf has high cellulose content (66.2%). Lower lignin content is normally found in non-wood fiber. Pineapple leaf fiber has a low lignin content of 4.2%. Lower lignin content is easier to discard from the pulp (Enayati *et al.*, 2009). Pineapple leaf fibers have lower ash content (4.5%). The low ash content indicates high yield of pulp (Lopez *et al.*, 2004). Pineapple leaf has very high moisture content (81.6%). This high moisture content will affect the mechanical and surface properties of the paper as less dimensional stability of the paper will be obtained (Khairi *et al.*, 2010). The hot water solubility and 1% sodium hydroxide solubility of pineapple are 39.7% and 32.5% respectively. The chemical composition of pineapple (*Ananas comosus*) leaf has is given in Table.

Table-2.4: Chemical composition of pineapple (*Ananas comosus*) leaf

Chemical components	Percentage
Cellulose Content	66.2
Hemi-cellulose Content	19.5
Holocellulose Content	85.7
Lignin Content	4.2
Ash Content	4.5

(Zawawi *et al.*, 2014)

#### 2.4.8 Pineapple in Bangladesh

Bangladesh is not a tropical country but the climate and the soils of many parts of Bangladesh are suitable for pineapple production. Mainly, it is grown in the hilly and high land area of Bangladesh where there is well drainage systems. Pineapple is extensively cultivated in the districts of Tangail, Rangamati, Chittagong, Bandarban, Dhaka, Mymensingh, Khagrachari, Sylhet and Moulvibazar. It is also grown in Rangpur, Rajshahi, Pabna, Dinajpur, Bogra, Patuakhali, Kushtia, Khulna, Jessore, Barisal, Kishoreganj, Jamalpur, Faridpur, Noakhali, Comilla etc (BBS, 2011).



## CHAPTER THREE: MATERIALS AND METHODS

### 3.1 Collection and Preparation of Samples

The samples of fresh crown leaves of pineapple were collected from pineapple farm of Madhupur Sal Forest. The collected samples were washed with water to remove all debris and suspended particles. Then the samples were cut approximately with size 2-3 cm using scissor. After that the samples were air-dried at ambient temperature for 7 days.

### 3.2 Determination of Moisture Content

The air dried samples were further dried in an oven at 110°C for 24 hrs to make no water particles exist. The moisture content of the samples was determined by following formula-

$$MC\% = \frac{Ww - Wd}{Wd} \times 100 \dots\dots\dots (1)$$

Where, Ww = Green Weight of Samples

Wd = Dry Weight of samples

MC% = Moisture Content

### 3.3 Pulping Procedure

Mini digester of Pulp and Paper Laboratory, Khulna University was used for cooking. Soda pulping method was applied for pulping of chipped pineapple leaves. Active alkali (AA) charge was selected as a variable in this experiment. In soda pulping, AA is defined as the hydroxide concentration, expressed in NaOH based on the oven dry raw materials. The following cooking conditions were maintained in the soda process:

**Table-3.1:** Cooking conditions of pineapple leaves

Cooking conditions	Unit
Active alkali charge (% NaOH)	17%, 19% and 21% based on dry raw material
Cooking temperature	120°C
Time to maximum temperature	50 min and 70 min
Liquor to raw material ratio	7:1

### **3.4 Pulp Washing and Blending**

After completing cooking the pressure inside the digester was released and the black liquor drained off. Then the cooking materials were washed up by water for 3-4 hrs to remove chemical adhere with materials. Later the materials were transferred to the blender. The materials were blended for 30 minutes revolting at 25000 rpm for preparing pulp. Eventually screening was done to prepare pulp for making hand sheet paper.

### **3.5 Determination of Yield**

In pulping operation the yield is the oven dry pulp mass expressed as a percentage of the oven dry wood mass. Yield was determined as the following formula:

$$\text{Yield (\%)} = \frac{\text{Dry product mass out}}{\text{Dry product mass in}} \times 100 \dots\dots\dots (2)$$

### **3.6 Manufacture of Handmade Paper**

At first the pulps were mixed with certain amount of water for preparing hand sheet paper. Then this mixture of pulp was shaken for 4-5 minutes approximately. A hand sheet mold was placed in a chamber and added water into the chamber until the level of the water was one inch above the screen. The bottom part of the mold was covered by a piece of cloth. Pulp was quickly poured into the mold. Dewatering was done by the water pump. After that the mold was placed in a tray and the cloth was unfastened from the mold. In the next step, the sheet was kept in air for drying for about 3-4 hours. Finally calendaring was done to make the surface smooth.

