Morphological and Chemical Characteristics of Different Non-wood Species and Their Effect on Pulping

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DEDICATED
TO MY PARENTS

CANDIDATE'S DECLARATION

I, Taslima Ferdous, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, certify that the research work titled "Morphological and Chemical Characteristics of Different Non-wood Species and Their Effect on Pulping" embodied in this PhD dissertation is my own work carried out by me under the supervision of Dr. Md. Abdul Quaiyyum, Professor, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, and Dr. Md. Sarwar Jahan, Director, BCSIR Laboratories, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka. The matter embodied in this thesis has not been submitted for the award of any other Degree or Diploma.

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SUPERVISOR'S CERTIFICATE

This is to certify that the thesis entitled, “Morphological and Chemical Characteristics of Different Non-wood Species and Their Effect on Pulping” is being submitted for examination in fulfilment of the requirements for the award of degree for Doctor of Philosophy (PhD) in Applied Chemistry and Chemical Engineering, embodies the original research work carried out by Taslima Ferdous, Registration number: 132/2017-2018 under our joint supervision and has not been submitted in part or full for any degree of this or any other university.

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ABSTRACT

Bangladesh is a densely populated agricultural country. As the allocated forestland for pulpwood production is very limited and a substantial quantity of crops residues is generated each year, the later can substitute pulpwood. But it is hard to use agriculture residues as pulping raw materials in conventional pulping process due to its high content of silica and fines. In this context, twenty-two residues of crops produced in Bangladesh were assessed in terms of their anatomical, chemical and morphological characteristics. The conventional soda-anthraquinone (AQ) pulping and alternate formic acid/peroxyformic acid (FA/PFA) pulping processes were evaluated for the suitability of the selected agricultural residues for pulp and paper production.

The non-wood samples showed a lot of variation in terms of anatomical, chemical and morphological characteristics. These samples showed a low to high level of α-cellulose (27.6-54.3%) and lignin content (~20%). Alkaline oxidation showed that the lignin of many of these non-wood residues was composed of high proportion of *p*-hydroxyphenyl propane unit. The ash content varied from 0.64% in dhaincha stalks to 15.1% in rice straws. Anatomically, most of the agricultural wastes consisted of parenchymatic cells in different proportions which generated fines in the pulping process. The fiber length of the samples varied from 0.62-1.91 mm and the range falls within the fiber length range of hardwood and softwood. The fiber wall thickness of most of these non-wood materials was thinner than wood.

The pulp yields in soda-AQ pulps of the samples were 21.01-64.39% with kappa number 4.92-42.43, while pulp yields in FA/PFA process were 34.5-60.7% with kappa number 10.9-24.1 depending on crops residues. A low pulp yield was obtained in soda-AQ process and the formic acid process produced better pulp yield from the non-wood raw materials because of the retention of silica. Bleaching of unbleached and oxygen delignified soda-AQ treated pulps were

evaluated in elemental chlorine free bleaching ($D_0/D_{HT}(E_P)D_1$) with varying chlorine dioxide (ClO_2) charge (kappa factor 0.15, 0.20 and 0.25) and temperature (70 and 85^oC). ClO_2 charge and temperature exhibited lower kappa number and higher brightness after alkaline extraction (EP) stage and high temperature ClO_2 delignification (D_{HT}) exhibited higher final pulp brightness. Residual hexeneuronic acid content in final pulp from most of the non-wood plants were lower and exhibited 1-2% higher pulp brightness in D_{HT} process than D_0 process. Oxygen delignified pulp and D_{HT} process discharged lower COD load in the effluent. The paper sheets prepared from the unbleached, bleached and refined unbleached pulps from both processes showed good physical properties.

Mathematical model between chemical and morphological characteristics with pulp yield and physical properties of the prepared paper sheets were developed. The pulp yield and kappa number were positively correlated with holocellulose content and lignin content, respectively. The papermaking properties of unbeaten pulps were depended on pulp fines, external fibrillation. Positive relation was observed for the fiber length with tear index of unbeaten pulp.

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ABBREVIATIONS

o.d.	Oven dried
FA	Formic Acid
PFA	Peroxyformic acid
AQ	Anthraquinone
HexA	Hexeneuronic acid
EP	Alkaline extraction
D	Chlorine dioxide
D_{HT}	High temperature chlorine dioxide delignification
COD	Chemical oxygen demand
UB	Unbleached
OD	Oxygen delignified

CHAPTER 1
GENERAL INTRODUCTION

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1.1. GENERAL INTRODUCTION

The process of extracting cellulosic fibers from plant material is termed as pulping. Generally, hardwood, softwood or non-wood plant materials are used for pulp production. The total fibrous raw materials used in the world for pulp production is wood (~90%) and the remaining (~10%) are non-wood. Out of the 10% non-wood used in the world, about 80% is used in Asia. This area suffers from lack raw material for pulp production because of many unavoidable reasons that include high population, less land, climate conditions, soil property, lack of proper technology etc. [1]. Generally pulping is conducted through chemical, mechanical (including thermomechanical) or semi-chemical pulping processes [2]. The pulp and paper industries obtain fibers from hardwood or softwood, the most abundant component of which is cellulose, a polysaccharide [3]. Wood also contains lignin, hemicellulose, extractives and a very little amount of inorganic metal components. Through the chemical pulping process, lignin and other non-cellulosic components are removed and the resultant pulp consists of natural lignocellulosic fiber materials. In addition to hardwood and softwood, numerous non-wood and recycled fibers are also used for pulp and paper production as these are good sources of cellulose [4].

The chemical composition of plant material gives an idea of its feasibility as possible raw material for papermaking. The fibrous component is the part of the plant that is required for papermaking. In fibers and cell walls cellulose is the main component. The other components of the cell wall include hemicellulose, pectins, lignin and proteins, and certain minerals. The composition and portion of the cell wall compounds differ in the individual species and even among plant parts. These variations affect the pulping ability of the plant material [1].

The low lignin content in non-wood plants lowers the requirement of chemicals for cooking and bleaching. Other than fibrous material, plants also contain other non-cellular elements,

including mineral compounds. While the inorganic compounds are essential for plant growth and development, they are undesirable in pulping and papermaking. The chemical composition of wood (Table 1.1) is one of the most important determining factor of pulp yield for various pulping processes.

Table 1.1. Wood components in hardwood, softwood and non-wood [2, 5-6]

Wood Components	Hardwood	Softwood	Non-wood
Cellulose (%)	40-50	40-45	40-45
Lignin (%)	20 - 25	25 - 35	15-30
Pentosans (%)	20-25	7-14	10-25
Ashes (%)	<1	<1	1-18

1.2. Principles of Pulping

Pulping involves unbinding of fibers from lignocellulosic plant material, by either mechanical or chemical processes. Chemical pulping is dependent upon chemical reactants and heat energy to soften and dissolve lignin to a varying degree and separates it from cellulose and hemicellulose. After chemical pulping, mechanical refining is required to separate the fibers. In the mechanical pulping, usually abrasive refining or grinding of wood is used to separate fibrous material. Before grinding, wood is pretreated with steam (or aqueous sulfite solution). In mechanical pulping the original chemical constituents of the fibrous material remain unchanged, except for removal of water solubles. The unbleached pulp, which is the material recovered from such processes, may be further treated by screening, washing, bleaching and purification operations [1,7].

Pulp is used as the most abundant raw material in the manufacture of paper and paperboard, and now-a-days it is also gaining its importance as a starting material of a variety of cellulose

products in the textile, food, and pharmaceutical industries. Like softwood and hardwood, non-wood is pulped in conventional processes, such as Soda, Soda-AQ or kraft pulping. Pulp produced in the conventional process from some of the important non-wood are shown in Table 1.2. As the pulping methods and conditions, raw material characteristics with harvesting time and the geographical location vary for non-wood, their pulping characteristics also differ in various studies. These are described in detail in literature review section.

Table 1.2. Conventional pulping of non-wood

Non-wood	Process	Pulp yield	Kappa number
Bamboo [8]	Kraft	43.4	11.2
Bagasse [9]	Soda	50.4	17.5
Corn stalk [10]	Soda-AQ	55.1	32.9
Jute fiber [11]	Soda-AQ	67.9	10.4
Rice straw [12]	Soda	35.32	15.83
	Soda-AQ	36.99	15.89
	Kraft	42.05	21.05
Wheat straw [13]	Kraft	39	10.8
Wheat straw [14]	Soda	47.7	24.1
	Soda-AQ	47.6	11.3
	ASAQ	47.0	8.4

1.3. Principles of Bleaching

Unbleached pulps contain high amount of lignin. Residual lignin in a pulp after cooking makes the pulp highly colored. The resin compounds are also colored impurities which are found in unbleached pulps along with dirt which is distinct as foreign matter having a noticeable complementary color in the pulp. So dark pulps are not suitable for the production of writing and printing papers.

Bleaching of fibers for decolonization has been accomplished since hundreds of years ago [15,16]. Karl Wilhelm Scheele first discovered chlorine as a bleaching agent in 1774. About twenty-five years later, Charles Tennant found that bleaching powder or calcium hypochlorite can be used as a bleaching agent in 1799. This invention made possible the transport of chlorine to an easily convertible form. It became the only available bleaching agent until 1804. After a paper mill in the USA used chlorine for bleaching in 1804, rapid innovations in bleaching technology occurred by 1930. The use of gaseous chlorine was initiated after 1930 which almost replaced hypochlorite as bleaching agent. The use of chlorine facilitated reduction of the cost of bleaching. Bleaching efficiency by using chlorine and chlorine dioxide facilitated improvement in equipment in 1940s. These developments led to the five-stage bleaching sequence that is still used extensively in the industry. The stages are, Chlorine(C), Alkaline extraction (E), Chlorine dioxide (D), Alkaline extraction (E) and Chlorine dioxide (D). The five-stage bleaching (CEDED) sequence produced pulp of high brightness with minimum loss in fiber strength [1,15-16].

In recent years, chlorine dioxide (ClO_2) has replaced elemental chlorine (Cl) to be used in bleaching. The advantage is the generation of less amount of adsorbable organic halides (AOX) in the effluent. But still the amount of AOX produced is enough to worsen the environment. That is why total chlorine free bleaching (TCF) processes are now being accepted and used to reduce waste effluent load. The TCF bleaching uses oxidizing agents such as oxygen, ozone and hydrogen peroxide which are less harmful for environment. The disadvantage is that the TCF bleaching require large capital investment, high cost of chemicals and pulp quality is of lower strength and brightness.

1.4. Non-wood

Agro-based fibers or wastes accumulated after the harvest of quarterly, half yearly or annual plants are generally termed as non-wood. About 10 % of global paper and board manufacture is based on crops residues and 90% of world production depends upon wood, either softwood or hardwood [17]. As the population of the world is growing day by day, growth in economic development would demand the increased need for various wood based commodities, resulting in decreased supply of raw materials for paper and pulp industries [18]. So, non-wood and recycled fibers have a good possibility to replace wood fibers [19,20]. Use of non-wood materials for the production of pulp and paper from has many advantages, such as these are easy to pulp, produce good-quality bleached pulp, and also they are excellent sources for specialty papers [21-23].

1.5. Types of non-wood biomass

Non-wood plant fibers can be divided into several groups depending on the location of the lignocellulosic component in the plant. These can be divided into the following four categories [24]:

1.5.1. Grass fibers

Gramineae or grass fiber includes bamboo, bagasse, corn stalks, rice straw, wheat straw, reed etc. This kind of raw material contain of nodes and internodes. But the heterogeneity of cellulose content within the raw materials makes the utilization of this kind of plant difficult in pulping processes.

The currently used grass fibers for papermaking are cereal straws, sugarcane, reeds and bamboo [25]. The source of fiber of these gramineae species are from the xylem of the vascular bundles of stems and leaves. The fiber can also be found in separate fiber strands where the layers are not a part of the vascular tissues [26-28]. Vascular bundles are usually in close proximity to

sclerenchyma cells. The vascular bundles usually have two rings as in cereal straw. The bundles can be found in the stem section like corn (*Zea mays L.*), bamboo and sugarcane [27]. The average length of grass fibers is 1–3 mm [28-29] and the ratio of fiber length to width varies from 75:1 to 230:1 [30].

The commonly used grass fiber commercially used is wheat (*Triticum aestivum L.*). Wheat is a monocotyledon and fibers of rye (*Secale cereale L.*), barley (*Hordeum vulgare L.*) and oat (*Avena sativa L.*) are similar to those of wheat [28] and they could also be used in papermaking. The commonly used grass fiber in Asia and Egypt is rice straw (*Oryza sativa L.*). Though there is similarity in physical structure of rice straw and wheat straw, but the percentage of leaves in rice straw is 35% more than that in wheat straw [31]. This kind of fiber is mixed with soft or hardwood in different proportions to make different kind of paper such as printing and writing paper, glassine and greaseproof paper, duplex and triplex paper, corrugating and wrapping paper [32].

Another important agricultural residue used for pulp manufacture is bagasse. Pulp from bagasse is used for all grades of papers [33]. But the main problem in pulping of bagasse is that 30% by weight of the stalk are pith, which is quite high percentage [31]. Usually, the entire plant is used for pulping to make paper when grass is used, and the pulp contains all the cellular and non-cellular elements [28]. The proportion of fiber cells is about 65 to 70% by weight in commercial grass pulp [28]. In addition to fiber cells, the grass pulp also contains fines the source of which are different vessel elements, tracheids, parenchyma cells, sclereids and epidermis. The presence of these elements makes the straw pulp more heterogeneous than wood pulp. The fines cause the drainage resistance of the pulp and thus the drainage time in papermaking is longer [34].

1.5.2. Bast fibers

Bast fibers refer to all fibers obtained from the phloem of the vascular tissues of dicotyledons plants. Fiber cells occur in strands termed fibers [27-28]. Hemp, kenaf, ramie (*Boechmeria nivea L.*) and jute (*Corchorus capsularis L.*) fibers are all bast fibers. Jute fibers are characterized by high cellulose content and relatively long in length. Chemical and morphological properties favor jute for use in pulp and papermaking [35]. It is primarily grown in Bangladesh, India, China and Thailand and the plant grows to a height of 2.5–3.5 meters. The length of the fiber cells of these plants varies from 2 mm (jute) to 120 mm (ramie) [27-28]. Bast fibers are isolated from the stem by a process termed retting. In retting operation enzymes are released by micro-organisms and these enzymes digest the pectic or the heteropolysaccharide element that surround the fiber bundles, and the fibers are thus released. Bast fibers provide high strength, permanence and other special properties which are needed for certain special kind of paper. Lightweight printing and writing papers, currency and cigarette papers are some of the examples of such papers [28,33].

1.5.3. Leaf fibers

Leaf fibre (also known as hardfibre) is normally obtained by scraping away the non-fibrous material of leaves and leaf sheaths of several monocotyledons, tropical and subtropical species [26]. Leaf fibre can have cellulose contents as high as 70% and they also have low lignin contents compared to wood [28]. Examples are pineapple and banana leaves. Manila hemp, or acaba, is derived from leaf sheaths of Musa textilis L., and is mainly used in cordage and for making strong but pliable papers. Sisal is produced from vascular bundles of several species in the genus *Agave* [36]. Leaves of esparto grass produce a fiber which is used to make soft writing papers [26].

1.5.4. Fruit fibers

Fruit fibers or seed hull fiber are obtained from unicellular seed or fruit hairs. One of the most common of plants fibres in use is cotton derived from the seed of plants of the cotton (Gossypium) family. Cotton has a three-walled structure consisting of a wax and pectin cuticle, a crystalline cellulose primary wall, a three-layer cellulosic secondary wall and a tertiary wall surrounding the lumen. [26]. The longest fibers of cotton (lint) are used as raw material for the textile industry, but the shorter ones (linters, 2–7 mm long), as well as textile cuttings and rags, are used as raw material for the best writing and drawing papers. Usually, the ratio of cellulose content is 90 % and the rest is resins, and mineral [28]. Another example of fruit fiber is Kapok, which is a fiber produced from fruit and seed hairs of two members of the family Bombaceae. Kapok fibers originate from the inner wall of the seed capsule. The cells are relatively long, up to 30 mm, with thin and highly lignified walls and a wide lumen [26].

In recent years, 46%, of the non-wood fiber used worldwide is straw, followed by bagasse (14%) and bamboo (6%) [37]. Other non-wood fibers such as cotton, hemp, sisal, and kenaf etc. are used for producing pulp and paper. Some characteristics of a few non-wood raw materials used for pulp production are summarized in Table 1.3.

Table 1.3. Summary of properties for non-wood plant fibers

Categories	Raw materials	Chemical properties			Physical properties	
		Cellulose w/w %	Hemicellulose w/w %	Lignin, w/w %	Fiber length (mm)	Fiber diameter (µm)
Agricultural residue	Banana stem [38]	59.18	17.50	18.21	1.55	22.00
	Rice straw [39]	41.20	19.50	21.90	1.41	8.00
	Bagasse [40]	42.34	28.60	21.70	1.51	21.40
	Wheat straw [41]	38.20	36.30	15.30	0.74	23.02
Annual plant	Bamboo [42]	43.00	39.00	31.00	2.70	14.00
	Elephant grass [43]	45.60	–	17.70	0.75	15.14
	Switch grass [44]	41.20	–	23.89	0.76	13.89
Non-wood crops	Kenaf bast [45]	55.50	17.70	12.50	2.90	28.16
	Plant fruit [46]	37.01	31.51	18.54	–	–
	Date palm rachis [47]	45.00	29.80	27.20	0.89	22.30
	Date palm leaves [47]	30.30	–	31.20	–	–

1.6. Chemical Characteristics of non-wood

The chemical structure of both wood and non-wood materials consists of three main components mainly, cellulose, hemicellulose, and lignin. Wood contains about 50% cellulose, 25% hemicellulose and 25 % lignin, but the proportion of the three main constituents vary in different species of wood and non-wood [7]. Also the chemical structure of non-wood plant fibers is different depending on the kind of the soil and growing conditions of the plants. The chemical structure of non-woods are categorized by a lower lignin content than wood and a higher pentosan or hemicellulose content. Stalk fibers are like hardwoods in chemical properties than softwoods. The major difference of non-wood with hard or softwood is the presence of higher ash and silica content of these non-woods.

1.7. Physical and Morphological Characteristics of non-wood

Non-wood fibers have unlimited variations in their physical and morphological properties. Softwoods contain tracheid and ray cells and other fines. The tracheid contains 90% fibers and only 10% are in ray cells. Hardwoods contain about 50% tracheid fibers and a large number of vessel and ray cells. Thus comparing with softwood, hardwood have more heterogeneous morphology.

Agro-based fibers which are commonly used for pulp production, for example rice and wheat straws, bagasse and corn stalks, have similarity to hardwood as the cellulose percentage is almost the same; but they contain a large quantity of very thin-walled cells, barrel-shaped parenchyma cells, and vessels and fine epidermal cells in a wide range of sizes [7]. Many non-wood fibers are like the short fiber hardwood, but some are long. In general, the length of the non-wood fiber is small, resulting in minor coarseness from these pulps. These fiber dimensions provide an idea of the possible effectiveness of these pulps in pulp and papermaking.

Previous studies have found that fiber lengths are not directly related to paper strength properties [48]. The minimum fiber length necessary to produce acceptable paper strength properties is dependent on many factors. Different fiber lengths provide different properties in paper. Though longer fiber length is required to impart strength properties in paper, but they tend to aggregate during pulping or beating operation hampers good sheet formation. Shorter fibers on the other hand provide excellent formation, but papers produced by using shorter fiber cannot be used for different applications.

1.8. Pulping characteristics of non-wood raw materials

The fiber features and the degree of difficulty of pulping for a particular raw material are important in deciding whether they can be used in certain pulping process,

The performance of fibrous raw material can be evaluated by the following factors:

(1) whether the fiber contents and forms are acceptable for pulping;

(2) the degree of difficulty for delignification in particular pulping process;

(3) the performance in certain pulping methods;

(4) the color of produced pulp and extent of bleaching difficulty;

(5) the drainage ability and the beating performance of pulp.

There are certain advantages of using non-wood fiber materials as pulp and papermaking raw Material [49-50]. These are as follows:

(1) it is the fast annual growing fiber resource, and it has lower lignin content than wood;

(2) pulp from non-wood can be produced at low temperatures with lower dosage of chemicals;

(3) a smaller plant can be feasible for manufacturing paper from non-wood;

(4) non-wood pulp is easy for the beating operation;

(5) the non-wood fiber materials pulping can bring additional economic benefits from the food crops, adding to the overall benefit of the producers.

1.9. Limitation of non-wood for pulping

Non-wood contains a high percentage of silica, hemicelluloses, and fines/parenchyma cells. The presence of these impurities in agricultural residues leads to serious technical challenges in the traditional pulping processes [51-52]. The silica present in the raw material transfer into the cooking liquor, which later on create difficulties in the recovery process of spent liquor. Silica forms scales in the recovery vessel which hampers heat transfer. The presence of silica also decreases causticizing efficiency, lime reuse/recycling, etc.

Another limitation in using non-wood raw material is that agricultural biomass is bulky in nature. As the packing density of most of the non-wood is low, transportation of this kind of raw material is difficult and costly. Also, the locations of agricultural waste are scattered,

thereby collection of raw materials is challenging. The total number of truck-miles to supply such kind of fibrous, bulky raw material to a mill is substantially higher than that of wood chips. Considering the raw material availability and collection, agricultural residue based non-wood pulp mills are small in number.

Another very important limitation of non-wood is that the resultant pulp has low drainage. Non-fibrous parenchymatic cells present in non-wood are part of the fines in the resultant pulp. These fines cause drainage problems and hamper paper machine runnability. Most non-wood contain lots of pith/parenchymatic cells, and fibers are mainly obtained from the vascular bundles in monocotyledonous stems and leaves. The parenchymatic cells lead to the formation of many fines during pulping process, hampering pulp washing, paper machine running and drying. Also, the high viscosity of black liquor from non-wood pulping is challenging.