## Steps of paper production

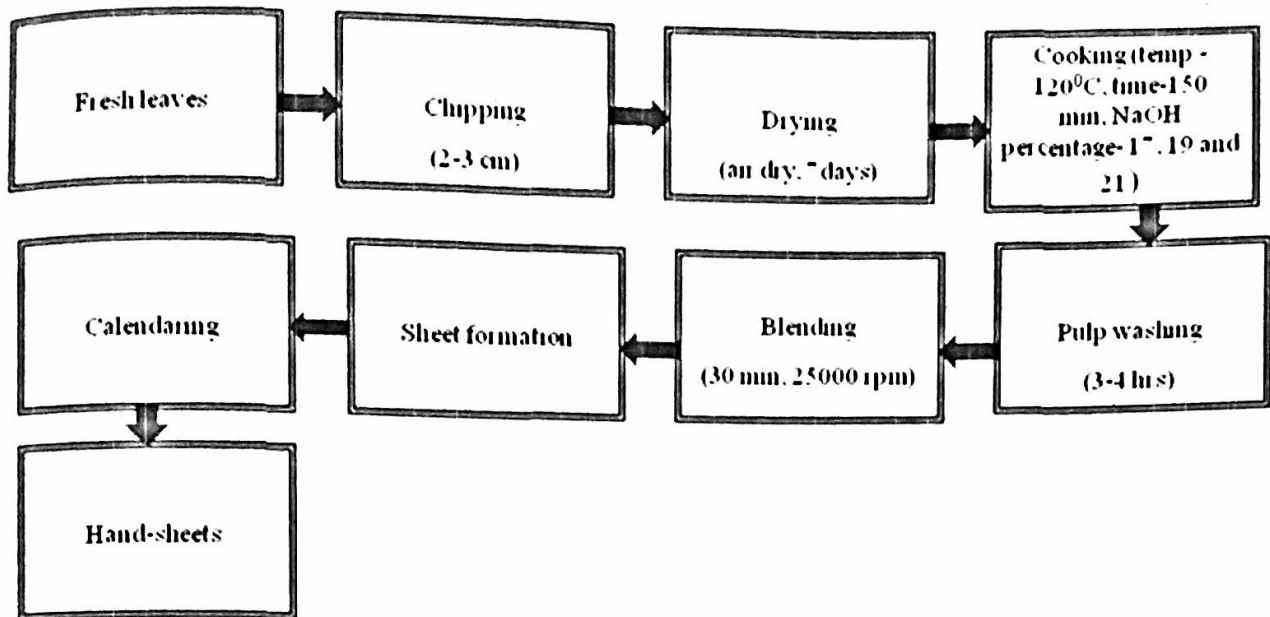


Fig3.1: Steps followed in this study for the production of paper.

### 3.7 Characterization of Paper

Physical and mechanical properties of paper such as tear strength, burst Strength, breaking length etc. were tested from recognized Pulp and Paper Laboratory.

#### Tensile Strength

Tensile strength can be measured by TAPPI tests T-404 and T-494. It indicates fiber strength, fiber bonding and fiber length. Tensile strength can be measured by following formula:

$$\text{Tensile Strength} = \frac{\text{Tensile Reading} \times 200000}{3 \times \text{GSM} \times 102} \text{ N. m/g} \dots \dots \dots (3)$$

#### Tear Strength

The most commonly used tearing test is T-414. Tearing strength is measured by following formula:

$$\text{Tearing Strength} = \frac{\text{Tear Reading} \times 1600}{\text{GSM}} \times 0.0980665 \dots \dots \dots (4)$$

## Bursting Strength

TAPPI method T-403 is the official test used for measuring the bursting strength of paper with thickness up to 0.6mm. It is measured by following formula:

$$\text{Bursting Strength} = \frac{\text{Burst Reading} \times 1000}{\text{GSM}} \times 0.0980665 \dots \dots \dots (5)$$

## CHAPTER FOUR: RESULTS AND DISCUSSION

### 4.1 Yield

It was found that, the average pulp yield at 17%, 19% and 21% NaOH concentration were 34.92%, 33.98% and 33.3% respectively (Fig 4.1). Highest pulp yield was achieved with the lowest value of active alkali. With an increase in active alkali the total pulp yield was decreased. The results are consistent with theoretical trends because higher concentration of alkali accelerates the dissolution of cellulose components. Shakhes *et.al* observed at same cooking time as the present study the tobacco stalks produced 46.43% yield at 20% alkali charges which was decreased to 39% at 25% alkali charges. Abdel-Aal reported that soda pulping of Buttonwood residues (*Conocarpus erectus L.*) by 17-23% of active alkali (NaOH) produced total pulp yields ranges between 48.36-55.46% whereas higher yield was achieved by lower alkali concentration (Abdel-Aal, 2013). Akpakpan *et.al* also found that both the frond and the petiole of *Nypa fruticans* produced lower yield with higher alkali concentration. Higher concentration of the cooking liquor, results in high rate of delignification and degradation of carbohydrate as a result the percentage of yield gradually decreased. Jahan *et.al* reported that the pulp yield of bamboo, rice straw, whole jute plant, bagasse and golpata fronds were 45.9, 38.8, 55.6, 50.5 and 37.2% respectively.

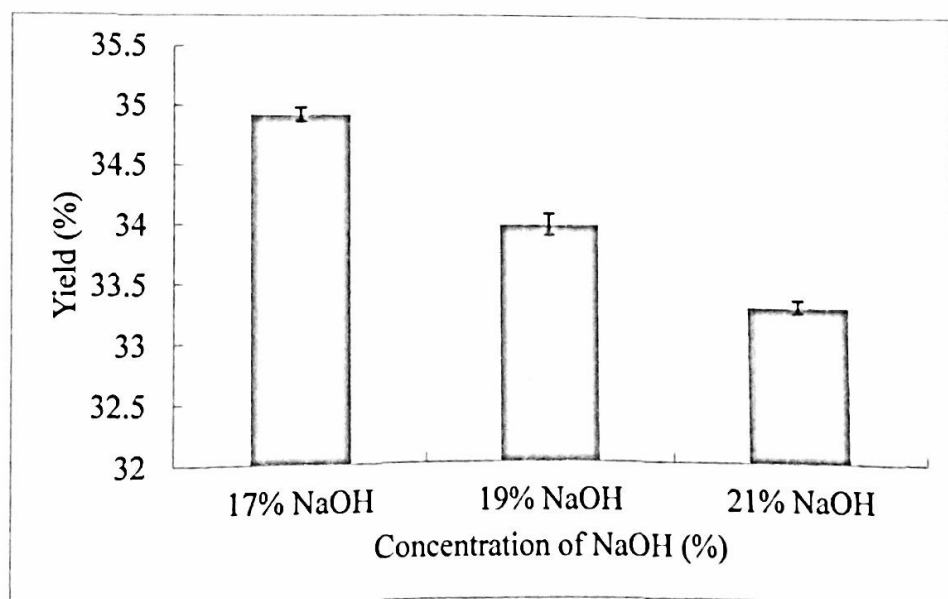
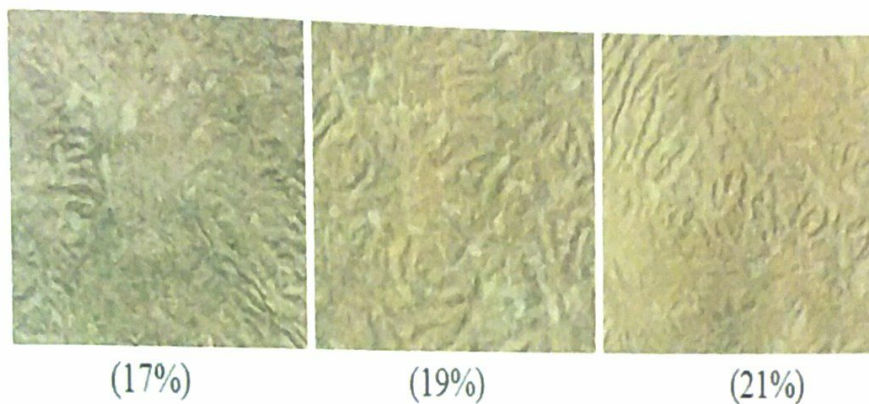


Fig 4.1: Yield (%) of pulp at different alkali concentration.