1.10. Global production of non-wood pulp

The earliest information of non-wood plant material for use as surfaces for writing can be found back in 3000 BC in Egypt, where the pressed pith tissue of papyrus sedge (Cyperus papyrus L.) was the most widely used writing material. Actual papermaking was discovered by Ts'ai Lun from China, in AD 105. He invented a way of making sheets using fibers from hemp rags and mulberry (Morus alba L.). Straw was used for the first time as a raw material for paper in 1800, and in 1827 the first commercial pulp mill began operations in the USA using straw [53]. Today many countries produce pulp and paper from non-wood (Table 1.4).

Table 1.4. Leading countries in non-wood papermaking pulp capacities (FAO 2002) [31].

Country	Non-wood pulping Capacity (1000 metric tons)	Pulping capacity (%) from Non-wood in country	Global pulping capacity (%) from Non-wood
1. China	17,672	84.2	70.7
2. India	2,001	61.3	8.0
3. Pakistan	491	100	1.96
4. Venezuela	260	65.0	1.1
5. Columbia	252	46.8	1.0
6. Mexico	230	24.1	0.92
7. Thailand	221	34.2	0.88
8. Turkey	191	27.4	0.76
9. Brazil	182	8.0	0.73
10. Greece	160	84.2	0.64
11. Italy	145	23.6	0.58
12. Argentina	141	12.8	0.56
13. Spain	141	7.2	0.56
14. Egypt	127	100	0.51
15. South Africa	113	7.0	0.45
16. Cuba	108	100	0.43
17. Iraq	101	100	0.40
18. Vietnam	100	40.0	0.40
19. Iran	90	25.0	0.36
20. Indonesia	86	1.4	0.34
21. Ecuador	77	100	0.31
22. Bangladesh	75	34.3	0.3
23. Romania	74	9.3	0.3
24. DPR Korea	50	47.2	0.2
25. Peru	50	100	0.2

The global production of paper and cardboard is about 419.7 million metric tons in 2017 [54]. More than half of the world's total paper is produced in China, the United States, and Japan. About 92% of total pulp production in the world is from softwood or hardwood and the rest of 8% of the comes from non-wood material [17]. China and India are advanced in using non-wood [55], and these two countries produce about 80% of global non-wood pulp. There has been changes in the consumption of paper products also. The requirement for writing, printing paper and newsprint is decreasing, while packaging, while the demand for tissue papers and other hygiene products are increasing [56].

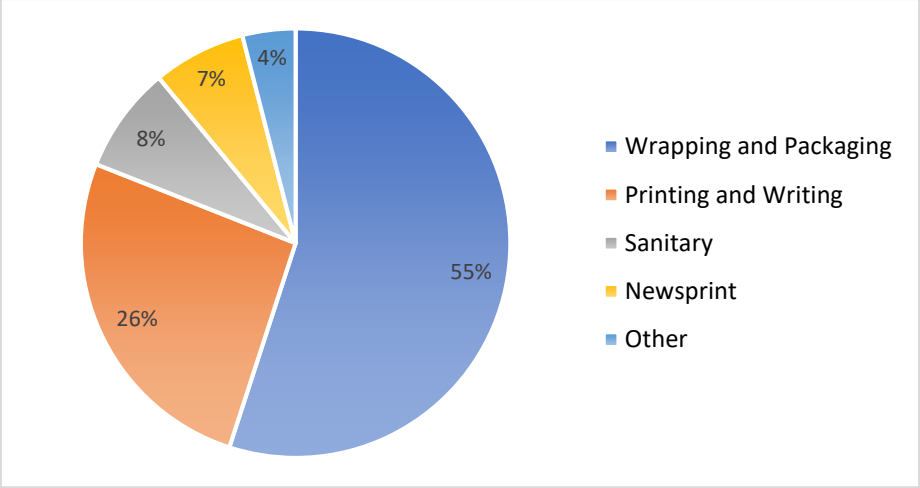

Figure 1.1. Global consumption by paper category, in tons in 2017 [57]

In many countries raw material for pulp production is scarce and sufficient quantities of wood is not available to meet the required demand for pulp production [58]. Thus due to the shortage of short fiber raw material (hardwood) and abundance of agricultural crops residues, active research has been under-taken to use non-wood raw material for paper production in recent years [59]. The predictable global availability of the most common agricultural residues for the year 2017 is given in Table 1.5 [17].

Table 1.5. The estimated global availability of agricultural residues (2017) [17].

Raw Material	Bone Dry Metric Tons (bdmt)
Cotton Linters	2,700,000
Cotton Staple	18,300,000
Cotton Stalks	68,000,000
Sugarcane Bagasse	102,000,000
Sorghum Stalks	252,000,000
Corn Stalks	750,000,000
Flax (oil seed)	2,000,000
Grass Seed	3,000,000
Oat	55,000,000
Barley	195,000,000
Rice	360,000,000
Wheat	600,000,000

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CHAPTER 2
LITERATURE REVIEW AND AIM OF THE WORK

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2.1. Introduction

The predominant pulping process for wood is Kraft or sulfate, while soda, sulfite and sulfate (and their deviations, such as Soda AQ) processes are industrially practiced for non-wood [1]. In order to overcome the limitations of non-wood pulping in conventional processes, many researchers are looking for alternative processes with easy and cheap recovery systems so that non-wood raw materials can used in a small pulp mill. For agricultural wastes, the predominant pulping process used is the soda-anthraquinine (AQ) process [2-7]. Among the alternative pulping processes, the organosolv process has several advantages. The organic solvent breaks up the lignocellulosic biomass to obtain cellulosic fibers for pulp and papermaking. Also high quality hemicelluloses and lignin degradation products can be generated from black liquors which lowers environment pollution [8-11]. The solvents used in the organosolv processes are either low-boiling solvents or high-boiling solvents. The low-boiling solvents used are methanol, ethanol, formic acid etc can be easily recovered by distillation. Also the high-boiling solvents (for example ethyleneglycol, ethanolamine), can be used at a low pressure and can be currently used at available facilities in prevailing conventional pulping processes. Thus, the equipment used in the classic processes, such as the soda and Kraft processes can also be used which would save capital cost [12-15]. Using the organic solvent process, pulps with high yield, low residual lignin content, high brightness and good strength can be produced [16-17]. Moreover, hemicelluloses and sulphur-free lignin fragments can be produced which are valuable by-products. The lignin fragments are useful for the production of lignin-based adhesives and other products that require high purity [18-20].

Considering all these factors the conventional soda-AQ pulping process and the environmentally benign alternative formic acid pulping process has been discussed in this chapter.

2.2. Earlier research on non-wood pulping

2.2.1. Soda-Anthraquinone (AQ) pulping process

As shown in Table 1.2, pulp is produced from non-wood using different chemical pulping processes. The soda-anthraquinone (AQ) pulping process has certain advantages and has been used conventionally by many researchers for pulp and paper production from non-wood plant materials [2-7].

In 1972 Bach and Fiehn reported one of the first applications of anthraquinone (AQ) or AQ-derivatives in pulping [21]. But AQ was used as an effective pulping catalyst in 1976 [22-24]. It was reported by Holton that AQ could be used to reduce the kappa number under identical cooking conditions [22]. In the early 1980s, a lot of research was done for the quantification of AQ to achieve low kappa value of pulp [25-29]. It was observed that at 0.2%-0.3% AQ charge on oven dry (o.d.) wood, softwood pulps of reasonable strength with kappa numbers as low as 15-17 could be obtained. Other researchers obtained similar results using AQ charges of 0.1%-.8% on o.d. wood [30].

MacLeod et al. found that by adding AQ to a conventional kraft process, the resulting pulp retained a larger percentage of carbohydrate material than the kraft pulp; resulting a higher pulp yield at a given kappa number [31]. Thus, AQ not only accelerated the kraft pulping reaction, it also stabilized and increased pulp yield.

Over the next decade, researchers worked laboriously to find the optimum use of AQ in industrial practice as a catalyst. It was found that AQ could be used for pulp production incremental [2-7], environmental improvement [25,29,32-33], cost reduction [5,34-36], and non-conventional alkaline pulping processes [2,36-39]. AQ was also found to be beneficial in pulping of several non-wood agricultural wastes [40-45].

During the late 1980s and into the 1990s, several successful mill trials by using AQ in the industries using kraft pulping processes was occurred and the process was adopted in many mills [46]. It was found that AQ provided almost zero capital solution to the demand for lower impact bleach plant operations with minimal effect on recovery [47]. Thus different pulp and paper mills frequently used AQ as a means to increase pulp production. As it had a major cost reduction, the limitation at recovery capacity was also possible to be avoided [48-49].

AQ proved to be an exciting addition to chemical pulping. Advances in AQ chemistry in pulping gave one of a very limited number of pulping chemistry development in decades [2]. The nature of the engineering process also magnified the potential financial benefit. Mills were designed so that all areas have about the same production capacity. The industries were able to operate at higher net production, improved capital efficiency and labor productivity as the restriction of using only one process was relieved.

Most paper products eventually find their way into food contact applications through recycling. So, the approval of the use of AQ in paper manufacturing was required by the U.S. Food and Drug Administration (FDA) [50]. AQ was approved as a pulp additive in 1987 [51] and later on it was rapidly accepted by the paper industry [52]. Most of these mills were using AQ to increase production [52].

2.2.2. Soda-AQ pulping Chemistry

The anthraquinone (AQ) pulping chemistry has been of great interest among the researchers. It was found that during alkaline pulping AQ operates as a redox catalyst and the chemistry is unlike hydroxide ions (OH^-) in the conventional soda process. During pulping, AQ reacts with reducing aldehyde end groups of carbohydrates and oxidizes them to create carboxylic acids [53]. The oxidation of aldehyde to carboxylic acid prevents the alkaline depolymerization reaction that occurs with the reducing sugar end groups. As the sugar end groups are not broken

down or depolymerized, the carbohydrate retains and this process results in an increased pulp yield. The interaction of these conditions allows the attainment of pulps with similar cooking times with higher yields and lower kappa number. The environment friendly AQ trials gave good results in terms of strength and yield, especially in case of bast fiber [53-56].

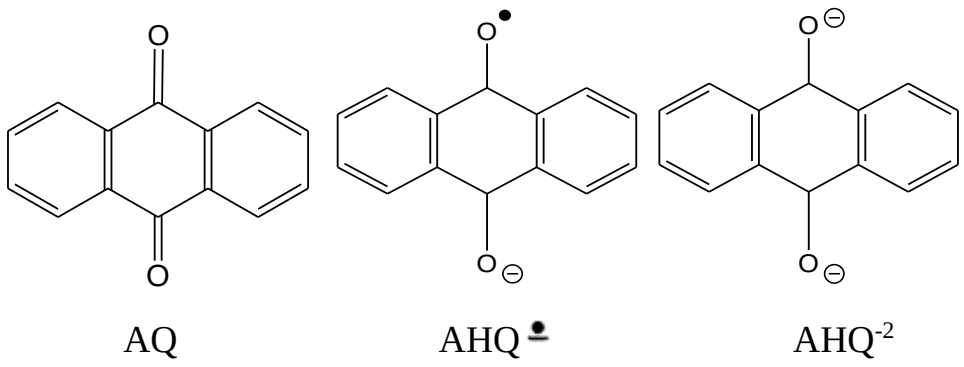


Figure 2.1. Different oxidation states of Anthraquinone (AQ) [56].

During pulping, AQ exists in several oxidation states, such as the oxidized form (AQ); the partially oxidized (partially reduced) semiquinone form, anthrahydroquinone radical anion ($AHQ^{\bullet -}$); and the fully reduced form, anthrahydroquinone dianion (AHQ^{-2}) [56].

The redox reactions that occur during soda-AQ process are shown in Figure 2.2. Here, AQ or $AHQ^{\bullet -}$ oxidizes carbohydrate aldehyde end units and reduces the alkaline carbohydrate degradation. In this stage AHQ^{-2} is formed. AHQ^{-2} reacts with lignin and lignin is fragmented which increases reaction rate and lignin is also removed by this process. Oxidation of AHQ^{-2} gives back AQ or $AHQ^{\bullet -}$. The important and significant advantage is that to occur these redox reactions, only a small amount (<0.1%) of AQ that is required.

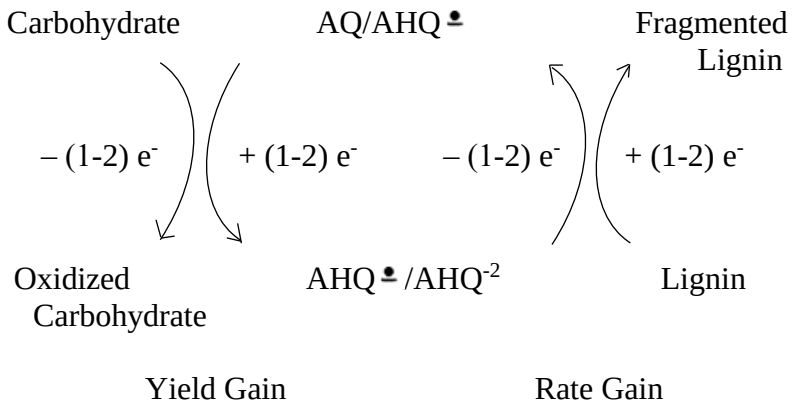
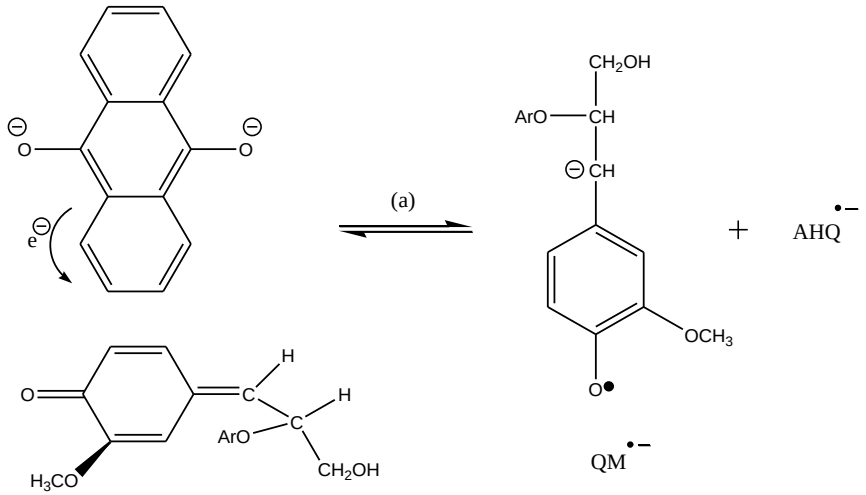
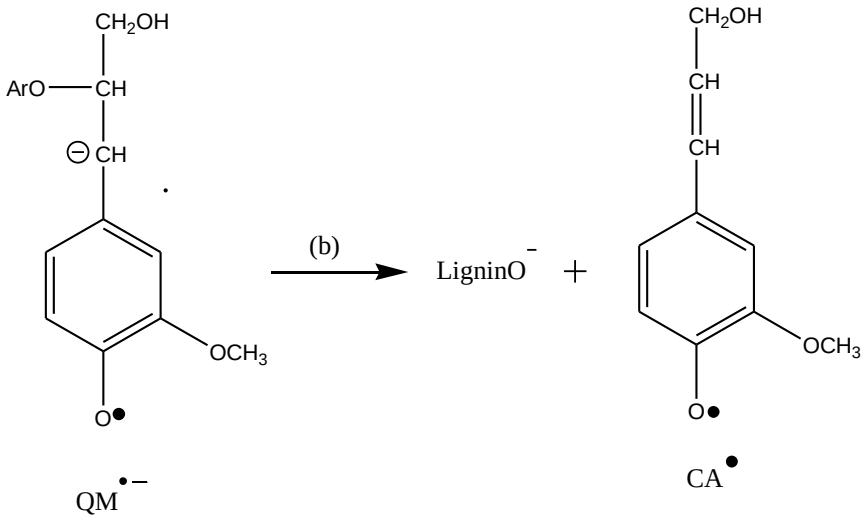


Figure 2.2. Anthraquinone redox reactions with wood components [8].

The steps proposed by Dimmel (1996) begin with one electron transfer from AHQ^{-2} to a lignin quinone methide (QM) (Figure 2.3; Eq. a). The resulting QM radical anion then breaks down to an ion and a radical fragment (Eq. b.). The latter picks up an electron from another AHQ^{-2} to give a second phenolate ion (Eq. c.). The AHQ^{-2} ions are regenerated when a carbohydrate is oxidized to $AHQ^{\bullet -}$ to an aldonic acid (Eq. d.). The sum of these equations (Eq. e.), indicates that electrons are transferred from carbohydrates to lignin, causing the former to be oxidized to relatively stable aldonic acid polymer end units, and the latter to be reduced, leading to fragmentation and sedimentation. The two effects account for the observed improved pulp yields and faster pulping rates [56].





$$AHQ^{-2} + CA^{\bullet} \xrightarrow{(c)} AHQ^{\bullet -} + CA^{-}$$

$$2AHQ^{\bullet -} + RCHO + 3HO^{-} \xrightarrow{(d)} 2AHQ^{\bullet -} + RCO_2^{-} + 2H_2O$$

$$\text{Lignin-QM} + \text{CarbohydrateCHO} + 3HO^{-} \xrightarrow{(e)} \text{LigninO}^{-} + CA^{-} + \text{Carbohydrate } CO_2^{-} + 2H_2O$$

Figure 2.3. Postulated SET reactions between AHQ ions and wood components; CA= coniferyl alcohol [56].

2.3. Alternative pulping processes

In order to overcome the problems associated with non-wood pulping in conventional processes, many researchers have worked on different alternative pulping processes previously. These include alkaline sulfite anthraquinone methanol (ASAM) process [57-58], inorganic acid pulping [59], ammonium sulfite pulping [60-64], IDE pulping method [65-66], alternative alkaline pulping [67-68], organic solvent pulping [8,69-73]. Table 2.1. shows previous studies of pulping of non-wood in alternative processes.

Table 2.1. Pulping of non-wood in alternative processes

Raw material	Process	Pulp yield (%)	Kappa number	Viscosity / DP	Tensile N.m/g	Tear $mN.m^2.g$	Burst $kP.m^2/g$
Bagasse [68]	NH_4OH-KOH-AQ	65.0	11.3		51.6	6.5	2.8
Rice straw [74]	KOH	42.82	34.93	888	2551**	0.33	1.45
Rice straw [75]	DEG	60.59	35.0	-	7220**	42.5**	68**
	DEG/EG	62.5	34.0	-	7800**	42.0**	62**
	DEG/EG/S	64.57	21.0	-	8140**	47.0**	63**
Rice straw [76]	Formic acid	44.4	25.1	-	3919**	3.95	2.39
Rice straw [77]	THFA	59.0	17.3	-	35.5	7.45	2.3
Bamboo [78]	FA based organosolv	40.5	29.4	899.1	-	-	-
Reed canary grass [79]	Milox	45.5	11.2	820	-	-	-
Wheat straw [80]	FA/AA/PA	39.3	23.2	1458*	4551**	3.45	2.51
Wheat straw [81]	Alcell	47.4	34.7	14.4	53.19	5.97	2.06
Wheat straw [82]	MEA-AQ	56.6	16.9		7100**	3.4	
Rye straw [82]	MEA-AQ	58.4	13.5		9050**	4.4	
Bagasse [83]	KOH	46.3	12.3	-	67.0	6.2	5.1
	KOH-AQ	49.1	11.0	-	69.9	5.6	5.4
Kash [83]	KOH	48.6	7.4	-	64.7	9.3	5.3
	KOH-AQ	48.9	7.3	-	65.2	8.9	5.2

**Breaking length and burst & tear factor

*Degree of polymerization, FA/AA/PA-Formic acid/Acetic acid/Peroxyacid, DEG- Diethyleneglycol, EG- ethyleneglycol, S-soda, THFA-Tetrahydrofurfuryl alcohol

2.3.1 Organosolv methods

In recent years, development of several organosolv methods capable of producing pulp with properties near to those of Kraft pulp has been reported. Prominent among the processes that use alcohols for pulping are those of Kleinert [8], Alcell [8,69-70], Organocell [69-71], ASAM [69-72] and ASAE [73]. Other processes based on other chemicals also worthy of special note are ester pulping [84-85], phenol pulping [8, 86], Acetocell [87], Milox [88-90], Formacell [91] and NAEM [92].

In the organic acid processes, typically formic acid and acetic acid are used to delignify lignocellulosic materials to produce pulp for paper [88,93-96]. In the acid pulping process, acidic delignification of raw materials removes lignin and a necessary part of the hemicellulose and nutrients, but the silica remains in the pulp. The pulping operation can be carried out at atmospheric pressure. There are several advantages of acid process. The acid used in the pulping process can be easily recovered by distillation and reused [12]. The cooking liquor is washed from the pulp, and cooking chemicals are recovered and recycled completely. Also, another major advantage is that cellulose, hemicellulose and lignin can be effectively separated. Formic acid can also be used to enhance acetic acid pulping. When formic acid is used in pulping, the temperature and pressure can be lower compared to those of alcohol or acetic acid pulping processes. Organic acid lignin is used as raw material for many value-added products, due to its lower molecular weight and higher reactivity [97-98]. Another major advantage of organic acid pulping is that silica retains of on pulp fiber which later on facilitates efficient recovery of cooking chemicals [99]. The organosolv pulping processes based on organic acid pulping are the Milox, Acetosolv and Formacell processes [87-91].

2.3.2. Formic acid/peroxyformic acid process (The Milox process)

In the Milox process, peroxyformic acid or peroxyacetic acid is used as the cooking chemical [100]. Peroxyformic or peroxyacetic acids are simple to prepare by equilibrium reaction between hydrogen peroxide and formic or acetic acids. These chemicals that do not react with cellulose or other wood polysaccharides in the same way as formic acid. When the process in performed into two or three stages, the hydrogen peroxide consumption can be reduced. The two-stage formic acid/peroxyformic acid process is reported previously to produce high viscosity and 90% ISO bleached pulp with 40-48 % yield [88-90]. The pulping process is carried out at atmospheric pressure and at temperatures below 100°C. It was found previously that the resulting pulps have low kappa numbers between 5 and 35 [12].

The hydrogen peroxide charge can be reduced by dividing the cooking method into two or three stages. The temperature is raised to the boiling point of the formic acid (105°C) and the cooking proceeds for 3-4 h. The softened chips are then washed with pure formic acid. The washed pulp is then reheated with peroxyformic acid at 60°C at about 10% consistency. Peroxide is applied to the liquor at 1%-2% of the original dry weight of the chips. Peroxide charge could be reduced to 2% by increasing peroxyacid treatment time or reducing residual lignin in the first formic acid stage through proper equipment (agitation) [101].

After peroxyformic acid cooking, the pulp is washed with strong formic acid, and washed under pressure with hot water at 120°C. This removes the chemically bonded formic acid. After washing and screening, the pulp is ready for bleaching [102].

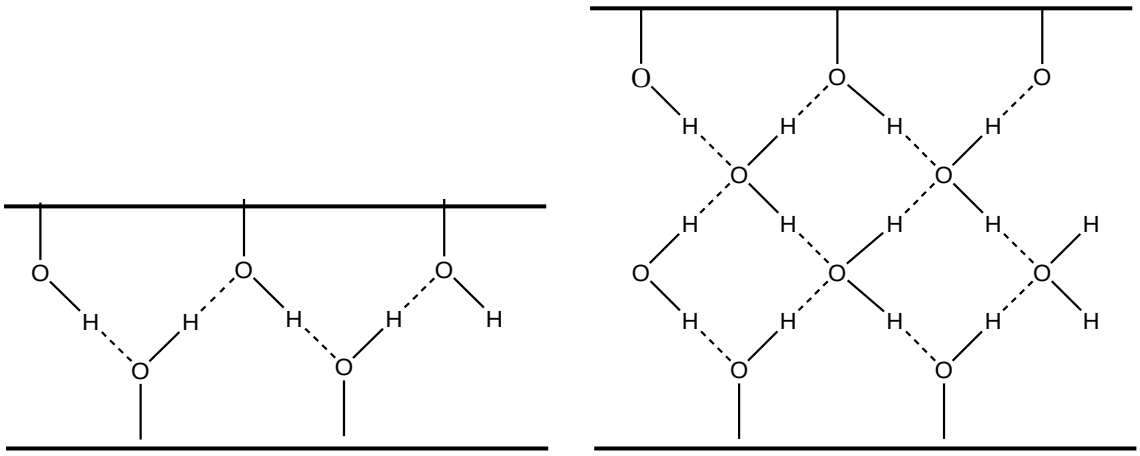
2.3.3. Chemistry of formic acid/peroxyformic acid pulping

During formic acid pulping, a certain amount of water helps initiation of reaction. The reaction below shows hydrolytic dissociation of organic acids in solutions and formation of solvated

protons, which facilitate the breakdown of plant matter in an organic acid environment when water is added.

$$RCOOH + H_2O \rightarrow RCOO^- + H_3O^+$$

During the pulping, the highly concentrated formic acid molecules latch onto the water molecules between the cellulose chains, which produces direct H-bonds between cellulose macromolecule and hydroxyl groups (Figure 2.4a). This causes poor mechanical properties of pulp and the blocks become stiff, breakable, inflexible and easily cut during refining, as opposed to hydrated fibers (Figure 2.4b). The addition of water is firstly used to break the links between the molecules of organic acid and then to favour the ionization and dissociation of these acids, which then supply the proton [103]. Thus, a certain amount of water helps the pulping improving the mechanical properties of paper.



(a) dehydrated fiber **(b) hydrated fiber**

Figure 2.4. Hydrogenous linkages between (a) dehydrated and (b) hydrated fibers [104].

The delignification of PFA can be explained by the action of the hydroxonium ion OH^+ formed during peroxyacid stage in acidic medium:

$$RCOOOH + H^+ \rightarrow RCOOH + OH^+$$

Hydroxonium ion (OH^+) is a strong electrophilic agent, which can react with lignin [105]. The peroxyacid under acidic condition act as delignifying and activating agent and not as bleaching agent [106].

2.4. Earlier research on non-wood bleaching

Bleaching is the treatment of pulps with chemical agents to increase their brightness by either lignin removal (delignification) or lignin decolorization. Bleaching of non-wood pulp has been practiced since early times. Pulps from agricultural wastes are easily bleachable because of their open fibrous structure and also due to the lower lignin content compared to wood pulps [107]. Such pulps require fewer chemicals than wood pulps.

The main parameters that influence the bleaching operation are the type of chemical, its dosage, pH value, temperature, and retention time. Chemicals used for bleaching cover oxidizing bleach, reductive bleach, sodium hydroxide, chelating agents and enzymes, which can be used alone or in combination. All lignin present in cellulosic raw material cannot be removed in a single bleaching stage, so pulp is usually bleached in multiple stages. The first two stages of bleaching primarily extract and release lignin, and the subsequent stages remove the lignin residues and finish the product.

In traditional non-wood pulping, the CEH (chlorination, alkaline extraction, and hypochlorite stage) three-stage bleaching process is usually adopted which causes heavy waste water pollution. Currently, the main clean bleaching technologies are elemental chlorine free bleaching (ECF) and total chlorine free bleaching (TCF). The main chemical used in ECF bleaching is chlorine dioxide. There are certain advantages of using chlorine dioxide as it has strong oxidation capacity. ECF bleaching technology is very mature in non-wood pulp bleaching [108]. Bleach used in TCF bleaching are generally oxygen, hydrogen peroxide and

ozone. For wheat straw pulp using TCF bleaching, the brightness of bleached pulp was found as high as 83.5% ISO without compromising the physical properties of the paper [102].

2.4.1. Bleaching Chemistry

2.4.2. Oxygen Bleaching Chemistry

Oxygen bleaching is a much gentler alternative to traditional chlorine bleaching. During oxygen-alkali bleaching, the phenolic hydroxyl group (Figure 2.5) (1) is deprotonated in alkaline media, to produce the phenolate anion (2). The phenolate ion provides high electron density that is required to initiate a one electron transfer. The reactive electrophilic (d-) sites (Figure 2.5) (2) are positioned at alternating carbons. Oxygen attacks at an electrophilic (d-) site and removes an electron, leaving a phenoxyl radical (3) and/or a mesomeric cyclohexadienonyl radical, while oxygen itself is reduced to the superoxide anion radical.

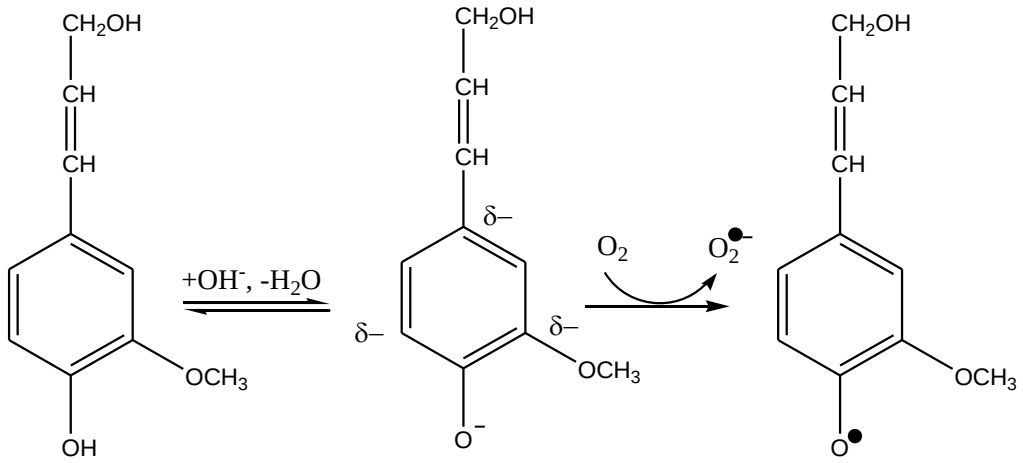


Figure 2.5. The initial step of oxygen-alkali bleaching at electrophilic (δ-) sites.

Under alkaline conditions the reaction of dioxygen with an activated lignin model compound (particularly a phenolate) generates a superoxide anion radical. [109-111].

$$\bullet O_2^- + OH\bullet \rightarrow OH^- + O_2 \quad (1)$$

$$HOO^- + OH\bullet \rightarrow OH^- + O_2 \quad (2)$$

$$OH\bullet + OH\bullet \rightarrow H_2O_2 \quad (3)$$

$$\bullet O_2^- + \bullet O_2^- + H_2O \rightarrow HO_2^- + O_2 + OH^- \quad (4)$$

$$\bullet O_2^- + H_2O_2 \rightarrow OH^- + OH\bullet + O_2 \quad (5)$$

$$HOO^- + H_2O_2 \rightarrow OH\bullet + \bullet O_2^- + H_2O \quad (6)$$

$$\bullet O_2^- + OH\bullet + H_2O \rightarrow HOO^- + OH^- \quad (7)$$

$$O_2 + \bullet O^- \rightarrow \bullet O_3^- + \bullet O^- \rightarrow O_2 + HOO^- \quad (8)$$

2.4.3. $D_0(EP)D_1$ Bleaching Chemistry

At slightly acidic conditions (pH 3-5) chlorine dioxide can be reduced to chloride ions [112]:

In this reaction five oxidation equivalents can be released. Therefore, 1M chlorine dioxide solution contains 5× 35.5 g/litre of active chlorine.

In alkaline media chlorine dioxide is reduced to chlorite ions involving a change of only one oxidation equivalent.

At slightly acidic conditions (pH 3-5) chlorine dioxide can be reduced to chloride ions:

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$$

In this reaction five oxidation equivalents can be released. Therefore, 1M chlorine dioxide contains 5 × 35.5 g/litre of active chlorine.

$$ClO_2 + e^- \rightarrow ClO_2^-$$

In alkaline media, chlorine dioxide is reduced to chlorite ions involving a change of only one oxidation equivalent:

Even at the usual (slightly acidic) bleaching conditions both chlorite ions and hypochlorous acid can be generated from chlorine dioxide in its reactions with pulp components (lignin).

Chlorite is not highly reactive, but it can disproportionate to hypochlorous acid and chlorate ions:

$$2ClO_2^- + H^+ \rightarrow HOCl + ClO_3^-$$

Here, hypochlorite is in equilibrium with chlorine. Contrary to hypochlorite and chlorine, chlorate is rather unreactive and it mainly remains in the bleaching effluent as such. Another reason for generation of chlorate is the oxidation of chlorite with chlorine or hypochlorite:

$$ClO_2^- + Cl_2 + H_2O \rightarrow ClO_3^- + 2\ Cl^- + 2H^+$$

$$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+$$

However, chlorite is reoxidized to chlorine dioxide.

$$2ClO_2^- + Cl_2 \rightarrow 2ClO_2 + 2\ Cl^-$$

$$2ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + HO^-$$

Sincea number species chlorine, hypochlorous acid, chlorite and chlorate, are formed as intermediates, the oxidation pathways of chlorine dioxide bleaching is complex.

2.5. Earlier research on morphology

To choose a fibrous raw material for pulp and paper production, information about the fiber morphology is very useful. The morphology of plant material provides important information which helps to determine the papermaking potential of various species [113-114]. The chemical and physical properties are based on the cell wall characteristics whereas the properties of the fiber depend on the type of cells from which the fiber is derived [115]. Anatomically, plant

fibers are composed sclerenchyma cells which are narrow and elongated in shape. Mature fibers have well-developed cell walls and their principal function is to support and protect the plant. Figure 2.6 is a cross section of a non-wood wheat plant. As can be seen from the figure, fibers develop from different meristems, and they are found mostly in the vascular tissue of the plant. Fibers sometimes occur in other tissues also [116-117].

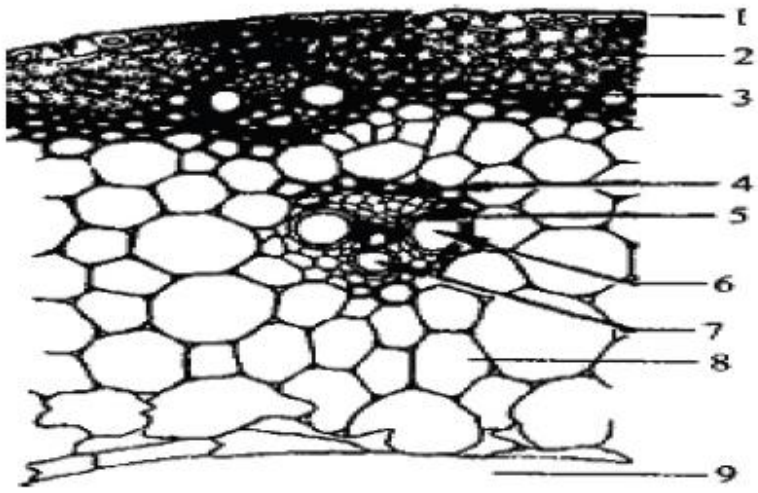


Figure 2.6. Cross section of wheat straw. (1) Outer epidermal cells, (2) Fibrous tissue band, (3) vessel, (4) bundle sheath, (5) vascular bundle, (6) xylem, (7) phloem, (8) parenchyma cell, (9) Internal epidermal membrane [117].

Fibers impart strength to the paper sheet. The vessel in plant material conducts water and dissolved minerals from the roots to the higher parts of the plant. As a result, the primary cell wall is partly strengthened, or almost entirely covered with a secondary wall which is also lignified. Large vessel elements cause problem in papermaking when hardwoods are used [118]. On the contrary, the function of parenchyma cell in plant is to store water, nutrient and assimilated products. In papermaking parenchyma cells with spherical and small cells are considered to decrease the raw material quality [119]. Parenchyma has low density and thus decreases the bulk density of the feed to the pulp digester. It also consumes chemicals without participating in paper strength and caused problem in pulp water drainage. The proportion of

parenchyma cell in fibers used for papermaking is between the range of 20–50% [120]. The image of the vessel element and parenchyma cell is presented in Figure 2.7.

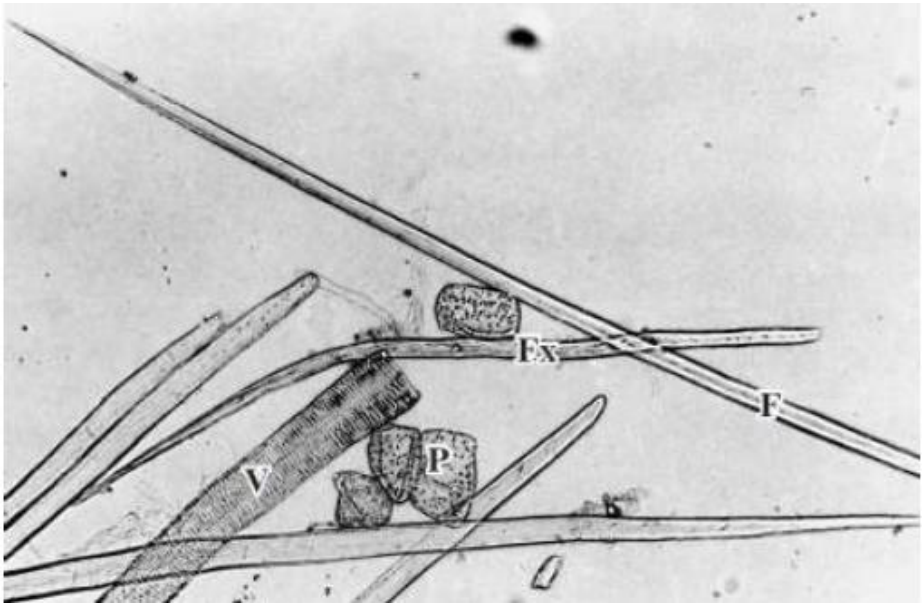


Figure 2.7. Image of fibre, vessel element and parenchyma cell in a *Cynara cardunculus* plant. [121]

Morphological characteristics are in evaluating pulp quality of fibers [121]. The significance of some parameters is described below.

2.5.1. Fiber Length

Fiber length is one of the major factors controlling the strength properties of paper. Fiber density and fiber strength are also important properties for good quality paper. According to Dinwoodie, fiber length is associated with the number of bonding site available on an individual fiber [122]. Montigny and Zoborowski showed that there is a simple straight-line relationship between the fiber length index of pulp and the tearing strength of the paper [123]. Also it was reported that long fibers have a strong positive correlation with tearing strength without any clear relationship with other paper properties [124].

2.5.2. Fiber Diameter

Fiber diameter is the thickness of individual fibers, its measurement is used to determine the end-use of the fibers [125 134]. In paper production, the importance of fiber diameter is usually based on its relationship with fiber length. This is called slenderness ratio or felting rate.

2.5.3. Lumen Width

Lumen is the inside space of a tabular structure. Lumen width is the distance between the diameters of the fiber. The important significance of lumen width on pulping process is that larger lumen width allows penetration of liquid into empty spaces of the fibers during beating improvising the quality of pulp [126].

2.5.4. Cell-wall thickness

Cell wall contain most of the cellulosic fiber. So it is important to determine the cell-wall thickness of the fibrous raw material to select it for pulp and paper production. The thickness of cell-wall increases with the age of the tree. Atchinson and McGovern showed that most non-wood fibers are thin-walled which invariably lower the coarseness of their pulp. Research shows that the thin-walled fibers are very important in the manufacture of many grades of papers [127]. Variations in fiber wall thickness occurs within individual trees and within trees of the same kind and for these indifferences, variations in density also occurs [128].

2.6. Derived fiber morphologies

Some common derived fiber morphologies used in assessing the fiber of lignocellulosic materials for pulp and paper productions are discussed below:

2.6.1. Slenderness Ratio

Slenderness ratio or felting power, is inversely proportional to the fiber diameter. It is the value obtained from the ratio of fiber length to fiber diameter. It has been found that if the slenderness

ratio of fibrous material is less than 70, it is not worth for quality pulp and paper production [120]. This is because a low slenderness ratio indicates reduced tearing resistance, which is partly due the fact that short thick fibers do not produce good surface contact and fiber-to-fiber bonding [129]. This expression for slenderness ratio is stated below.

$$\text{Slenderness ratio} = \frac{\text{Fibre length}}{\text{Fibre diameter}}$$

2.6.2. Flexibility ratio

This measures the ratio of lumen to fiber diameter. It is one of the important factors which determine the suitability of pulp for paper making. It expressed the actual proportion of lumen out of a total circumference of a fiber in percentage.

Flexibility is the key to the development of burst and tensile strength as well as the development of the paper properties that affects printing [130-131]. The expression for flexibility ratio is stated in equation 2.

$$\text{Flexibility ratio} = \frac{\text{Lumen width}}{\text{Fibre diameter}} \times 100$$

Based on flexibility ratio, Bektals et al. classified plant fibers into the following four groups [132].

High elastic fibers: This represents woods with flexibility ratio greater than 75%. Density of such wood is low, usually less than 0.45g/cm3 thin walled and large lumen. Fibers of such wood can collapse easily and flatten to produce good surface area contact, thus, there is a good fiber-fiber bonding.

Elastic fibers: This constitutes woods with fiber flexibility between 50-75%. Density is medium with cell-wall and lumen of equal dimension. The fiber collapsed partially to give relative contact and fiber bonding.

Rigid fibers: This constitutes woods with fiber flexibility between 30-50%. The cell-walls are thicker with medium to high density fibers seldom flatten and have poor surface contact and fiber-to fiber bonding.

High rigid fibers: Wood with fiber flexibility less than 30%. This is generally applicable to over matured tress. Fibers are very thick-walled with narrow lumina, very poor surface contact and fiber to-fiber bonding.

2.6.3. Runkel ratio

This measures the amount of wood in respect to the cavity or lumen of the fiber. It is twice the thickness of the cell-wall divided by the width of the lumen as shown in equation 3.

$$\text{Runkel ratio} = \frac{2 \times \text{Cell wall thickness}}{\text{Lumen width}}$$

Ademiluyi and Okeke classified fiber value according to the runkel ratio and concluded that as runkel ratio increases, the paper quality produced decreases with Runkel ratio less than one being the best while those greater than one are of poorer quality [133]. Fibers with higher runkel ratio are stiffer, less flexible and form bulkier paper of low bonded areas than fibers with lower runkel ratio [120].

2.7. PROBLEM STATEMENT

In 2017, the total production of paper and cardboard was approximately 419.7 million metric tons worldwide. The market value of paper and pulp is expected to increase within the five-year period of 2019 and 2024. The estimation is a rise from 63.3 billion U.S. dollars to about 79.6 billion U.S. dollars by 2024 [135]. This increasing trend is mainly from developing countries like China. On the other hand, the GDP growth in Bangladesh is above 6% since last 15 years, which indicates that the living standard of people has improvised. The per capita paper and board consumption in Bangladesh is about 5 kg, whereas in advanced countries it is 250 kg/capita, and the Asian average is about 45 kg/capita [136]. The forest resources is very limited in Bangladesh which is a major downside for pulp and paper production in this country. More than half of the demand of pulp and paper is fulfilled by import. As a consequence, the country needs alternative fibrous raw materials sources. In this regard, many researches have been working on finding out suitable alternative raw material sources for pulping [137-143].

Wood has been the principal source of cellulosic fibre for pulp and paper manufacture for years. The increased demand of paper consumption has already caused massive deforestation in the world. The consequence is the ecological imbalance and climate change which are already very obvious. Thus, along with wood, non-wood can be a good alternative paper pulp manufacturing in many countries where agricultural residue are available [143].

Bangladesh as an agricultural country generates a substantial quantity of agricultural residues [144]. Annual growth in agricultural sector in Bangladesh was reported by World Bank at 2.7863% in 2016, which indicates that the crops residues quantity increased consequently over the years [145]. A significant solution to the raw materials problem of a forest deficient and agriculture dependent country could be the use of agricultural residues for pulp manufacturing [146]. Therefore, to reduce the load on our forests, some agriculture residues available in Bangladesh have been carefully selected to study their suitability as pulping raw material.