From the variance analysis and LSD (Table A-2.1), it was observed that there was significant difference ( $F=392.98$ ,  $df=20$  and  $p<0.05$ ) among the pulp yield at different concentration. According to these results, the most appropriate cooking parameter for the pineapple leaf was 17% NaOH.

#### 4.2 Pictorial View

The pictorial view of 17%, 19% and 21% alkali treated unbleached hand sheet are given in bellow-

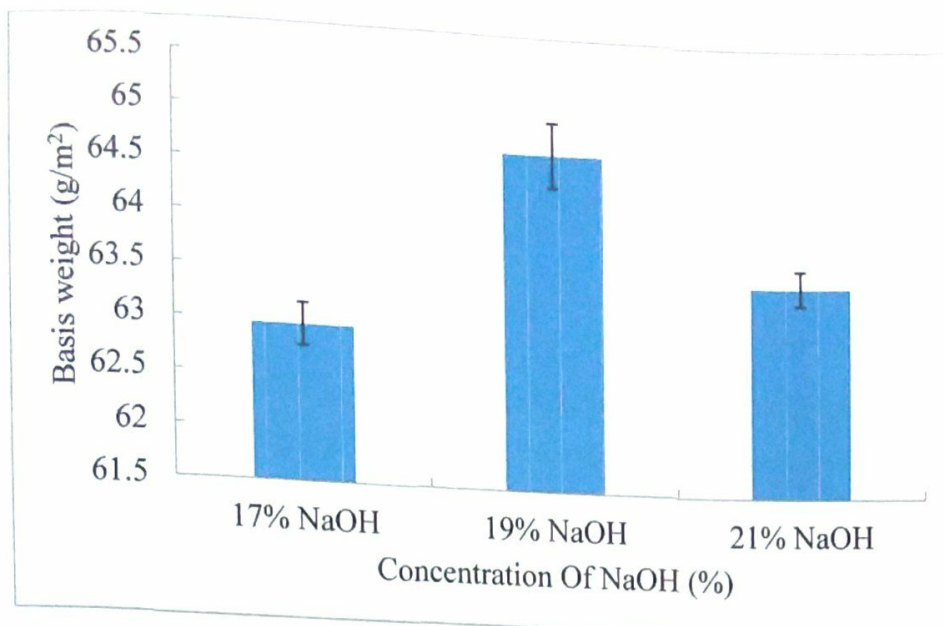


**Fig 4.2:** Pictorial view of paper treated by different concentration of NaOH (%)

#### 4.3. Basis Weight

The averages observed at 17%, 19% and 21% AA were 62.96, 64.69 and 63.51  $g/m^2$  respectively for basis weight of paper from pineapple leaf (Fig 4.3). In case of sabai grass 12% and 14% alkali charged pulp induced the basis weight of 67.86 and 69.17 respectively (Tyagi *et.al*, 2004). Fagbemi *et.al* found that the basis weight of paper from kenaf bark and corn husk were 82.06 and 93.3 $g/m^2$  respectively.