2.8. AIM OF THE WORK

1. To study the chemical, morphological and anatomical properties of non-wood available in Bangladesh.
2. To evaluate conventional soda-anthraquinone pulping and alternate formic acid/ peroxyformic acid pulping of the crops residue.
3. To study the alkaline peroxide bleaching of produced formic acid pulp.
4. To investigate low and high temperature chlorine dioxide bleaching of produced soda-anthraquinone pulp.
5. To evaluate the physical properties of the prepared paper sheets from the produced pulps.
6. To develop mathematical model between chemical and morphological characteristics with pulp yield and physical properties of the prepared paper sheets.

The overall aim of this study is to evaluate the possibility of using agricultural residues as source of fibrous raw material for pulp and paper production in Bangladesh.

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CHAPTER 3

CHEMICAL AND MORPHOLOGICAL CHARACTERISTICS

3.1 Introduction
3.2. Experimental
3.2.1. Raw materials
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3.1. INTRODUCTION

The fibrous constituent is the most important part of the plant. Since plant fibres consist of cell walls, the composition and amount of fibres is reflected in the properties of cell walls [1-2]. Cellulose is the principal component in cell walls and in fibres. The non-cellulose components of the cell wall include hemicelluloses, pectins, lignin and proteins, and in the epidermal cells also certain minerals [2]. Due to harvesting time, geographical location and variety of non-wood crops residue, the morphology and chemical compositions also differ and they affect the pulping properties of the plant material [3]. Some of non-woody fibre plants contain more pentosans (over 20%), holocellulose (over 70%) and less lignin (about 15%) as compared with hardwoods [4]. They have also higher hot water solubility, which is apparent from the easy accessibility of cooking liquors. The low lignin content in grasses and annuals lowers the requirement of chemicals for cooking and bleaching [4].

Except for the fibrous material, plants also consist of other cellular elements, including mineral compounds. While the inorganic compounds are essential for plant growth and development, they are undesirable in pulping and papermaking [6].

3.2. EXPERIMENTAL

3.2.1. Raw materials

Twenty-two crops residue that grows abundantly in Bangladesh and are either wasted or used as cattle feed or fuel for burning have been selected for pulping raw material in this study. Wheat straw, corn stalks, mustard stalks, eggplant stalks, chia stalks, banana pseudo stem, banana leaf, banana peduncle, bagasse, bamboo, kash (kans grass), okra stalks and kaun (millet) straw were collected from Katiadi, Kishoreganj. Jute and jute stick, dhaincha stalks, rice straw, bamboo, red lentil stalks were collected from Trishal, Mymensingh. Pineapple leaves, cassava stalks, cotton (*Gossypium*) stalks were collected from Hobiganj, Sylhet and mulberry stalks were collected from Rajshahi district.

These are listed below.

1. Bagasse (*Saccharum*)
2. Bamboo (*Bambusoideae*)
3. Banana (*Musa Cavendish*) pseudo stem
4. Banana (*Musa Cavendish*) leaf
5. Banana (*Musa Cavendish*) peduncle
6. Cassava (*M. esculenta*) stalks
7. Chia (*Salvia hispanica*) stalks
8. Corn (Z. mays) stalks
9. Cotton (*Gossypium*) stalks
10. Dhaincha (*Sesbania aculeata*) stalks
11. Eggplant (*Solanum melongena*) stalks
12. Jute (*Corchorus*) fiber
13. Jute (*Corchorus*) stick
14. Kash (*Saccharum spontaneum*) stalks
15. Kaun (*Seetaria- ltalika*) straw
16. Mulberry *(Morus)* stalks
17. Mustard (*Brassica juncea*) stalks
18. Okra (*A. esculentus*) stalks
19. Pineapple (*A. comosus*) leaves
20. Red lentil (*L. culinaris)* stalks
21. Rice (*Oryza sativa)* Straw
22. Wheat (*T. aestivum*) straw

3.2.2. Determination of chemical characteristics

3.2.2.1. Preparation of Test Specimen

The test specimen consisted of at least 1 gram of oven dry extractive-free raw material, prepared according to TAPPI standard, that had previously been ground to pass a 40-mesh sieve and then retained on a 60-mesh sieve.

3.2.2.2. Cold water solubility (T 207 cm-99)

2 gm o.d. sample was dissolved in 300 ml distilled water and constant stirred for 48 hours at 23± 2^0C. It was then filtered, washed, dried and weighed.

3.2.2.3. Hot water solubility (T 207 cm-99)

2 gm o.d. sample was dissolved in 100 ml hot distilled water in the Erlynmeyer flask with reflux condenser and it was placed in a boiling water bath for 4 hours. It was then filtered, washed, dried and weighed.

Calculation:

Hot or cold water solubility, % = $\frac{A-B}{A} \times 100$

Where, A = Initial weight of the test specimen, gm (o.d.)

B = Weight of test specimen after extraction, gm (o.d.)

3.2.2.4. 1% NaOH solubility (TAPPI T-257)

Hot alkali solution extracts low molecular weight carbohydrates consisting mainly of hemicellulose and degraded cellulose in wood materials. 1 gm o.d. sample was dissolved in 100 ml 1% NaOH solution was placed in a boiling water bath maintaining temperature 97 ^{0}C to 100 ^{0}C with constant stirring for 1 hour. It was then filtered, washed, dried and weighed.

Calculation:

Solubility, % = $\frac{A-B}{A} \times 100$

Where, A = Weight of test specimen before extraction, gm (o.d.)

B = Weight of test specimen after extraction, gm (o.d.)

3.2.2.5. Solvent extractive (Tappi T 204 om-88)

Soluble materials or extractives in wood consist of those components that are soluble in neutral organic solvents. Since the pulping process usually removes most water-soluble and volatile

compounds that are also soluble in organic solvents, the solvent extractable material in pulp is considered to consist primarily of resin and fatty acids and their esters, waxes, and unsaponifiable substances. No single organic solvent is capable of removing all these substances, and different solvents remove different combinations.

The extractions were done in Soxhlet extraction apparatus for over a period of 4-5 hours. After extraction the samples were filtered and dried and the solvent was evaporated and dried in an oven for 1 hour at 105 ± 3°C. Every sample were weighed to the nearest 0.1 mg.

Calculation:

Extractives, % = $\frac{We-Wb}{Wp} \times 100$

Where, W_e = oven-dry weight of extract, g

W_p = oven weight of wood or pulp, g

W_b = oven-dry weight of blank residue, g

3.2.2.6. Determination of Holocellulose [5]

Holocellulose is the lignin fibrous material comprising all of the hemicellulose and cellulose.

100 mL $NaClO_2$ (3.5%) was added to 1 gram o.d. sample in 250 mL beaker. The pH of the solution was maintained at 4 by addition of CH_3COOH-CH_3COONa buffer solution. Then it was set up on a water bath and heated for about 3-4 hours until the disappearance of yellow color. It is then filtered through sintered crucible, washed with distilled water and kept overnight in an oven at 105°C.

Calculation:

Holocellulose, % = $\frac{A}{W} \times 100$

Where, A = weight of oven dry holocellulose (g)

W = weight of oven dry test specimen (g)

3.2.2.7. Determination of α-cellulose (Tappi T 203 om-93)

α-cellulose is the pulp fraction resistant to 17.5% sodium hydroxide solution under conditions of the test. Beta-cellulose is the soluble fraction which is re-precipitated on acidification of the solution; gamma-cellulose is that fraction remaining in the solution.

Test specimen was treated a definite amount of 17.5% NaOH solution for 45 minutes. The concentration of NaOH was then reduced to 8.3% and the mixture is treated for another 30 minutes. The α-cellulose was separated by filtration through crucible, washed, dried and weighed.

Calculation:

α-cellulose= $\frac{A}{W} \times 100$

Where, A= weight of oven dry α-cellulose (g)

W= weight of oven dry test specimen (g)

3.2.2.8. Lignin (Tappi T 211 om-83)

Lignin is an aromatic, amorphous substance containing phenolic methoxyl, hydroxyl, and other constituent groups which forms a part of the cell wall and middle lamella in wood. In this method of determination, lignin (also known as "Klason lignin") is the part of wood or pulp constituent insoluble in 72% sulfuric acid.

72% H_2SO_4 was added to the beaker containing the 1 gm of o. d. test specimen. The material is stirred frequently for 2 hours and then transferred to a flask to autoclave for 4 hours. The insoluble material (lignin) was allowed to settle and was siphoned off through a filtering crucible. The crucible with lignin was dried in an oven at 105±3°C to constant weight, cooled in a desiccator and weighed.

Calculation:

Lignin, % = $\frac{A}{W} \times 100$

Where, A = weight of lignin, g

W = oven-dry weight of test specimen, g.

3.2.2.9. Pentosan content (Tappi T 223 cm-10)

Pentosan content in pulp indicates the retention or loss of hemicellulose in general during pulping and bleaching processes, and since hemicellulose contributes to the strength of paper pulps, high pentosan content is desirable.

In this method, test specimen was treated with hot hydrochloric acid (12%) to hydrolyze the pentosan to pentose, which are then dehydrated to furfural. The furfural from the pentosan was collected in the distillate, allowed to react with bromine at 0°C. and the excess bromine was determined by titration with thiosulfate solution.

Calculation:

Pentosan = $\frac{7.58N(V2-V1)}{W} - 1.1\%$

Where, N= Normality of sodium thiosulfate

V1= volume of thiosulfate needed for blank

V2= Volume of thiosulfate needed for sample

W= weight of moisture free sample

3.2.2.10. Ash content (T 211 om-02)

Ash is the material remaining after the sample is ignited at a specified temperature and is calculated on the basis of the dry weight of the original sample.

Calculation:

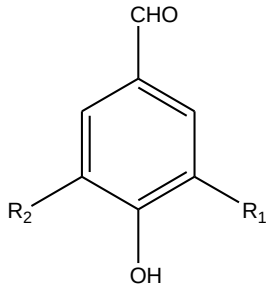
Ash, % = $\frac{A}{W} \times 100$

Where, A = weight of ash, g

W = oven-dry weight of test specimen, g.

3.2.2.11. Alkaline nitrobenzene oxidation

Alkaline nitrobenzene oxidation is a technique used for a long time for the conversion of isoeugenol to vanillin [6-7]. When Alkaline nitrobenzene oxidation is applied to lignin materials, the major oxidation products obtained are phenolic aldehydes such as p-hydroxybenzaldehyde (1), vanillin (2) and syringaldehyde (3) (Figure 3.1). These products are derived from oxidative degradation of the corresponding 4-hydroxyphenylpropane units and the corresponding 4-O-alkylated (a-O-4and b-O-4) lignin substructures. The relative amount of the uncondensed p-hydroxyphenyl, guaiacyl and syringyl units that constitute the original lignin can be obtained from the molar ratio of these derived products. Thus, a significant parameter that has long been used for wood lignin characterization is the syringyl to guaiacyl (S/G) ratio [6]. Leopold in 1950 found the optimal reaction conditions for nitrobenzene oxidation of lignins [8]. The nitrobenzene oxidation of lignins that has been conducted in laboratories later on are usually according to the modifications of the original procedure developed by Leopold [6-8].



1: R_1 = H, 2: R_1 = OCH_3, R_2 = H, 3: R_1 = R_2 = OCH_3

Figure 3.1. Nitrobenzene oxidation products [9]

Procedure

10 mg extractive free milled plant materials were taken in a bomb and 4 ml of 2M NaOH and 0.25 ml nitrobenzene were added, and the mixture was kept at 170 ^{o}C for 2 hr. A 0.1M NaOH solution internal standard solution containing 3-ethoxy-4-hydroxybenzaldehyde (0.2-0.4g/1, 1

ml) was added. The reaction mixture was treated with dichloromethane (15 ml) for three times. The aqueous phase was acidified with hydrochloric acid (4M) to pH~1 and treated twice with dichloromethane (20 ml) and once with ethyl ether (15 ml). Then the solvent was washed with water. The insoluble inorganic materials were removed by filtration and the solution was evaporated to dryness and silylated with BSA at 105^{o} C for 5 min. The final silylated compounds were analyzed by gas chromatography, GC-FID: Shimadzu 17 A under the following conditions,

Injection volume: 1µ1.

Gas Column: NB-l (GL science) fused-silica capillary column (length, 30m; 0.25mm i.d.),

Column temperature: 150^{o} C, 15 min -3^{o} C/min•180^{o}C -10^{o}C/min•280^{o} C

Injection temperature: 250^{o} C

Detector temperature: 280^{o} C

Column flow rate of He gas 1.9 ml/min

Splitting ratio 60: 1

3.2.3. Determination of *morphological and anatomical characteristics*

For the measurements of fiber morphological properties, first these samples were macerated in a solution containing 1:1 HNO_3 and $KClO_3$. A drop of macerated sample was taken in a slide and fiber length and diameter were measured in image analyzer Euromex-Oxion using Image Focus Alpha software. For measuring fiber length and fiber width, 200 fibers were measured from the slides and average reading was taken [10].

For anatomical analysis, the three samples were sectioned with sliding microtome and transversal section slide was prepared and investigated under an image analyzer. SEM image of cross section was recorded using a scanning electron microscope (Model EV018, Carl Zeiss AG, Germany).

3.2. RESULTS AND DISCUSSION

3.2.1. Chemical characteristics

3.2.1.1. Solubilities

The chemical characteristics of twenty-two non-wood raw materials are shown in Table 3.1. The cold water treatment removes a part of extraneous components like tannins, gums, sugars, inorganic matter and colored compounds present in lignocellulosic biomass and the hot water treatment removes starches. The higher water solubility adversely affects the pulp yield [11]. Cold water and hot water solubilities of pineapple leaves were highest (35.36 and 40.17 respectively) compared to other raw materials followed by cassava stalks, rice straw, wheat straw, cotton stalks and banana leaf. The higher cold and hot water solubilities indicated the presence of higher inorganic, tannins, gums, sugars etc. and starch is also extracted in hot water. Bagasse, jute stick, mulberry stalks, dhaincha stalks showed comparatively lower cold and hot water solubilities than other raw materials.

One percent alkali solubilities indicate the presence of lower molecular carbohydrates and other alkali soluble materials. One percent alkali solubilities of chia plant was higher than dhaincha, mustard stalks and lentil stalks and slightly lower than cotton stalks. Very high one percent NaOH solubility of pineapple leaves (52.52%), wheat straw (44.89), cassava plant (40.74%) followed by bagasse (39.6) and okra plant (37.98%) was observed. Dhaincha stalks (17.68%) and mulberry stalks (21.00%) showed the lowest amount of one percent NaOH solubility. The higher NaOH solubility of pineapple leaves, wheat straw, cassava plant and okra plant was possibility due to the presence of low molar mass of carbohydrates and other alkali soluble materials.

According to Sharma et al., higher one percent alkali, cold and water solubilities may affect pulp yield and cooking chemical consumption [12]. Thus, a very high water and alkali solubility of pineapple leaves and cassava stalks indicated lower pulp yield.

3.2.1.2. Ash content

The mineral components of lignocellulosic biomass are represented as ash content. Ash content in the twenty-two crops residues were found to be from 0.67% in bagasse to 15.1% in rice straw. Higher ash content is undesirable during chemical recovery of the pulping process. Presence of transition metals such as Mn, Fe and Cu negatively affects pulp bleachability in peroxide and oxygen bleaching [13]. Andrade et al. reported a high ash content of 4.0% in whole bagasse which is higher than the present study [14]. Pydimalla et al. also found >1% ash in whole bagasse [15]. Ash contents in the corn stalk of two varieties of North Carolina, USA were 3.61 and 7.10% [16], while our value for ash content of corn stalks was 4.48%. It appears that harvesting time, and the geographical location affect the morphology and chemical composition of the non-wood.

As shown in Table 3.1, banana pseudo stem and banana leaf had high amount of ash content (approximately 6%), which is a big concern in alkaline pulping [17]. The ash content in banana peduncle (1.77%) was much less than banana stem and leaf. This ash content is still high for industry processing, though approximately 50% of them can be extracted by washing before pulping.

3.2.1.3. Extractives

Acetone extractives include waxes, fats, resins etc. Lower extractives content is desirable for better pulp yield. Acetone soluble content adversely affects the paper machine runnability. High extractive contents in lignocelluloses are undesirable for pulping, bleaching and papermaking. It also affects the quality of paper because it leaves stains in the resulting paper sheets and paper manufactured from such type of fibrous material might show reduced water absorbency [12]. So, it is desired to low content of extractives in pulping raw materials. As shown in Table 3.1., acetone extractives of mulberry plant were the highest (3.55%) and banana

pseudo stem was the lowest (0.08%). Acetone solubility in these crops residues was much lower than the reported data [18].

3.2.1.4. Holocellulose and α-cellulose

Holocellulose and α-cellulose contents in lignocellulosic biomass are the prime factors in selecting pulping raw material, which positively affect the pulp yield in chemical pulping process. Cellulosic raw materials also determine physical strength properties of paper [10]. Total carbohydrate content is defined as Holocellulose. The holocellulose content is directly related to pulp yield and papermaking properties [19]. Therefore, high holocellulose content is desirable for better pulp yield and papermaking properties [19]. It is observed from Table 3.1 that the holocellulose content of the crops residues varied from 57-66% except jute (77.9%), banana peduncle (73.7%) and dhaincha stalks (71.2%). The lowest holocellulose content was in pineapple leaves (41.6%) and cassava stalks (50.2%).

The α-cellulose contents in ligncellulosics positively influence pulp yield during chemical pulping [20-21]. The cellulose content also determines physical strength properties of paper [21-22]. As shown in Table 3.1, the highest α-cellulose content in banana peduncle was 45.2%, while the lowest α-cellulose content in okra plant was 29.6%. This higher α-cellulose is expected to produce higher pulp yield. Nieschlag et al. found out that raw materials containing about 34% α-cellulose and more are suitable for pulp and paper manufacture. [23].

3.2.1.5. Lignin

Lignin is undesirable polymer for pulp production. Lower lignin content of raw materials is desirable for delignification at relatively milder pulping conditions (lower temperatures and chemical charges) to reach a desirable kappa number. It is observed from the Table 3.1 that lignin contents were varied from 14.6% in jute fiber to 28.4% in eggplant stalks. Lignin content in wheat straw and rice straw was relatively higher as compared to other studies [24]. This was

because of high ash content. No reports have been found on the chemical characteristics of eggplant stalks, kaun straw and chia stalks. Lignin content in chia stalks was 23.2%. The lignin content in corn stalks was very close to the result obtained by Ates et al. [25]. But the lignin content in different portions of banana fiber was much higher than the result obtained in previous published data [26]. This can be explained by variation of banana species. Klason lignin content in these raw materials was close to hardwood lignin content [27]. Finally, it can be said that that these crops residues are characterized by relatively moderate amounts of Klason lignin.

Acid soluble lignin (ASL) is composed of low molecular weight degradation products from sulphuric acid treatment of klason lignin with the syringyl nucleus [28-29]. ASL in the raw materials were from 2.04% in eggplant to 5.03% in pineapples leaves. ASL content in the non-wood samples was almost similar to the reported value by Andrade et al [30].

3.2.1.6. Pentosan

Most of the non-wood hemicellulose contains mainly xylan, which is reflected by pentosan. Hemicellulose content affects pulp yield and especially papermaking properties. Sitch and Marshall [8] showed that the presence of hemicellulose reduced average fiber length during beating, thus indicating a correlation between fiber flexibility and hemicellulose content, thus pulps of high strength were prepared.

Pentosan content in these crops residues varied from 11.6% in jute to 22.3% in kash stalks. Pentosan is an important characteristics papermaking pulp, which facilitates H-bonding during sheet formation. Bai et al., 2012 showed that addition of hemicelluloses increased tensile index, burst index, tear index and folding endurance of paper sheet [31]. The results were attributed to the role of hydroxyl group (OH–) in hemicelluloses molecular which brought about more H-bond formation between cellulose and hemicelluloses and benefited the bonding between the fibers.

Table 3.1. Chemical characteristics of crops residues

Raw Materials	Hot water solubility (%)	Cold water solubility (%)	NaOH solubility (%)	Ash Content (%)	Extractives in Acetone (%)	Holo cellulose (%)	α-cellulose (%)	Klason Lignin (%)	Acid Soluble Lignin (%)	Pentosan (%)
Bagasse	8.45	12.13	39.6	0.67	2.2	62.2	39.3	20.4	2.28	16.9
Bamboo	12.88	11.43	26.90	3.27	0.54	65.5	46.9	26.9	2.88	18.4
Banana pseudo stem	18.26	12.10	32.34	6.85	0.08	66.2	40.2	24.1	2.74	13.4
Banana leaf	21.38	22.57	36.62	6.97	1.44	64.9	41.4	20.7	2.36	13.3
Banana peduncle	13.98	20.43	29.96	1.77	0.54	73.7	45.2	20.4	2.56	14.8
Cassava stalks	33.17	28.37	40.74	2.49	1.10	50.2	36.4	20.6	3.64	14.8
Chia stalks	20.53	16.30	34.58	2.58	1.82	60.5	30.5	23.2	2.73	13.2
Corn stalks	14.62	18.13	38.92	4.48	0.87	59.5	35.1	19.7	2.09	17.8
Cotton stalks	22.54	20.07	37.6	3.54	1.06	66.0	35.7	23.3	3.64	18.0
Dhaincha stalks	10.30	11.43	17.68	0.64	0.74	71.2	39.7	24.1	3.98	14.6
Eggplant stalks	17.96	12.10	25.75	1.66	0.29	63.2	35.0	28.4	2.04	14.3
Jute	13.45	12.38	21.77	1.22	0.74	77.9	54.3	14.6	2.89	11.6
Jute Stick	9.89	19.18	30.97	0.73	1.03	69.2	37.7	27.1	2.46	19.7
Kash stalks	18.49	17.82	38.09	1.07	2.01	66.2	43.3	19.8	3.17	22.3
Kaun straw	15.95	15.22	42.2	7.3	1.2	56.6	35.9	19.3	3.03	17.6
Mulberry stalks	10.39	13.07	21.00	3.15	3.55	70.2	38.8	26.3	2.58	16.2
Mustard stalks	21.91	18.37	32.46	5.04	0.59	62.9	33.7	18.1	2.17	18.9
Okra stalks	21.9	13.15	37.98	0.77	1.54	56.8	29. 6	18.7	3.62	15.1
Pineapple leaves	35.36	40.17	52.52	8.48	3.43	41.6	27.6	17.9	5.03	19.8
Red Lentil stalks	21.05	20.82	32.82	6.79	1.31	59.2	36.5	23.8	3.52	15.2
Rice straw	27.65	16.10	51.1	15.1	2.1	61.7	38. 7	22.9	4.08	18.0
Wheat straw	22.85	18.16	44.89	9.12	0.57	65.6	37.0	25.1	2.59	18.0

3.2.1.7. Alkaline Nitrobenzene Oxidation

Lignin is composed of syringyl (S), guaiacyl (V) and p-hydroxyphenyl (H) unit. Alkaline nitrobenzene oxidation (ANO) is a popular technique to analyze the structural composition of lignin. This is done by cleavage of ether linkages and oxidation of three constitutive monomeric lignin units of guaiacyl, syringyl, and *p*-hydroxyphenyl leading to a number of degradation products from non-condensed units [32]. *p*-hydroxy bezaldehyde syringyldehyde and vanillin were the main products of whole bagasse and corn stalks lignin in almost equal proportion.

Table 3.2 shows the yield of alkaline nitrobenzene oxidation products from twenty-two non-wood raw materials. The predominant product was identified to be syringaldehyde (S), which comprised 24.56% for dhaincha stalks and 24.07% for red lentil stalks. It resulted from the degradation of non-condensed syringyl unit. Therefore, dhaincha stalks and red lentil stalks lignin contains more condensed structure than other plant lignins. Vanillin (V) appeared as the second major degradation products resulted from the noncondensed guaiacyl unit, which consisted of 11-17%. Okra plant lignin had the highest amount of vanillin. 17.1%. The presence of small quantities of p- hydroxybenzaldehyde from noncondensed p-hydroxyphenyl unit (H) was found in all these non-plant lignin (1-12%). Similar results have been reported in abaca fibre, oil palm fibre lignins [33,34]. But pineapple leaves showed the highest amount of H unit, 21.1%.

Reported data indicate that the syringyl to guaiacyl (S/V) ratio of the lignin is a governing parameter for ease of delignification [35]. The highest relative ratio of S to V in jute (3.10) and the lowest was in banana pseudo stem (0.69). The results appeared to be in general agreement with the range of S to V ratios obtained from hardwood lignin [35].

Table 3.2. Alkaline nitrobenzene oxidation of crops residues

Raw materials	S (%)	V (%)	H (%)	V+S+H (%)	S/V
Bagasse	12.59±0.22	13.71±0.58	12.22±0.24	38.52±0.05	0.92
Bamboo	10.81±0.10	10.65±0.24	9.04±0.65	30.50±0.31	1.02
Banana pseudo stem	4.34±0.07	6.23±0.87	10.80±0.89	21.37±0.83	0.69
Banana leaf	4.40±0.31	3.92±0.06	8.89±0.75	17.21±0.38	1.12
Banana peduncle	11.42±0.45	8.27±0.87	3.90±0.95	23.59±0.42	1.38
Cassava stalks	18.06±0.24	11.63±0.88	2.01±0.12	31.70±0.57	1.55
Chia stalks	18.06±0.00	12.77±0.29	5.58±0.07	36.41±0.39	1.42
Corn stalks	13.29±0.21	11.63±0.32	12.86±0.66	37.78±0.78	1.142
Cotton stalks	22.11±0.32	17.92±0.41	1.42±0.23	41.46±0.32	1.23
Dhaincha stalks	24.56±0.48	16.50±0.56	2.70±0.59	33.45±0.58	1.63
Eggplant stalks	18.63±0.85	11.40±0.26	3.42±0.81	43.76±0.37	1.48
Jute	23.98±0.90	7.73±0.43	5.27±0.97	36.98±0.43	3.10
Jute Stick	14.55±0.30	11.33±0.99	6.19±0.38	32.06±0.69	1.28
Kash stalks	14.47±0.35	5.77±0.95	8.90±0.67	29.14±0.53	2.51
Kaun straw	12.75±0.25	5.63±0.11	7.89±0.35	26.27±0.49	2.26
Mulberry stalks	14.80±0.89	12.98±0.51	9.07±0.07	36.84±0.43	1.14
Mustard stalks	17.77±0.80	14.65±0.43	4.23±0.16	36.65±0.39	1.21
Okra stalks	17.93±0.05	17.07±0.28	2.71±0.13	37.72±0.20	1.05
Pineapple leaves	21.01±0.85	12.67±0.02	21.88±0.50	55.56±0.36	1.66
Red Lentil stalks	24.07±0.93	9.41±0.25	10.47±0.98	43.95±0.35	2.56
Rice straw	21.55±0.78	10.29±0.18	5.44±0.68	37.28±0.29	2.09
Wheat straw	12.38±0.28	6.03±0.08	3.33±0.3	21.74±0.06	2.05

S- Syringyldehyde, V- Vanilin, H- p-hydroxybenzaldehyde

3.3.2. Morphological characterization

The role of morphological characteristics such as fiber length width, wall thickness, lumen diameter and their derived values such as flexibility coefficient, slender ratio and runkel ratio of twenty-two non-wood samples are given in Table 3.3. The fiber lengths banana leaf (midrib), jute and banana peduncle were 1.91, 1.85 and 1.50 mm, which was longer than other non-woods samples which were in the range of 1.36-0.0.58 mm). The fiber length banana leaf was similar to previous fiber length study of bamboo (1.91 mm) [12]. The fibre lengths of eggplant stalks (0.58 mm), jute stick (0.62 mm), cassava stalks (0.65 mm), and mulberry stalks (0.65 mm) were shorter than reported data [12,36]. A higher fibre length contributes higher tearing strength of paper [37]. The fibers in a paper web are randomly distributed, and depending on the length of the fiber, the number of fiber crossings increases or decreases. A longer fiber crosses higher number of fibers and web becomes stronger resulted higher wet and dry web strength. Fibre diameter pineapple leaves was lowest (5.34 μm) and hight fiber diameter was found in banana peduncle (28.32 μm). The fiber wall thickness of these non-wood plant was thin (1.91-3.83 μm). Paper formed by thin-walled fibre would be dense, and well formed [36].

The central cavity in the fiber is known as fiber lumen which is void. The wider lumen diameter was observed for banana peduncle fibers (21.7 μm) and narrower for rice straw (5.6 μm). Depending on the extent of void space, the fiber may flatten to different extents, as the fiber is refined. The higher the extent of collapsibility, the higher is the bonded area. Table 3.3 also presents derived vaues of the samples. Cassava stalks showed the lowest slender ratio (25.49). There is a positive correlation between slenderness ratio and folding endurance [38-39]. Generally, it is considered that if the slenderness ratio for the fibre is less than 70 than pulp would have poor strength [40]. The shorter and wider fiber produces a poor slenderness ratio, which in turn reduces tearing resistance. This is partly because short and

thick fibers do not produce good surface contact and fiber-to-fiber bonding [41]. Generally, the acceptable value for slenderness ratio of papermaking is more than 33, respectively [42].

The highest and lowers runkel ratios were found for kaun straw (1.015) and cassava stalks (0.208), respectively. Fibers which have Runkel ratio less than 1.0 are considered as thin-walled fibers [43] and fibers having Runkel ratio above 1.0 are considered as thick-walled, stiffer and rigid in nature and form bulky and more opaque paper with lower bonded area [44]. Based on the results, these non-wood plants had comparatively thin walled fibres (Table 3.3).

The fibre diameter and cell wall thickness control the fibre flexibility. The flexibility coefficient of cassava stalks and okra plant stalks were 79% and 77%, respectively, while it was 56% for eggplant stalks and 47% for kaun stalks. Fibers that have low fleaxibility coefficient do not collapse easily which facilitates them to maintain their tabular structure on pressing consequently. Such type of fibers produces paper sheets of higher tear, bulk and opacity [45]. Fibre flexibility influences the number of interfiber bonds because more flexible fibres have more interfiber contact [46].

Table 3.3. Morphological characteristics and derived values of crops residues

Raw materials	Fiber length, L (mm)	Fiber width, D (µm)	Fiber wall thickness, w (µm)	Lumen diameter, d (µm)	Slender ratio (L/D)	Runkel ratio (2w/d)	Flexibility coefficient (d/DX100)
Bagasse	1.36	16.2	1.9	10.95	79.2	0.317	73.45
Bamboo	1.17	12.06	1.48	8.5	97.01	0.348	70.48
Banana pseudo stem	1.22	14.81	1.51	11.6	82.37	0.27	78.3
Banana leaf	1.92	13.75	2.52	8.7	139.63	0.57	63.3
Banana peduncle	1.5	25.18	1.27	21.7	59.57	0.16	86.2
Cassava stalks	0.65	25.5	2.09	20.13	25.49	0.204	78.9
Chia stalks	0.67	15.55	1.91	11.11	43.1	0.34	71.43
Corn stalks	0.9	15.7	1.78	9.11	57.3	0.33	66.9
Cotton stalks	0.9	17.2	2.21	12.23	52.3	0.36	71.1
Dhaincha stalks	0.73	19.5	2.12	15.34	37.4	0.28	78.7
Eggplant stalks	0.58	13.2	2.49	7.34	43.84	0.678	55.61
Jute	1.85	13.53	3.5	5.90	136.73	1.086	43.60
Jute Stick	0.62	16.84	3.2	10.02	36.81	0.627	60.57
Kash stalks	0.86	13.6	2	8.7	63.2	0.408	72.1
Kaun straw	0.814	13.9	3.3	6.5	58.56	1.015	46.76
Mulberry stalks	0.65	16.3	2.21	11.31	39.88	0.391	69.38
Mustard stalks	0.87	13.7	2.53	8.24	63.5	0.61	60.1
Okra stalks	1.14	21	1.75	16.22	54.29	0.339	77.23
Pineapple leaves	1.06	15.34	2.8	9.25	64.48	0.605	60.29
Red Lentil stalks	0.74	14.3	2.32	9.43	51.7	0.49	66
Rice straw	0.78	11.6	1.83	5.6	83.87	0.56	60.21
Wheat straw	0.97	9.3	1.99	7.15	83.62	0.65	61.63

3.3.3. Anatomical characterization

Sample from twenty-two plant was studied on an optical microscope and also on a scanning electron microscope (SEM). Figure. 3.2. and Figure. 3.3. show light micrograph of cross section of non-wood samples at a magnification of 10X. All of the non-woods contain fibrous as well as non-fibrous components. The non-fibrous components included parenchyma, vessel and epidermal cells. The presence of non-fibrous components directly affects the quality and recovery of cooking chemicals.

Micrographs of different straw fibers show thin taper off to pointed ends with parenchyma cells. Vessel elements were also found which are coil like. The ground tissue consists of parenchyma cells, which are large, barrel-shaped and thin-walled. When the thin wall and poorly lignified parenchyma are formed into sheets, they impair drainage and easily flatten during refining causing further drainage problems [36]. The parenchyma cells are easily deformed and generate fines, leading to decreased freeness and increased water retention by the pulp. But as the thin-walled parenchyma collapses during pulping, they aid in bonding of the fibers, contributing to the tensile strength of the unbeaten pulps. The epidermis layer and ground tissue form a major part of fines fraction in the pulp which are perhaps the most undesirable elements of the stalk for pulping. These cells dissolved very slowly and incompletely during the pulping process, creating the problem of fluff in the dryer or printing machine, due to the larger surface area of the non-fibrous cells.

Like many non-wood materials, non-fibrous cellular materials, such as parenchyma tissues, vessel elements and epidermal tissues were present in straws (rice straw, kaun straw, wheat straw), in addition to cellulose fibres (Figures 3.2, 3.3). Micrograph of kaun fibers show thin tapper off to pointed ends with parenchymatous cells, which is almost similar to wheat straw fibers (Fig. 1). But rice straw fibers were thinner and shorter than the other two fibers. Coil like

vessel elements were also found in kaun straw. The parenchyma tissues in these photomicrographs are seen as large, barrel shaped, iso-diametric and thin-walled.

The tightly packed unevenly thickened collenchyma cells with cellulose and pectin depositions in their primary walls were found all the twenty-two lignocelluloses. This became lignified and thickened, to form sclerenchyma cells at maturity and provided rigidity to the straw part and an extra source of fibers. A cap of bast fibers on the phloem side of the vascular bundles represented the most valuable, fibrous material in straws (Figures 3.4 and 3.5).

The light microscopy observation of chia plant revealed the occurrence of four distinct tissue systems: vessels, fibers, parenchyma cells and collenchyma. Cortex parenchyma is present under the epidermis. The collenchyma cells are found, which is composed of cellulose and pectin, subsequently it is lignified and form sclerenchyma cells that is composed of lignin and cellulose. The vessels (tracheal tubes) are diffused through the xylem. The fibers originating from outer part are thick wall and those are from inner part was thin wall is call parenchyma. As shown in Fig.3.3, mustard plant also showed similar structure. Dhaincha fibres were similar in uniformity, straightness and wider and less non-fibrous cell than other non-woods.

In case of banana stem, peduncle and leaf (midrib), the fibers, vessels and a large portion of parenchyma cells were seen in the light microscopy. The vessels are diffused through the xylem. The outer part was thick wall of fibers and inner part was thin wall call parenchyma. The presence of non-fibrous components directly affects the quality of pulp and recovery of cooking chemicals. Therefore, special technology must be developed based on the morphology of each non-conventional raw material.

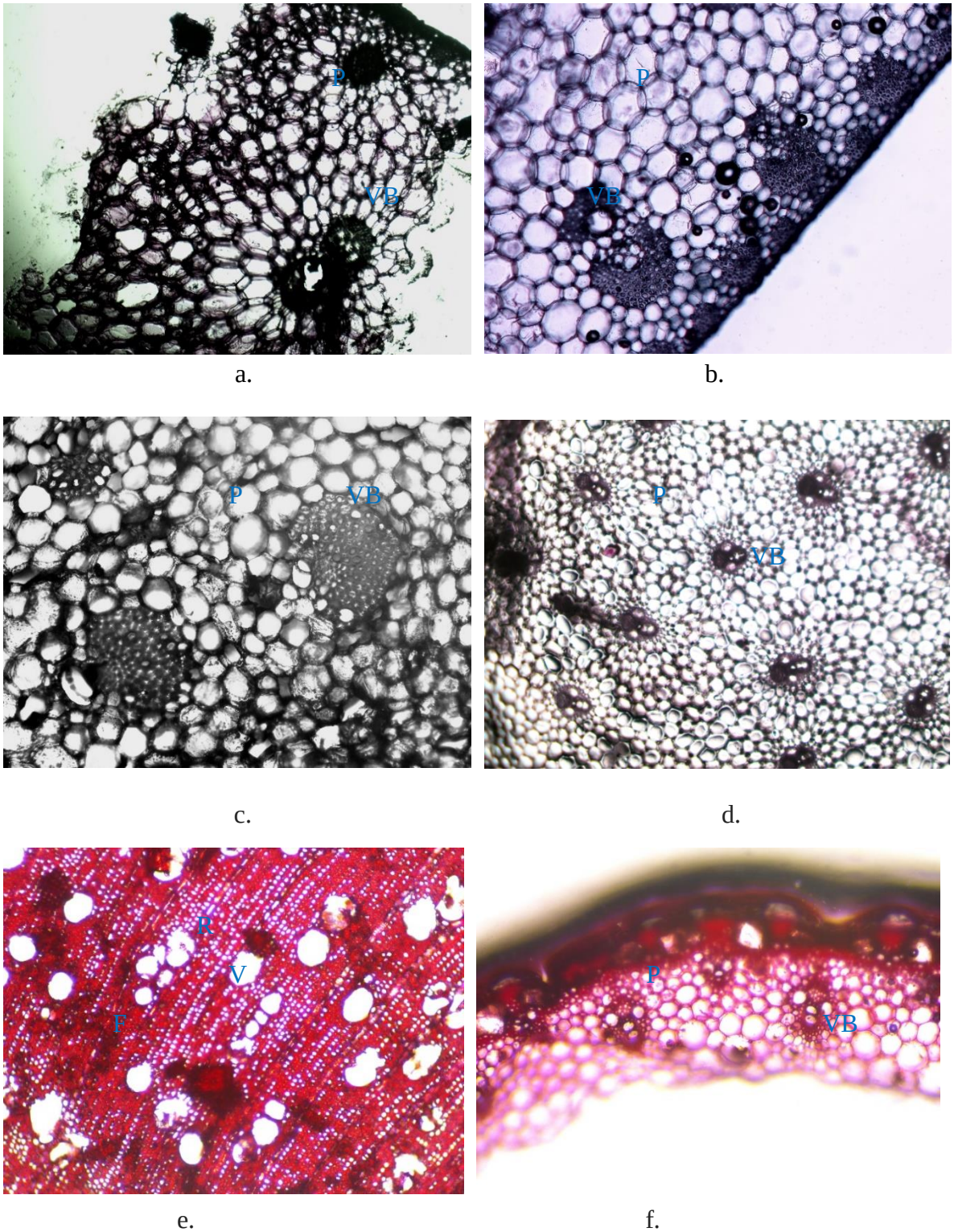
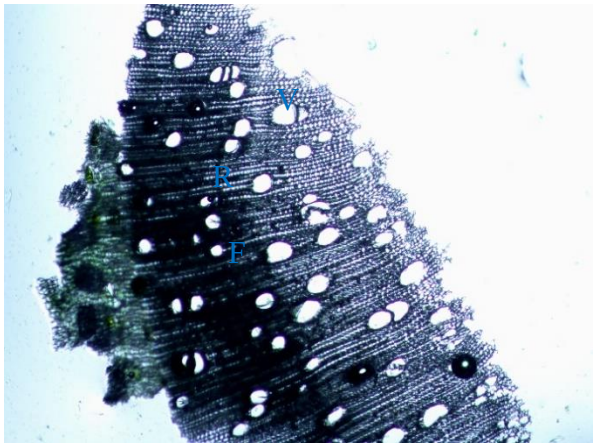


Figure 3.2. Micrograph of a) Banana Pseudo stem, b) Banana leaves, c) Banana peduncle, d) Corn stalks, e) Eggplant stalks and f) Wheat straw. (P-Parenchyma, S- Sclenchyma, VB-Vascular bundle, R- Ray cell, F-Fiber, V-Vessel)



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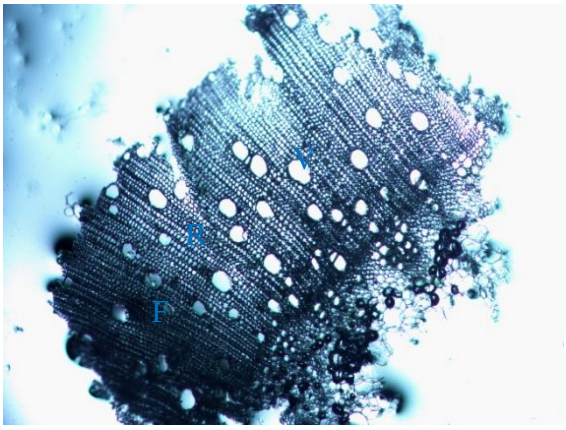

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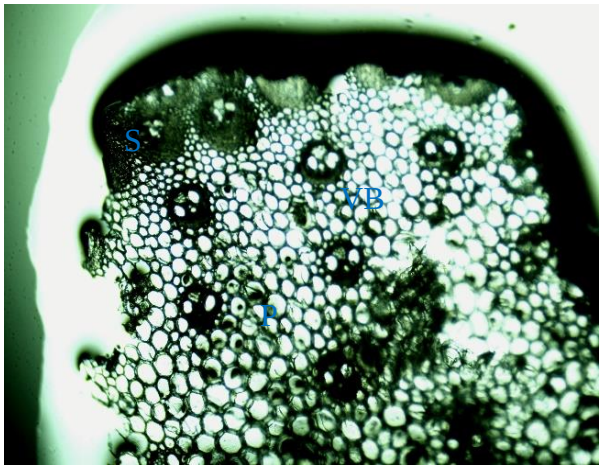

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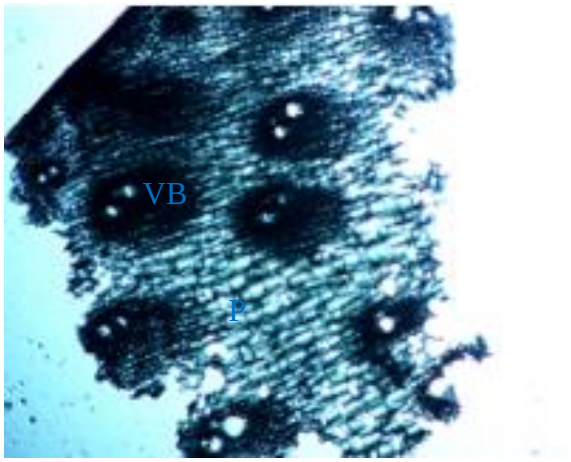

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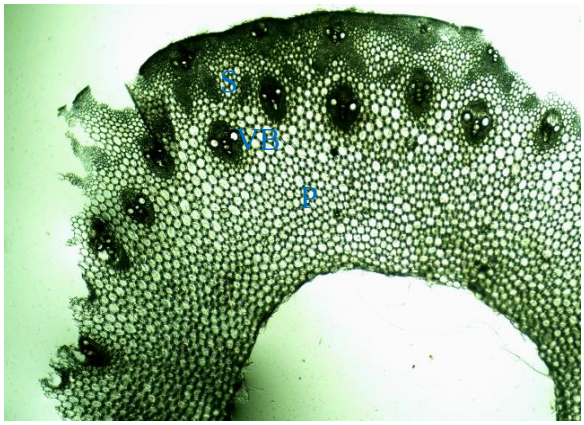