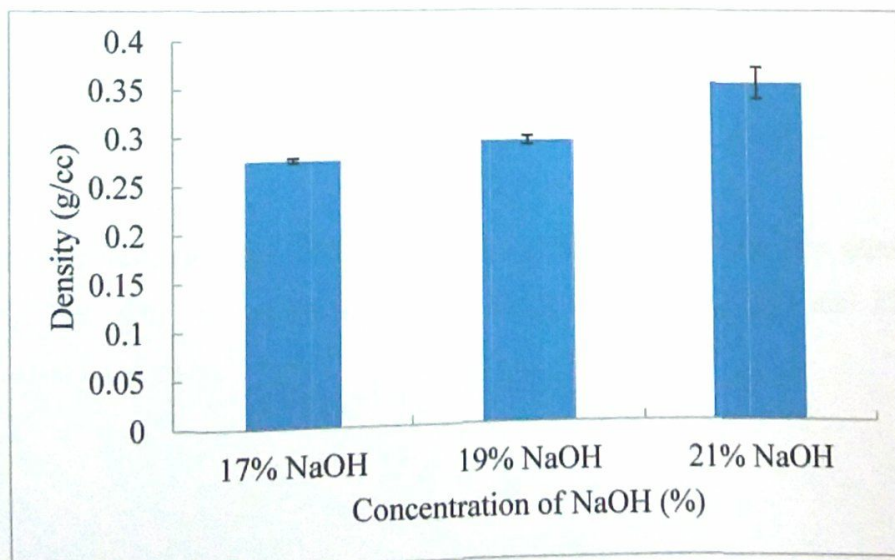


**Fig 4.3:** Effect of NaOH concentration on basis weight of paper.

From the variance analysis and LSD (Table A-2.2), it was observed that, there was significant difference ( $F=14.31$ ,  $df=20, 16$  and  $P<.05$ ) of basis weight among 17%, 19% and 21% alkali treated unbleached hand sheet.

#### 4.4 Density

The averages observed at 17%, 19% and 21% AA were 0.275, 0.294, 0.355 g/cc respectively for density (Fig 4.4). The density also increased with an increase in alkali concentration. Tyagi *et.al* reported the similar results in sabai grass. That study found that pulp obtain from 12% soda pulping condition had the density of  $452 \text{ kg/m}^3$  while  $501 \text{ kg/m}^3$  was gained through 14% pulping condition.



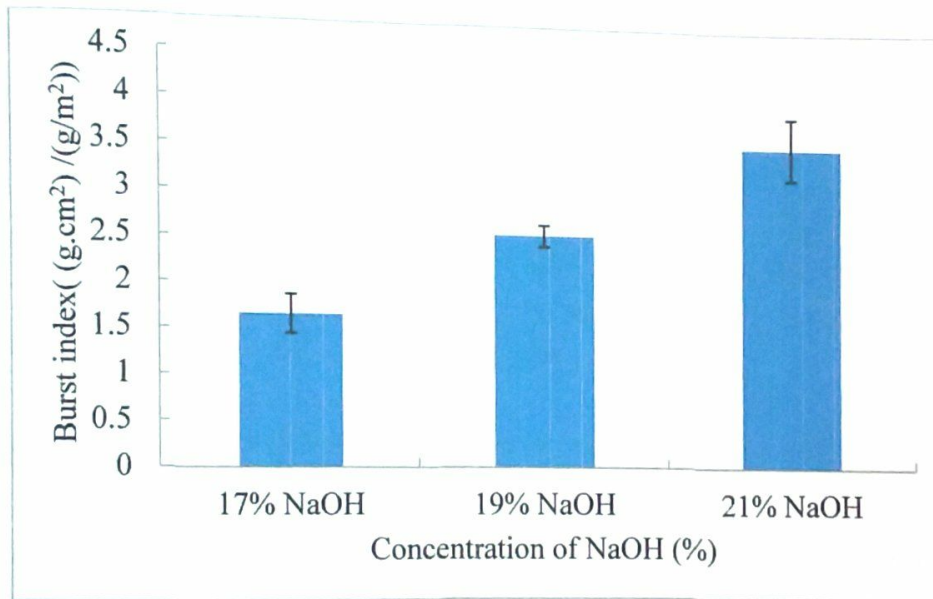
**Fig 4.4:** Effect of NaOH concentration on density of paper.



From the variance analysis and LSD (Table A-2.3), it was observed that, there was significant difference ( $F=16.74$ ,  $df =20, 16$  and  $P<.05$ ) of density among 17%, 19% and 21% alkali treated unbleached hand sheet.

#### 4.5 Burst Index

The averages for burst index were 1.66, 2.55 and 3.56 ( $\text{g.cm}^2$ )/( $\text{g/m}^2$ ) for 17, 19 and 21% active alkali, respectively (Fig 4.5). A study conducted by Ahmadi *et.al* (2009) on semi-chemical alkali treatment of rapeseed residues mentioned the same result as higher NaOH concentration increase burst index. That study found that the burst index of paper ranges from 1.7-2.04  $\text{kPa.m}^2/\text{g}$  at 8-16% alkali concentration. Jahan *et.al* reported that the burst index of paper made from bamboo, rice straw, whole jute plant, bagasse and golpata fronds were 4.9, 3.8, 7.0, 3.6 and 4.5  $\text{kPa.m}^2/\text{g}$  respectively.