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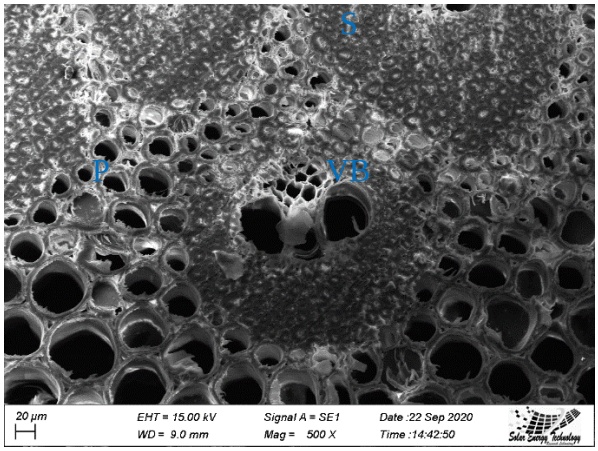
Figure 3.3. Micrograph of a) Dhaincha, b) Jute stick, c) Kash stalks d) Bagasse, e) Rice straw, and f) Pineapple leaves. (P-Parenchyma, S-Sclenchyma, VB-Vascular bundle, R- Ray cell, F-Fiber, V-Vessel)



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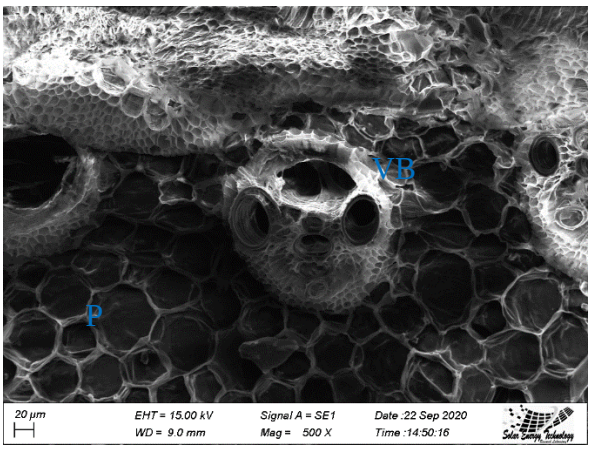

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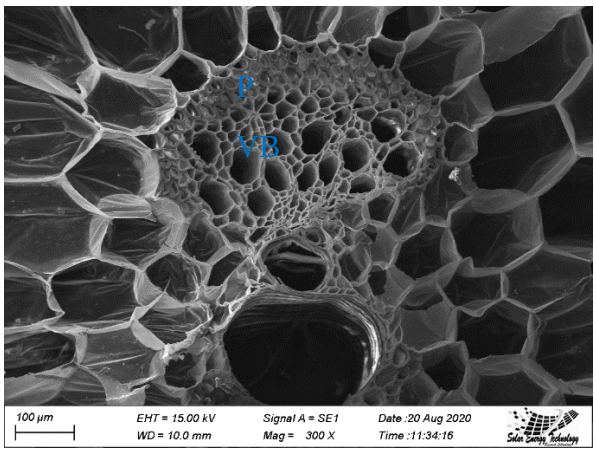

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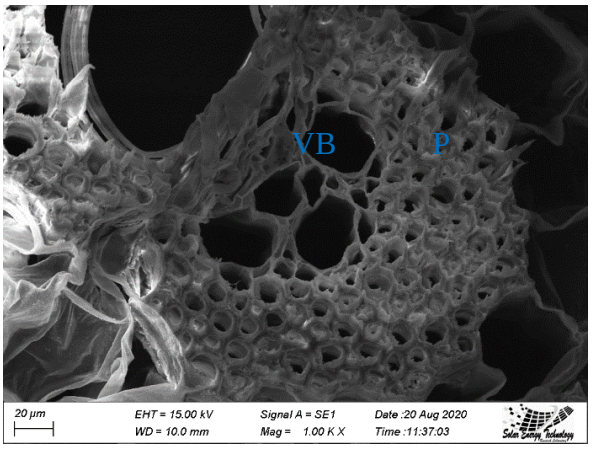

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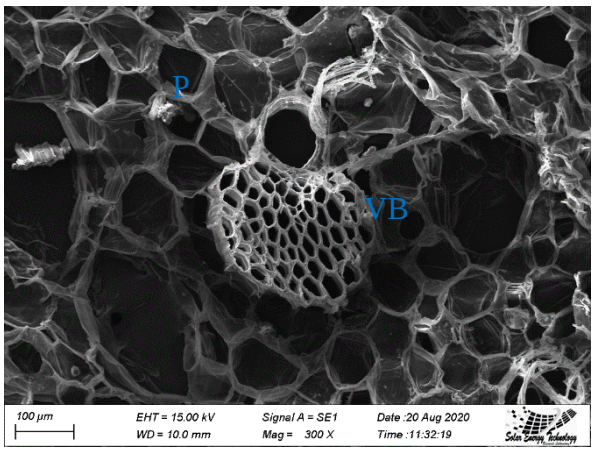

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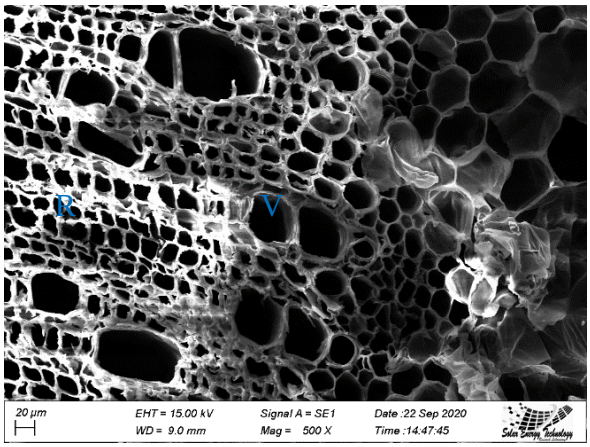

f.

Figure 3.4. Cross section of a. Kash stalks, b. Rice straw, c. Banana Pseudo Stem, d. Banana Leaf, e. Banana Peduncle and f. Jute (P-Parenchyma, S-Sclenchyma, VB-Vascular bundle, R-Ray cell, F-Fiber, V-Vessel)

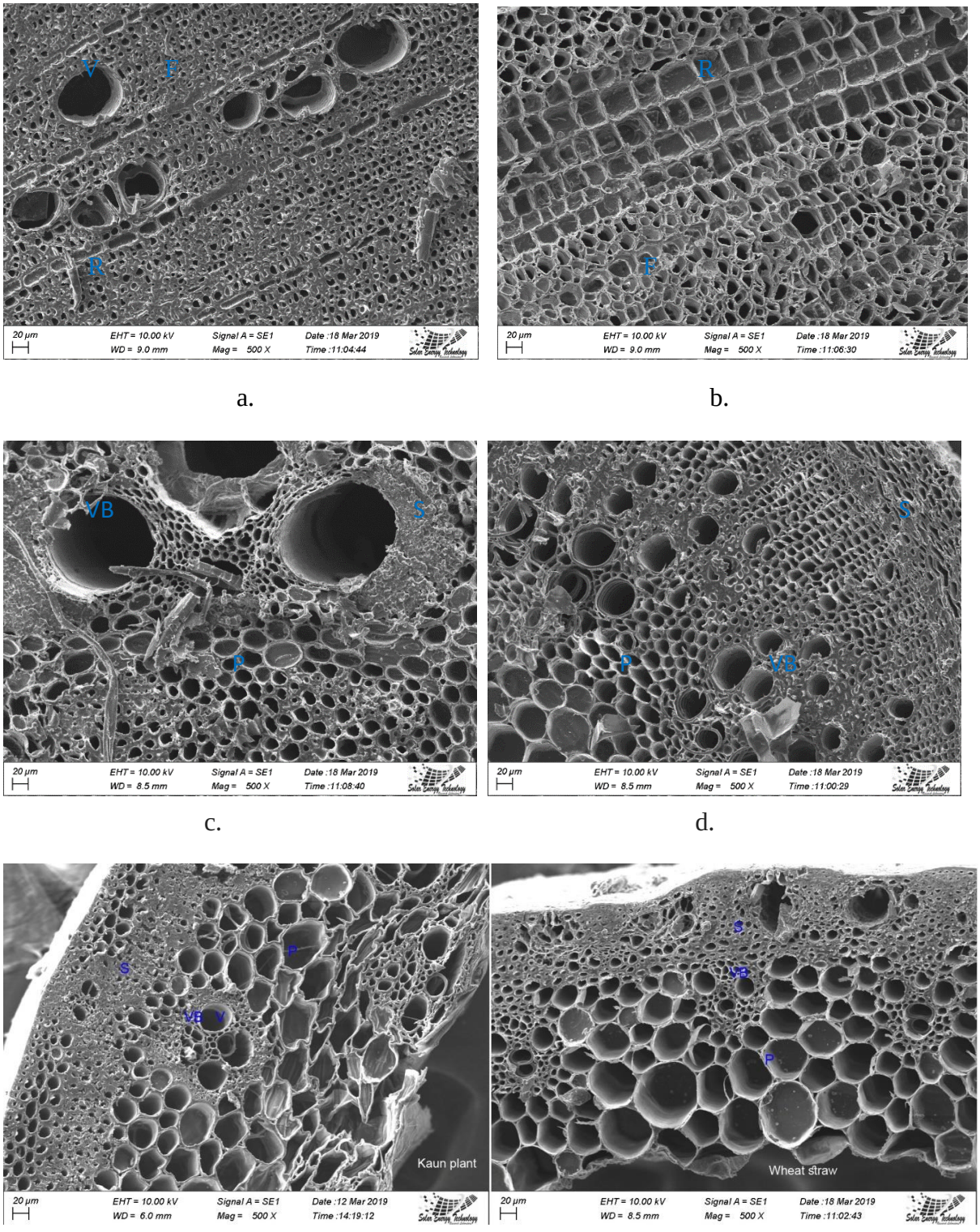

Figure 3.5. Cross section of a) Eggplant stalks, b) Okra stalks, c) Bamboo, d) Chia stalks, e) Kaun straw and f) Wheat straw. (P-Parenchyma, S-Sclenchyma, VB-Vascular bundle, R-Ray cell, F-Fiber, V-Vessel)

3.4. Conclusions

In this study twenty-two crops residues were evaluated by chemical and morphological characterization. A lot of variation in the chemical and morphological properties of the samples was observed. It was found that the α-cellulose contents in these samples were quite acceptable to consider as pulping raw materials. Most of these residues are high in ash content, which is challenging. The lignin of these samples was found to be composed of mostly p-hydroxy phenylpropane unit and syringyl unit.

The morphological and anatomical characterization showed that all of the non-woods contain fibrous as well as non-fibrous components. The non-fibrous components included parenchyma, vessel and epidermal cells which actually contribute to the fine content in pulp. The ground tissue consisted of parenchyma cells, which are large, barrel-shaped and thin-walled leading to create problems in drainage. The presence of the non-fibrous components directly affected the quality and recovery of cooking chemicals. The fiber length of the samples varied from 0.62-1.91 mm and the range falls within the fiber length range of hardwood and softwood. The fiber wall thickness of most of these non-wood materials was thinner than wood.

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CHAPTER 4
FORMIC ACID PULPING, PULP QUALITY ANALYSIS AND PHYSICAL PROPERTIES OF PAPER SHEETS

4.1. Introduction
4.1.1 Why formic acid pulping
4.2. Experimental
4.2.1. Raw materials
4.2.2. Preparation of cooking liquor
4.3. Pulping
4.3.1. Formic acid treatment
4.3.2. Peroxyformic acid treatment
4.3.3. Bleaching
4.3.4. Evaluation of pulps
4.3.5. Physical property of paper sheets
4.4. Results and discussion
4.4.1. Formic acid treatment
4.4.2. Peroxyformic acid treatment
4.4.3. Bleaching and physical properties of paper sheets
4.4.4. Pulp quality analysis
4.5. Conclusions
4.6. References

4.1. INTRODUCTION

Conventionally agricultural residues are pulped by alkaline processes. The main challenges of non-wood pulping in conventional pulping processes are 1) high amounts of silica cause silica-related operational difficulties in the process, 2) high amounts of fines/parenchyma cells decrease the drainage, and 3) the bulky nature of raw materials increases the collection/transportation cost, thus alternative pulping processes are under development. In alkali processes, pulp yield and properties are good but the main drawback is the dissolution of silica in the black liquor, which causes problem during recovery of the cooking reagents. A pulp mill cannot be environment friendly without chemical recovery system. Therefore, organic solvent-based delignification has been exhaustively studied in recent years as an alternative to the traditional processes of chemical pulp production because of strict regulations on environmental discharges [1-4].

The detail of organic acid fractionation of crops residues is shown in Figure 4.1 [5].

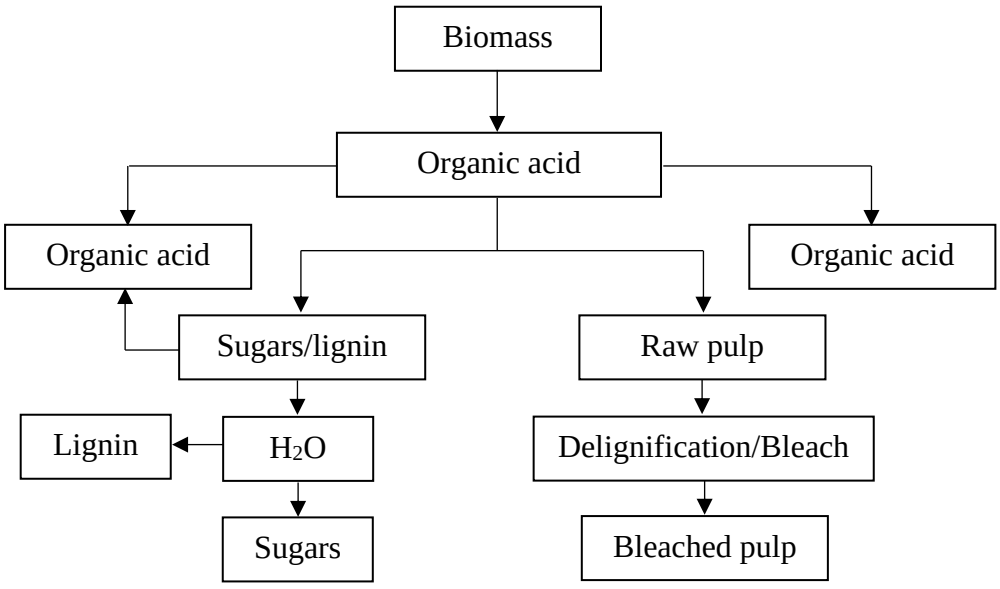


Figure 4.1. Flow diagram of lignocellulosic biomass fractionation in organic acid process in biorefinery concept [5]

The dissolved lignin and hemicelluloses in the spent liquor of organic acid pulping can be separated easily [1,6-8], and organic acid can be recovered by distillation and reused in the process [9]. Organic acid lignin is characterized a by higher phenolic group [10-11], consequently improved reactivity in using resins [12]. This lignin can also be used for many value-added products due to its lower molecular weight and higher reactivity [13-15]. The spent liquor lignin can also be used for producing carbon fibers [16], activated carbon [17] etc.

4.1.1. Why Formic Acid Pulping

The organosolv pulping conditions have effects on the delignification of fibrous materials. Acidic organosolv pulping is facilitated by the hydrolysis of ether linkages between lignin and carbohydrate. The dissolved lignin decreases with increasing cooking time when the fibrous materials are pulped with organic acids, indicating that lignin condensation occurs during cooking. Condensation during pulping occurs to a greater extent with formic acid than with acetic acid [18].

In formic acid delignification, a significant amount of materials can be dissolved at relatively low processing temperature [19-21]. Formic acid partially depolymerises lignin and hemicellulose, producing oligomers that are soluble in the liquid mixture. Cellulose and liquor are separated by filtration, and the dissolved lignin can be recovered easily. Also, the distillation of the spent liquor enables the recovery of formic acid. The leftover rich sugar fraction can be fermented for alcohols.

The two-stage process uses cooking with formic acid alone, followed by treatment with formic acid and hydrogen peroxide [22]. When the Milox method is used to delignify agricultural plants, the resulting pulp contains all the silica present in the plant. This enables the use of a similar chemical recycling system as in a corresponding wood pulping process. The silica is dissolved during the alkaline peroxide bleaching. [9]. The two stage peroxyacetic acid process gives higher delignification than three-stage process and vice-versa with peroxyformic acid.

The Milox process is a sulphur free process and bleaching can be achieved totally without chlorine chemicals [22].

4.2. EXPERIMENTAL

4.2.1. Raw materials

The twenty-two raw materials were air dried in the sun and were cut into chips of 2-3 cm size for cooking.

4.2.2. Preparation of cooking liquor

For each sample, cooking was performed three times at boiling temperature of formic acid for 4 hrs using three different concentrations of formic acid. Reagent grade formic acid (98-99%) was used to make 70, 80 and 90% (v/v) acid concentration. For 500 gm oven dried (o.d.) sample, the liquor ratio was maintained 10.

4.3. PULPING

4.3.1. Formic acid treatment (FA)

The crops residues were refluxed with formic acid (FA) in a hotplate. The reaction time was maintained 4 h at boiling temperature. After desired reaction time, pulp was filtered in a buckner funnel and washed with fresh formic acid followed by distilled water. Then the pulp yield was determined gravimetrically. The lignin content in pulp was determined by Tappi Test Methods (T 222 om-98).

Figure 4.2. Experimental setup for formic acid cooking

4.3.2. Peroxyformic acid treatment (PFA)

FA-treated pulp was further delignified with peroxyformic acid (PFA) at 80 °C. The reaction was carried out in a thermostatic water bath. The PFA was prepared by adding 90% formic acid with 4% H_2O_2 (on o.d. FA pulp). The time was kept constant for 120 min. After completion of the pulping, a pulp was filtered off and washed with 80% fresh formic acid and finally with water. Pulp yield was determined gravimetrically on raw material. The kappa number of the resulting pulp was determined in accordance with Tappi test methods (T 236 om-99). All experiments were carried out thrice and average reading was taken.

4.3.3. Bleaching

Bleaching experiments of unbleached pulp (50 g) were carried out at 10% pulp concentration. The pH was adjusted to 11 by adding NaOH. The hydrogen peroxide was varied to 4% on o.d. pulp. The bleaching temperature was 80 °C for 1 h. A similar procedure was followed in the 2nd stage of peroxide bleaching.

4.3.4. Evaluation of pulps

4.3.4.1. Determination of Moisture Content of pulp

The test of moisture content is the most important general analytical method in the cellulose field, because almost all cellulose materials are sold on a basis which requires weight correction either to zero moisture content or to standard moisture content.

1-2 gram pulp was taken to previously oven dried and weighed containers. The open containers were heated 2-4 hours in the oven until a constant weight was obtained. Determinations were run in triplicate. The percentage of moisture content was calculated by the following formula:

$$\text{Percentage} = \frac{(wt.\ of\ air\ dried\ sample - wt.of\ oven\ dried\ sample)}{wt.of\ air\ dried\ sample} \times 100$$

4.3.4.2. Kappa number of pulp (T236-60)

The kappa number is the volume (in millimeters) of 0.1 N potassium permanganate solution consumed by 1 gram of moisture free pulp under the condition specified by this method.

1 gm o.d sample was added in 100 ml distilled water. 50 ml of 4 N sulfuric acid, 50 ml of potassium permanganate and distilled water were added to make the solution 500 ml. After 10 minutes of stirring, 10 ml KI was added to the solution and titrated with 1 N sodium thiosulfate using starch indicator to make the solution colourless**.**

Calculation:

Kappa number (k) = P×f/w

Where,

p= (b-a) N/concentration of potassium permanganate
f= factor for correction to a 50% permanganate consumption, dependent in the value of p
w= weight of moisture free pulp in the specimen, gram
P= amount of 0.1N permanganate actually consumed by test specimen, ml
b= amount of thiosulfate consumed in the blank determination

a= amount of thiosulfate consumed by test specimen
N= normality of thiosulfate

4.3.4.3. Determination of fibre dimension of pulps

The fibre dimension of pulps was analysed in Fiber Quality Analyser (Model FQA-360, OpTest Equipment Inc., Ontario, Canada). The mean length, mean width, curl index, kink index, percentage of external fibrillation, coarseness and percentage of fines present in pulp samples were measured using in-built software.

4.3.5. Physical property of paper sheets

Handsheets of about 2 gm/m^2 were made in a Rapid Kothon Sheet Making Machine according to German Standard Methods no 106. The sheets were tested for tensile, burst, tear according to TAPPI Standard Methods.

4.3.5.1. Tensile strength of paper (T494)

The maximum tensile force developed in a test specimen before rupture on a tensile test carried to rupture under prescribed condition. Tensile strength (according to TAPPI) is the force per unit width of the test specimen. Tensile index is the tensile strength in N/m divided by gram.

4.3.5.2. Tear resistance of paper

The tear resistance is the force required to continue the tearing of an initial cut in a single sheet of prepare. The tear index is the quotient of tearing resistance by basis weight.

Calculation: $x = a/w$

Where, x = the tear index, Nm^2/kg

w = grammage (substance) g/m^2

a = the tearing resistance, Nm

4.3.5.3. Burst index of paper

The bursting index of paper is the maximum uniformly distributed pressure, applied at the right angle to its surface that a piece will stand under a standardized condition. The burst index is the bursting strength divided by basis weight.