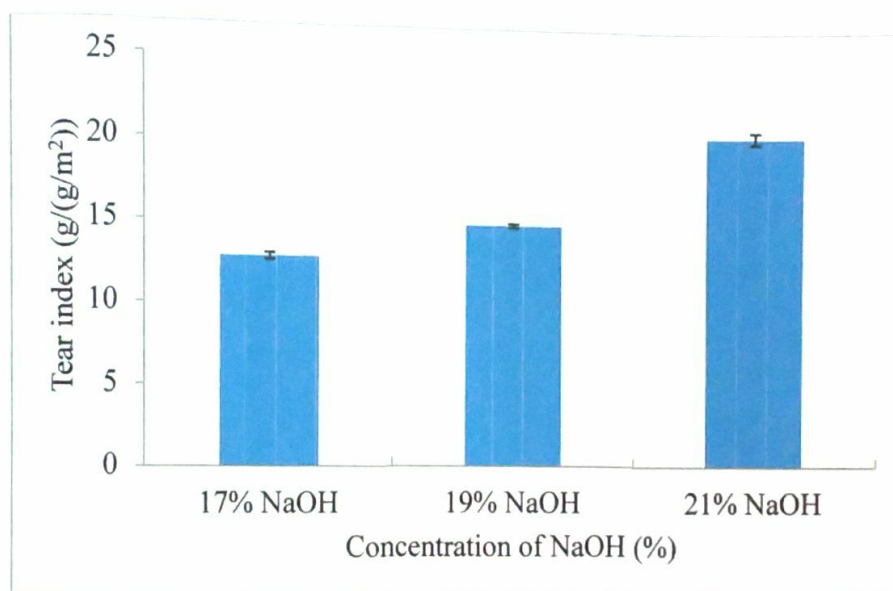


**Fig 4.5:** Effect of NaOH concentration on burst index of paper.

The variance analysis and LSD (Table A-2.4) showed that, there was significant difference ( $F=80.53$ ,  $df =20, 16$  and  $P<.05$ ) of tear index among 17%, 19% and 21% alkali treated unbleached hand sheet.

#### 4.6 Tear Index

It was found that, the average tear index was 12.83 (g/(g/m<sup>2</sup>)) for 17% AA, followed by 14.88 (g/(g/m<sup>2</sup>)) for 19% and 20.42 (g/(g/m<sup>2</sup>)) for 21% (Fig 4.6). Here the highest alkali concentration represents the highest value of tear index. Rosli *et.al* (2009) and Ahmadi *et.al* (2009) reported that an increase in NaOH (%) concentration increase the tear value of paper. An increase in NaOH (%) concentration accelerates the removal of impurities and surface hemicelluloses and lignin. This factor may be a possible cause for enhancement of tear index.



**Fig 4.6:** Effect of NaOH concentration on tear index of paper.

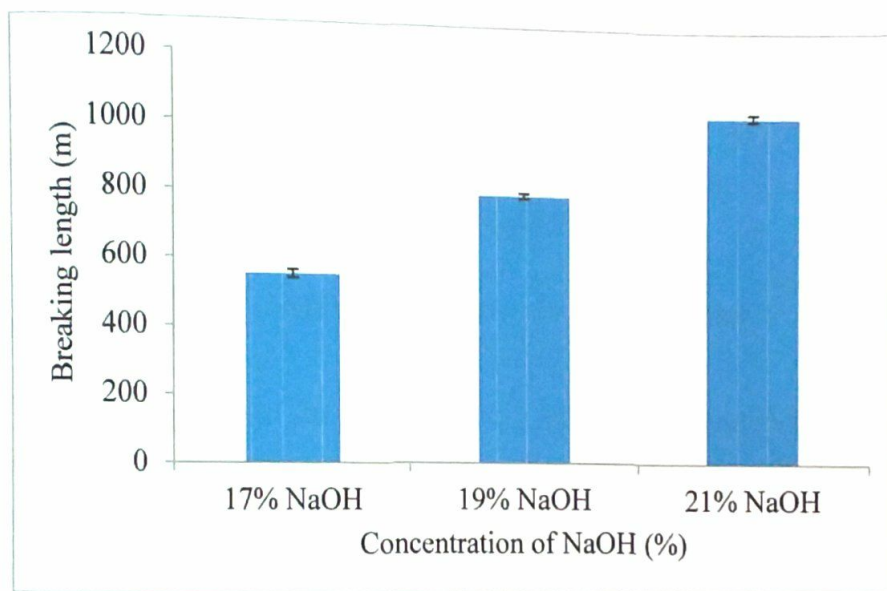
From the variance analysis and LSD (Table A-2.5), it was observed that, there was significant difference ( $F=263.43$ ,  $df=20, 16$  and  $P<.05$ ) of tear index among 17%, 19% and 21% alkali treated unbleached hand sheet.