Calculation: $x = a/w$

where, x = burst index, KPa m^2/kg

a = bursting strength, KPa (=k. kN/m^2)

(a = b× 98.07; Where, b = bursting factor, kg/cm^2)

w = basis weight, g/m^2

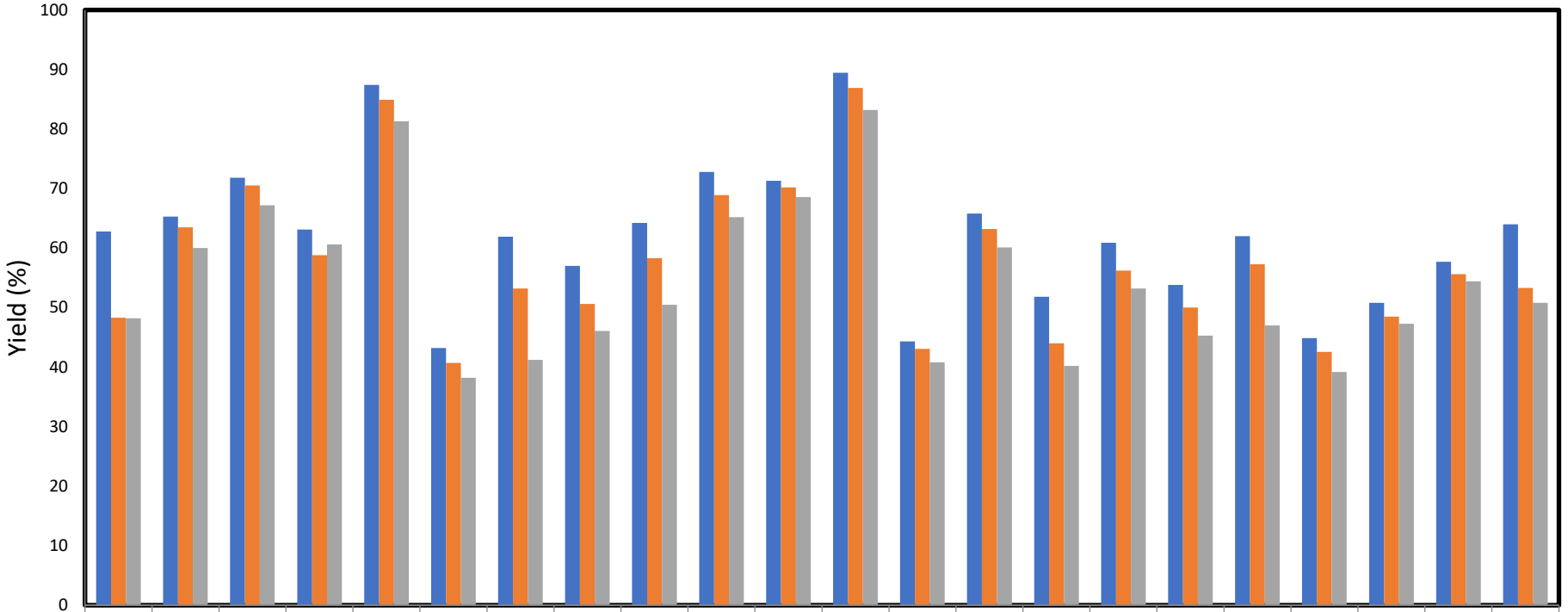
4.4. RESULTS AND DISCUSSION

4.4.1. Formic acid treatment

Delignification of chopped crops residues was carried out by varying formic acid charge and results of yield and residual lignin after formic acid treatment are shown in Figures 4.2-4.3. From previous studies it was observed that organic acid delignification needs 4 h to get desirable delignification degree, where raw materials were defibrated [2]. Therefore, formic acid treatment was kept constant at 4 h in this investigation. Yield and residual lignin decreased with increasing formic acid charge. Residual lignin did not reach to the desired level until formic acid charge was 90%. Complete defibration of crops residues was considered as desire level of residual lignin. Residual lignin content in mustard stalks was 11.0%, while the same in banana pseudo stem was 13.7%. There was no correlation found between lignin content in the raw materials and delignification degree with formic acid. The difference in lignin structure of the raw material was mainly responsible for delignification degree in formic acid treatment. [23] showed that the higher syringyl unit indicates higher delignification rate. [24] studied organic acid delignification mechanism by using model lignin. The α-aryl ether bonds of

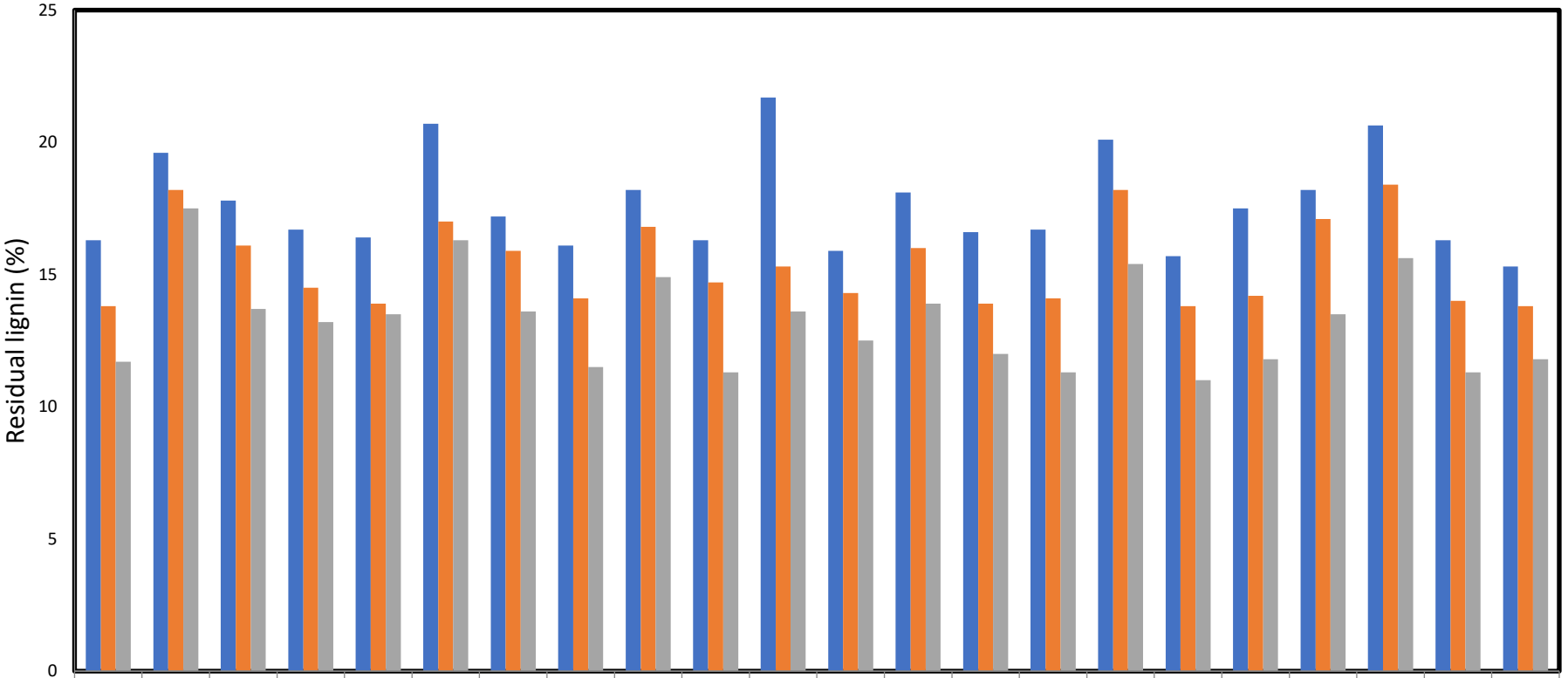
arylglycerol-1, 3-aryl ethers were ruptured by acid treatment and generated carbonium ions in the first steps. Most of the carbonium ions immediately lose three protons to form vinyl ether which is then hydrolysed, but some undergo intra or intermolecular nucleophilic attack by aromatic rings to produce condensation products.

The highest yield after 90% formic acid treatment was 81.3% in banana peduncle and the lowest yield was 41.2% in chia plant. This can be explained by α–cellulose content in the original raw materials. Eggplant stalks showed 68.6% yield after 90% formic acid treatment, which was not consistence with the α–cellulose content in the original raw materials. The higher residual lignin can be explained by higher yield.



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana pedunclе	Cassava stalks	Chia stalks	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash stalks	Kaun straw	Mulberry stalks	Mustard stalks	Okra stalks	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
FA70	62.8	65.3	71.8	63.1	87.4	43.22	61.9	57	64.21	72.81	71.3	89.47	44.34	65.8	51.8	60.88	53.8	62	44.89	50.8	57.7	64
FA80	48.3	63.5	70.5	58.8	84.9	40.7	53.2	50.6	58.3	68.9	70.2	86.9	43.06	63.2	44	56.2	50	57.3	42.57	48.5	55.6	53.3
FA90	48.2	60	67.2	60.6	81.3	38.22	41.2	46.1	50.49	65.2	68.6	83.21	40.8	60.1	40.2	53.2	45.3	47	39.2	47.3	54.4	50.8

Figure 4.3. Effect of formic acid concentration on yield of crops residues



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana peduncle	Cassava stalks	Chia stalks	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash	Kaun plant	Mulberry stalks	Mustard stalks	Okra plant	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
FA70	16.3	19.6	17.8	16.7	16.4	20.7	17.2	16.1	18.2	16.3	21.7	15.9	18.1	16.6	16.7	20.1	15.7	17.5	18.2	20.64	16.3	15.3
FA80	13.8	18.2	16.1	14.5	13.9	17	15.9	14.1	16.8	14.7	15.3	14.3	16	13.9	14.1	18.2	13.8	14.2	17.1	18.4	14	13.8
FA90	11.7	17.5	13.7	13.2	13.5	16.3	13.6	11.5	14.9	11.3	13.6	12.5	13.9	12	11.3	15.4	11	11.8	13.5	15.62	11.3	11.8

Figure 4.4. Effect of formic acid concentration on the delignification of crops residues

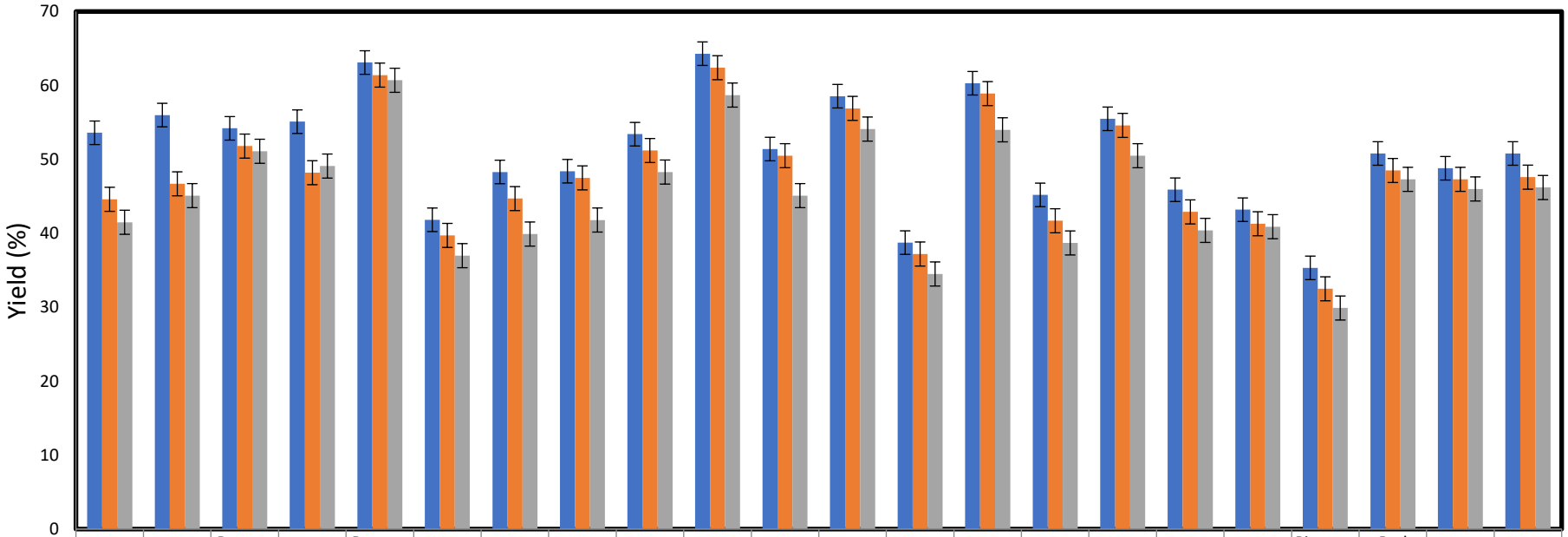
4.4.2. Peroxyformic acid (PFA) treatment

Formic acid treated crops residues were cooked with peroxyformic acid (formed by 90% formic acid and 4% hydrogen peroxide) for 2 h at 80^{o}C. Previous studies showed that longer cooking time in PFA pulping resulted in lignin condensation reaction, which increased kappa number [4]. Therefore, in this study, PFA treatment time was kept constant for 2 hours.

The kappa number estimates the amount of chemicals required during bleaching of wood pulp to obtain a pulp with a given degree of whiteness. Since the amount of bleach needed is related to the lignin content of the pulp, the kappa number can be used to monitor the effectiveness of the lignin-extraction phase of the pulping process. the kappa value is approximately proportional to the residual lignin content of the pulp. The kappa number as well as pulp yield of PFA treated pulp decreased accordingly as the yield and residual lignin content decreased in 70, 80 and 90% treatment of FA (Figures 4.5-4.6). 90% FA treated crops residues produced pulps of almost similar kappa number than the conventional alkaline pulping process.

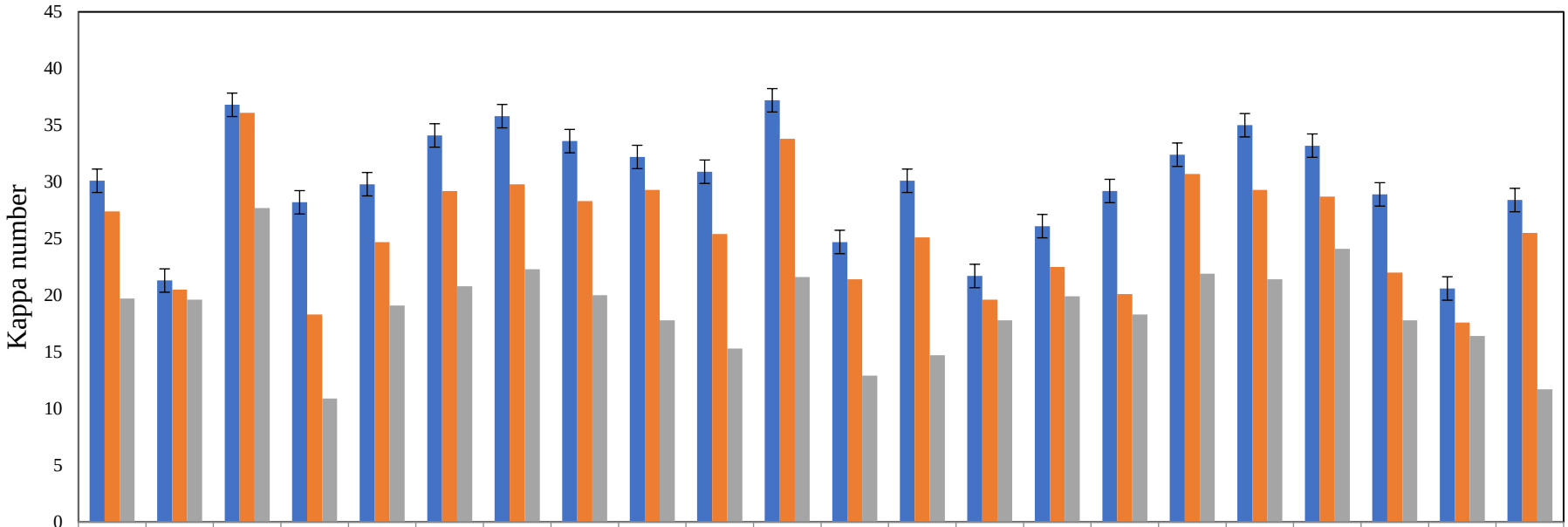
As shown in Figure 4.6, kappa number of PFA banana leaf pulp was only 10.9, while the same raw material produced pulp with kappa number 23-17 in kraft process [25]. A higher kappa number was observed for banana pseudo stem, which is still better or equal kappa number as compared to conventional pulping [24]. The kappa number of mustard stalks was 21.9 which is very close to the kappa number obtained by organic acid mixture treatment followed by peroxyacid pulping [26]. A very high pulp yield of 60.7% was obtained from banana peduncle after PFA cooking with kappa number 19.1. This higher pulp yield can be explained by higher α-cellulose content in banana peduncle (Table 3.1.). The lowest pulp yield (39.9%) was obtained from chia plant as its α-cellulose content was lower. Pulp yield from corn stalks was 41.1%, which was much lower than the other studies in conventional pulping processes [25,27-28]. This can be explained by different variety and location of raw material, which differentiate chemical characteristics of the corn stalks.

Pulp yield from kash was 54.0% with kappa number 17.8, which was very close to soda-AQ pulping [29]. Crops residues with high ash content such as rice straw, wheat straw showed higher pulp yield as compared to conventional pulping. This can be explained by the retention of silica on pulp during organic acid pulping [1]. There are no reports found on pulping of eggplant plant, chia plant and kaun plant. Therefore, these raw materials for conventional pulping need to be studied further.



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana pedunclе	Cassava stalks	Chia stalks	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash stalks	Kaun straw	Mulberry stalks	Mustard stalks	Okra stalks	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
FA70	53.6	56	54.2	55.1	63.1	41.83	48.3	48.4	53.41	64.3	51.4	58.55	38.75	60.3	45.2	55.49	45.9	43.2	35.33	50.8	48.8	50.8
FA80	44.6	46.7	51.8	48.2	61.4	39.72	44.7	47.5	51.2	62.4	50.5	56.9	37.2	58.9	41.7	54.6	42.9	41.3	32.5	48.5	47.3	47.6
FA90	41.5	45.1	51.1	49.1	60.7	36.98	39.9	41.8	48.29	58.7	45.1	54.1	34.5	54	38.7	50.5	40.4	40.9	29.9	47.3	46	46.2

Figure 4.5. Pulp yield after peroxyformic acid treatment of FA treated of crops residues



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana pedunclе	Cassava stalks	Chia plant	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash	Kaun plant	Mulberry stalks	Mustard stalks	Okra plant	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
FA70	30.1	21.3	36.8	28.2	29.8	34.1	35.8	33.6	32.2	30.9	37.2	24.7	30.1	21.7	26.1	29.2	32.4	35	33.2	28.9	20.6	28.4
FA80	27.4	20.5	36.1	18.3	24.7	29.2	29.8	28.3	29.3	25.4	33.8	21.4	25.1	19.6	22.5	20.1	30.7	29.3	28.7	22	17.6	25.5
FA90	19.7	19.6	27.7	10.9	19.1	20.8	22.3	20	17.8	15.3	21.6	12.9	14.7	17.8	19.9	18.3	21.9	21.4	24.1	17.8	16.4	11.7

Figure 4.6. Kappa number after peroxyformic acid treatment of FA treated of crops residues

4.4.3. Bleaching and physical properties of paper sheets

PFA treated pulps were bleached by two stages of alkaline peroxide bleaching. Pulp bleachability was improved with increasing FA charge during FA treatment. Organic acid pulps from bagasse (85.0%) and rice straw (81.3%) showed the best bleachability among these 14 crops residues. Corn stalks, wheat straw and banana peduncle pulps reached to above 75% brightness in two stages alkaline peroxide bleaching, while mustard stalks and banana pseudo stem pulps did not show good bleachability. In other study of organic acid pulping, kash pulp reached to 83% brightness at 4% peroxide charge, while the brightness of banana stem and dhaincha pulps were 79 and 75%, respectively at the same peroxide charge [30]. Brightness can be increased to above 80% by increasing peroxide charge by 2% in each stage.

Bleached pulps were blended in warring bender for 5 min and handsheets were prepared for determining papermaking properties. As shown in Table 4.1, corns stalks pulp showed the highest tensile index (66.9 N.m/g) followed by chia plant (60.0 N.m/g), wheat straw (59.9 N.m/g) and kash (55.0 N.m/g) pulps. Longer fiber length, lower coarseness, higher fines and degree of external fibrillation may explain higher tensile index (Table 4.2). It was observed that though jute stick did not produce high pulp yield, but tensile index was better than jute fiber because of the presence of high hemicellulose content in jute stick. The coarse fibers have a greater tendency to flocculate during sheet making that is detrimental to formation [31], which consequently produced lower tensile index. The fines of chemical pulps have a strong tendency to intensify the interaction between fibres [32-33] showed that external fibrillation, increased tensile index about 20%. But [34] showed that external fibrillation resulted in increased density without affecting tensile strength. Tear index and burst index of these pulps did not reach to desired level except wheat straw and chia plant pulps. This may be attributed by the poorly bonded fibers with fines [35]. Similar behavior of low tear and burst index of organic acid pulps were observed in elsewhere [30,36].