#### 4.7 Breaking Length

The averages observed at 17%, 19% and 21% AA were 553.72, 794.43 and 1037.28 m respectively for breaking length (Fig 4.7). The study showed that, the average values for breaking length at 21% active alkali gave the highest value, while the lowest average was observed at 17% active alkali. Ahmadi *et.al* (2009) and Tyagi *et.al* (2004) also found in their



studies higher concentration of alkali charges increase the breaking length. Ahmadi *et.al* found 4.48 km as highest value of breaking length at 16% alkali concentration while 3.63 km at 8% alkali concentration as lowest value. Tyagi *et.al* observed 3.844 km at 12% soda concentration and 5.37 km at 14% soda concentration in handsheets made from sabai grass (*Eulaliopsis binata*). Jahan *et.al* reported that the breaking length of paper made from bamboo, rice straw, whole jute plant, bagasse and golpata fronds were 5511, 6590, 7336, 5600 and 7228 m respectively.

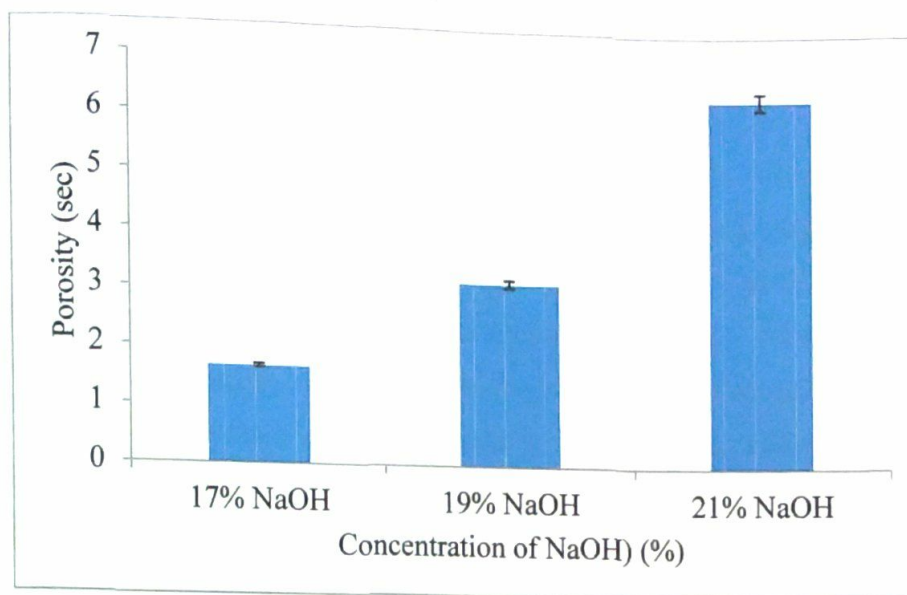


**Fig 4.7:** Effect of NaOH concentration on breaking length of paper.

From the variance analysis and LSD (Table A-2.6), it was observed that, there was significant difference ( $F=538.03$ ,  $df =20, 16$  and  $P<.05$ ) of breaking length among 17%, 19% and 21% alkali treated unbleached hand sheet.

#### 4.8 Porosity

The averages observed at 17%, 19% and 21% AA were 1.67, 3.17 and 6.4 sec respectively for porosity (Fig 4.8).



**Fig 4.8:** Effect of NaOH concentration on porosity of paper.

From the variance analysis and LSD (Table A-2.7), it was observed that, there was significant difference ( $F=686.56$ ,  $df =20, 16$  and  $P<.05$ ) of tear index among 17%, 19% and 21% alkali treated unbleached hand sheet.

## CHAPTER FIVE: CONCLUSION

### 5.1 Conclusion

The study shows that waste pineapple (*Ananas comosus*) leaf may be a good substitute of wood for the production of pulp and pulp products. The pulping of pineapple leaf with NaOH requires lower heating conditions (i.e. time and temperature). The study also shows that increases in active alkali result in a decrease in pulp yield. The results regarding pineapple leaf at different active alkali concentrations suggest that the density, tear index, burst index, breaking length and porosity at 23% active alkali are higher than those at 20% active alkali and that those at 20% active alkali are higher than those at 17% active alkali. All of these properties are more or less similar to other conventional non-wood raw materials available in Bangladesh. Thus it can be concluded that pineapple leaf should be considered as a suitable raw material for pulp and paper production which means a new comprehensive utilization of pineapple leaf wastes. Such innovative utilization will help to mitigate local demands of pulp products as well as diminish pressure on woody materials.

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## APPENDICES

### Appendix-1: Laboratory test results

Active Alkali (%)	Yield (%)	Basis Weight (g/m <sup>2</sup> )	Burst Index (g.cm <sup>2</sup> )/(g/m <sup>2</sup> )	Tear Index (g/(g/m <sup>2</sup> ))	Breaking Length (m)	Porosity (sec)
17	34.92	62.96	1.66	12.83	553.72	1.67
19	33.98	64.69	2.55	14.88	794.43	3.17
21	33.30	63.51	3.56	20.42	1037.28	6.4

**Appendix-2: ANOVA with LSD (Tukey)**

**Table A-2.1: ANOVA for Yield**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	9.24721	2	4.623605	136.1027	1.36E-11	3.554557
Within Groups	0.611486	18	0.033971			
Total	9.858695	20				

**Table A-2.2: LSD for Yield**

Treatment	N	Mean	Grouping
17	7	34.91	A
19	7	33.98	B
21	7	33.29	B

**Table A-2.3: ANOVA for Basis Weight**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	10.89809524	2	5.449047619	14.30971238	0.0001907	3.554557146
Within Groups	6.854285714	18	0.380793651			
Total	17.75238095	20				

**Table A-2.4: LSD for Basis Weight**

Treatment	N	Mean	Grouping
19	7	64.68	A
21	7	63.51	B
17	7	62.95	B

**Table A-2.5: ANOVA for Density**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.02413	2	0.012065	16.74318	7.8023E-05	3.554557
Within Groups	0.012971	18	0.000721			
Total	0.037101	20				

**Table A-2.6: LSD for Density**

Treatment	N	Mean	Grouping
21	7	0.35	A
19	7	0.29	B
17	7	0.28	B

**Table A-2.7: ANOVA for Burst Index**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	12.57591	2	6.287957	80.52962	1.05E-09	3.554557
Within Groups	1.405486	18	0.078083			
Total	13.9814	20				

**Table A-2.8: LSD for Burst Index**

Treatment	N	Mean	Grouping
21	7	3.55	A
19	7	2.55	B
17	7	1.66	C



**Table A-2.9: ANOVA for Tear Index**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	215.9027	2	107.9514	263.4358	4.69E-14	3.554557
Within Groups	7.376086	18	0.409783			
Total	223.2788	20				

**Table A-2.10: LSD for Tear Index**

Treatment	N	Mean	Grouping
21	7	20.42	A
19	7	14.88	B
17	7	12.82	C

**Table A-2.11: ANOVA for Breaking Length**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	818450	2	409225	538.0382	8.83E-17	3.554557
Within Groups	13690.57	18	760.5873			
Total	832140.6	20				

**Table A-2.12: LSD for Breaking Length**

Treatment	N	Mean	Grouping
21	7	1037.3	A
19	7	794.43	B
17	7	553.7	C

**Table A-2.13: ANOVA for Porosity**

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	81.74381	2	40.8719	686.5565	1.02E-17	3.554557
Within Groups	1.071571	18	0.059532			
Total	82.81538	20				

**Table A-2.14: LSD for Porosity**

<b>Treatment</b>	<b>N</b>	<b>Mean</b>	<b>Grouping</b>
21	7	6.40	A
19	7	3.17	B
17	7	1.67	C