Table 4.1. Physical properties of bleached pulp

Raw materials	Tensile index (N.m/g)	Tear index (mN.m2/g)	Burst index (kPa.m2/g)	Elongation (%)	TEA (J/m2)	Brightness (%)
Bagasse	35.3±1.9	2.4±0.4	1.0±0.1	1.3±0.1	14.3±2.1	85.0±4.0
Bamboo	31.6±2.0	5.0±0.8	1.2±0.1	2.4±0.3	27.7±2.2	78.8±4.1
Banana pseudo stem	41.8±1.8	2.0±0.6	1.0±0.2	2.1±0.4	34.1±3.6	60.0±2.4
Banana leaf	50.2±2.7	3.1±0.7	1.8±0.4	1.9±0.3	38.9±2.9	70.9±3.6
Banana peduncle	51.7±2.3	4.1±1.0	2.0±0.3	1.9±0.2	40.7±2.8	77.6±3.4
Cassava stalks	16.3±6.7	2.80±0.6	0.19±0.2	1.4±0.1	6.3±3.0	54.14±2.9
Chia stalks	60.0±4.1	5.7±1.1	3.4±0.6	3.3±0.5	80.0±4.8	73.8±4.1
Corn stalks	66.9±4.2	4.4±0.8	2.9±0.5	2.4±0.3	64.1±4.3	75.2±3.1
Cotton stalks	39.2±5.0	5.8±0.7	2.1±0.8	2.1±3.0	41.7±2.9	56.3±2.9
Dhaincha stalks	30.0±2.2	3.4±0.6	3.1±0.4	2.3±3.3	12.0±2.5	58.38±1.7
Eggplant stalks	35.7±2.3	4.5±0.9	2.1±0.3	2.3±0.3	46.0±4.1	72.2±3.4
Jute	29.7±2.2	4.98±0.3	0.63±0.3	1.7±0.3	21.3±5.2	82.46±3.5
Jute Stick	32.7±2.4	4.2±0.5	1.5±0.2	1.8±0.1	27.7±4.0	78.92±2.7
Kash stalks	55.0±3.2	3.3±0.3	2.0±0.3	2.1±0.3	42.4±3.2	73.8±3.3
Kaun straw	27.5±2.1	3.6±0.5	0.56±0.1	1.6±0.2	15.1±2.0	72.9±3.0
Mulberry stalks	22.5±0.6	4.98±0.9	0.19±0.2	2.3±0.2	23.2±2.5	44.62±4.0
Mustard stalks	54.1±3.2	3.1±0.6	1.4±0.2	1.7±0.2	32.4±3.5	53.5±4.3
Okra stalks	46.8±1.8	3.2±0.8	1.9±0.2	1.5±0.3	25.2±2.3	76.2±3.6
Pineapple leaves	27.5±1.2	2.1±0.9	3.1±0.5	1.4±0.7	29.4±2.8	70.0±3.2
Red Lentil stalks	14.2±1.2	4.04±0.5	3.3±0.5	1.1±0.1	5.9±1.8	54.79±3.0
Rice straw	45.0±3.1	2.6±0.3	1.9±0.4	2.1±0.3	33.6±3.4	81.3±4.1
Wheat straw	59.9±3.1	5.9±1.0	1.2±0.2	1.4±0.2	24.9±2.3	76.7±3.6

4.4.4. Pulp quality analysis

Table 4.2. shows the length weighted fiber length, average width, fine percentage, curl, kink indexes, degree of fibrillation and coarseness of pulp samples from twenty-two non-wood. Such measurements are essential, since they directly impact the properties of the pulps and the quality of the produced papers. The fines content which are the fibers consisting of length below 0.2 mm in non-wood materials is considerably higher than the wood [37].

All these non-wood plant except dhaincha contains many fines, which generated from nonfibrous parenchymatic cells (Figures 3.2-3.5). Dhaincha pulp clearly has the lowest fines content (16.13%) followed by chia plant soda-AQ pulp (31.25%). The low fines content in dhaincha pulp is consistent with the micrograph picture (Figure 3.3). Mustard stalks had the highest amount of fines 48.17% followed by lentil stalks, 37.7%. The length weight fiber length of chia plant pulp was shorter than dhaincha pulp and longer than mustard and lentil stalks pulps.

Longer fiber length, lower coarseness, higher fines and degree of external fibrillation may explain higher tensile index (Table 4.1) of the samples. The coarse fibers have a greater tendency to flocculate during sheet making that is detrimental to formation [38], which consequently produced lower tensile index. The fines of chemical pulps have a strong tendency to intensify the interaction between fibres. Retulainen et al. and Kang et al. showed that external fibrillation, increased tensile index about 20% [32,39]. But Hartman showed that external fibrillation resulted in increased density without affecting tensile strength [40]. Tear index and burst index of these pulps did not reach to desired level except wheat straw and chia plant pulps. This may be attributed by the poorly bonded fibers with fines [41]. Similar behavior of low tear and burst index of organic acid pulps were observed in elsewhere [30,42].

All these non-wood plant except eggplant stalks contains many fines, which generated from nonfibrous parenchymatic cells (Figure 3.5). Banana pseudo stem had the highest amount of fines 68.2%, followed by bamboo 60.8%, kaun straw 59.2% and eggplant stalks pulp showed the lowest amount of fines of 18.2%. The lowest amount of fines in eggplant plant pulp can be explained by wood like anatomical structure (sclerenchyma). The high fines content may correspond to the fibers that are more flexible. The length weight fiber length of bamboo pulp was longest. Bamboo consists of bast fiber and stick and the fiber length of bast fibre was more than 3 mm, which contributed for average longer fibre length [43]. Paper formation has large effect on fines and fiber length. Reducing fibre length has little direct effect on the sheet structural and optical properties, but does reduce papermaking properties [44]. The coarseness of these non-wood plants fibre had a lot of variation (3.4–14.8 mg/100 m). This parameter is related to the fiber wall thickness and influences the fiber collapse degree and development of bulk [45]. Curl and kinks index of bagasse and bamboo pulp were higher. Curl and kinks are fiber deformations that contribute to a more developed network, generating less inter-fiber bonds and leading to a potential develop bulk, porosity, and smoothness in the final product.

Table 4.2. Fiber quality of organic acid pulps from crops residues

Raw materials	Fines (%)	Length Weighted (mm)	Mean Curl Index	Mean Kink Index (mm^{-1})	Mean Width (μm)	Degree of External Fibrillation (%)	Coarseness (mg/m)
Bagasse	51.4	0.617	0.200	3.1	18.3	1.74	0.148
Bamboo	60.8	1.407	0.230	2.8	15.3	1.60	0.042
Banana pseudo stem	66.8	0.489	0.140	2.42	17.0	0.62	0.134
Banana leaf	57.8	0.909	0.184	2.83	15.5	0.78	0.114
Banana peduncle	53.5	0.529	0.116	2.13	21.1	1.63	0.075
Cassava stalks	53.2	0.436	0.040	0.938	26.9	1.0	0.034
Chia stalks	44.6	0.591	0.159	2.62	16.5	1.24	0.079
Corn stalks	46.6	0.683	0.175	2.82	17.3	1.18	0.077
Cotton stalks	29.8	0.764	0.139	2.12	17.7	1.41	0.087
Dhaincha stalks	18.3	0.777	0.063	1.23	24.1	1.14	0.079
Eggplant stalks	18.2	0.449	0.067	1.4	16.4	1.7	0.058
Jute	40.7	1.068	0.107	1.20	15.6	1.03	0.080
Jute Stick	78.9	0.456	0.079	1.41	24.7	2.00	0.059
Kash stalks	54.0	0.779	0.101	1.88	18.4	1.55	0.187
Kaun straw	59.2	0.503	0.133	2.70	12.6	1.00	0.138
Mulberry stalks	36.7	0.434	0.064	1.35	19.0	1.4	0.04
Mustard stalks	51.0	0.722	0.175	2.64	19.6	1.13	0.164
Okra stalks	31.6	1.236	0.101	1.75	21	1.4	0.143
Pineapple leaves	43.8	0.817	0.082	1.70	10.5	0.83	0.061
Red Lentil stalks	43.4	0.345	0.143	2.16	16.3	2.16	0.024
Rice straw	42.1	0.564	0.068	1.89	10.4	0.96	0.059
Wheat straw	53.5	0.869	0.174	2.74	15.4	0.77	0.106

4.5. Conclusions

In this study twenty-two crops residues were evaluated in organic acid pulping. The α-cellulose contents in these samples were quite acceptable to consider as pulping raw materials. Most of these crops residues was high in ash content, which was challenging to use those as pulping raw material. Therefore, formic acid pulping was assessed in this study. The formic acid concentration had a remarkable effect on the delignification of crops residues. Peroxyformic acid treatment reduced the residual lignin remarkably. Pulp yield after peroxyformic acid treatment was better than the conventional pulp. Organic acid pulps from bagasse, bamboo, rice straw, wheat straw, banana peduncle, okra plant and corn stalks showed comparatively good bleachability in two stages alkaline peroxide bleaching. Crops residues generated very high amount of fines in organic pulping. A good tensile index of most of the bleached pulp was observed, while tear and burst index suffered. Considering all parameters, especially pulp yield, delignification, papermaking properties and bleachability, kash and banana peduncle showed the best raw materials for organic acid pulping.

4.6. References

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CHAPTER 5
SODA-AQ PULPING,
PULP QUALITY ANALYSIS
AND
PHYSICAL PROPERTIES OF PAPER SHEETS

5.1 Introduction
5.2. Experimental
5.2.1. Preparation of cooking liquor
5.2.2. Pulping
5.2.3. Determination of chemical characteristics
5.2.5. Evaluation of pulps
5.3. Results and discussion
5.3.1. Pulp yield
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5.6. Conclusions
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5.1. INTRODUCTION

For the production of pulp from wood and annual plants, various processes are carried out where the digesting liquor contains free caustic soda, sodium salts of alkyl benzenesulfonic acids, and of aromatic or aliphatic carboxylic acids. Gordon et al. in 1997 reported that delignification improved when anthraquinone or its derivatives are added to the cooking liquor during digestion [1].

In the present investigation Soda-AQ pulping process was carried out to produce pulp from all the twenty-two crops residue [2]. In the soda-anthraquinone (AQ) process, AQ operates as a redox catalyst unlike hydroxide ions (OH^-) in the conventional soda process, which promotes the transfer of electron from carbohydrate to lignin. This process accelerates the degradation and solubilization of lignin which results in faster pulping. The end group oxidation stabilizes the carbohydrates against the attack of alkali which generates higher pulp yield [3-5]. Thus the process provides a means to achieve a selective separation of lignin from cellulose and hemicellulose in non-degraded forms using comparatively less chemicals than other methods (kraft and sulfite methods).

5.2. EXPERIMENTAL

5.2.1. Preparation of cooking liquor

The active alkali was varied from 16-20 % as NaOH on oven dried (O.D.) sample in the liquor ratio of 1:5. AQ was 0.1 % of O.D. raw material. The cooking was continued for 2 hrs at the maximum temperature (170 °C).

5.2.2. Pulping

The twenty-two samples were cooked by soda-AQ process with varying alkali charge. Soda-AQ pulping was done in a 5-liter capacity thermostatically controlled electrically heated rotary digester. The cooking was continued for 60 min at the maximum temperature (170 °C). At the

end of pulping, pressure was relieved to atmospheric pressure, pulp was taken out from the digester, washed till free from residual chemicals, and screened by flat vibratory screener (Yasuda, Japan).

5.2.3. Determination of chemical characteristics

The screened pulp yield, total pulp yield and screened reject were determined gravimetrically as percentage of o.d. raw material. The kappa number (T 236 om-99) of the resulting pulp was determined in accordance with Tappi Test Methods as described before. Three replicates of all experiments were done and average reading was taken.

5.2.4. Evaluation of pulps

Pulps from kaun straw, wheat straw and rice straw were beaten in a valley beater to different freeness (^oSR) and hand sheets of about 60g/m^2 were made in a Rapid Kothen Sheet Making Machine. The freeness or drainability was determined according to ISO 5267-1 Schopper-Riegler method. The sheets were tested for tensile (T 494 om-96), burst (T 403 om-97) and tear strength (T 414 om-98) according to TAPPI Standard Test Methods.

5.3. RESULTS AND DISCUSSION

5.3.1. Pulp yield

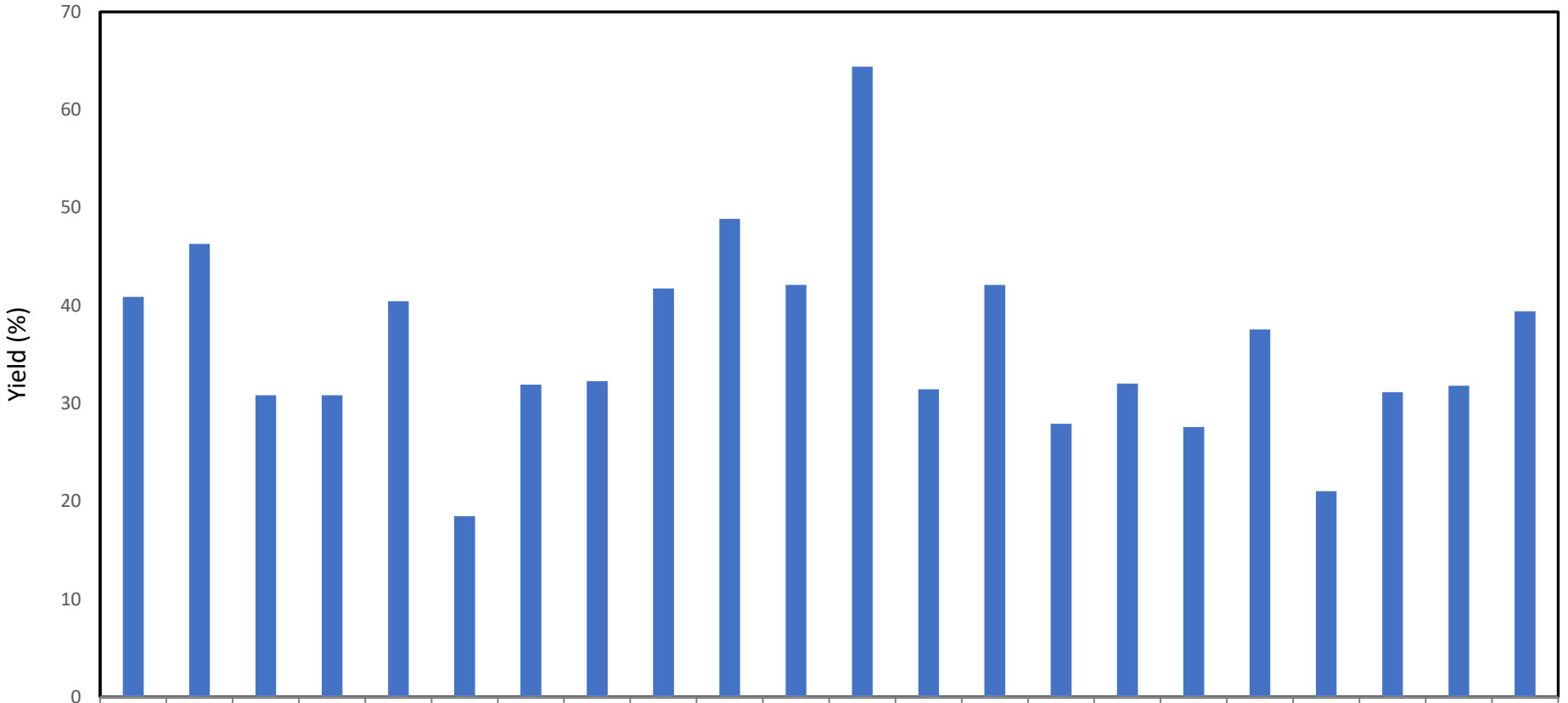
The twenty-two non-wood raw materials were cooked by soda-AQ process with varying alkali charge and results are shown in Table (Appendix I). The optimum pulp yield and corresponding kappa values are shown in Figures 5.1 and 5.2.

The pulp yield decreased with alkali charge as was expected (Appendix I). For straw pulps, screened pulp yield of kaun straw pulp at 12% NaOH charge was 29.8%, which was 2% and 11.6% lower than the pulp yield from rice straw and wheat straw, respectively, under the same cooking conditions. In these conditions, the screened reject was 0.8%, 0.5% and 0% for kaun

straw, wheat straw and rice straw, respectively. Screened pulp yield from kaun straw decreased to 28.5% with no reject with increasing alkali charge to 16%. According to water and alkali solubilities data (Table 3.1), kaun straw was supposed to give higher pulp yield compared to rice straw. The lower pulp yield of non-wood samples can be explained by some hemicellulose components which are soluble in alkaline pulping conditions. A lower pulp yield can also be explained by lower holocellulose and α-cellulose c

The pulp yields from mulberry, okra, cassava, mustard stalks and pineapple leaves were much lower than other crops residues. This was because of the lower holocellulose and α-cellulose content of these crops residues (Table 3.1). Jute and bamboo showed the highest pulp yield of ~ 64% at 14% alkali charge. The other samples showed pulp yield between 28-49%.

It is seen that pulp yield in FA followed by PFA pulping was higher than that of soda-AQ pulping. The higher pulp yield in FA/PFA process can be explained by retention of silica on the pulp fiber, which was dissolved in alkaline process [6,7]. At kappa number 17, the pulp yield of rice straw and wheat straw was 46% in FA/PFA process while the pulp yield of kaun straw was 38.7% at kappa number 19.9 in FA/PFA process and 30.6% at kappa number 18.4 in soda-AQ process.



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana pedunclе	Cassava stalks	Chia stalks	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash stalks	Kaun straw	Mulberry stalks	Mustard stalks	Okra stalks	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
Yield (%)	40.88	46.29	30.82	30.82	40.44	18.46	31.9	32.27	41.74	48.86	42.11	64.39	31.43	42.09	27.9	32.01	27.59	37.55	21.01	31.12	31.8	39.4

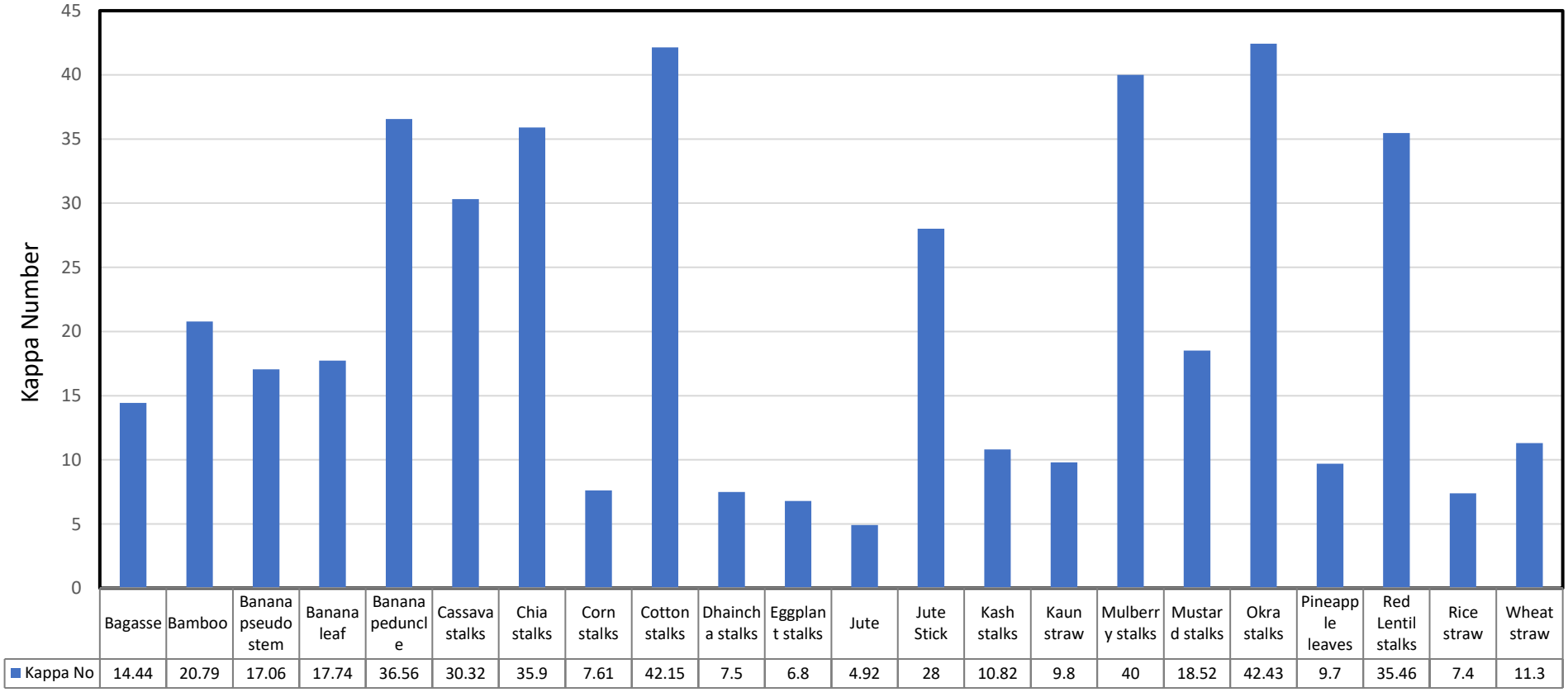
Figure 5.1. Pulp yield of soda-anthraquinone treated pulp at different alkali concentration

5.3.2. Kappa number

The kappa number is an estimation of the amount of chemicals required during bleaching of wood pulp to obtain a pulp with a given degree of whiteness. The amount of bleaching chemical required is directly related to the lignin content of pulp. So, the kappa number is used to estimate the efficacy of the lignin-extraction phase of the pulping process. The kappa value is approximately proportional to the residual lignin content of the pulp.

It was observed that the degree of delignification is higher for rice straw as compared to kaun straw and wheat straw (Figure 5.2). Kappa number of rice straw pulp was only 8.5 at 12 % alkali charge, while kappa number of kaun straw and wheat straw pulps was 18.4 and 19.9, respectively at this alkali charge. As shown in Table (Appendix I), the samples were cooked by soda-AQ process with varying alkali charge from 12% to 18%. The kappa number decreased sharply at an optimum alkali charge for the non-wood samples. This indicates that the sample already reached to its residual delignification stage at optimum alkali charge and increasing the alkali charge does not add to further delignification.

As shown in Figure 5.2, at optimum cooking conditions kappa number of jute pulp was lower than other plants. It indicates the lowest residual lignin content of the pulp from jute samples. The highest residual lignin was found in okra and cotton stalks followed by mulberry stalks, red lentil stalks and banana peduncle pulps.



	Bagasse	Bamboo	Banana pseudo stem	Banana leaf	Banana pedunclе	Cassava stalks	Chia stalks	Corn stalks	Cotton stalks	Dhaincha stalks	Eggplant stalks	Jute	Jute Stick	Kash stalks	Kaun straw	Mulberry stalks	Mustard stalks	Okra stalks	Pineapple leaves	Red Lentil stalks	Rice straw	Wheat straw
Kappa No	14.44	20.79	17.06	17.74	36.56	30.32	35.9	7.61	42.15	7.5	6.8	4.92	28	10.82	9.8	40	18.52	42.43	9.7	35.46	7.4	11.3

Figure 5.2. Kappa number of soda-anthraquinone treated pulp at different concentration

5.4. PULP QUALITY ANALYSIS

Table 5.1 shows the weighted length, average width, fine percentage, curl, kink indexes, degree of fibrillation and coarseness of pulp samples from twenty-two non-wood pulps.

Such measurements are essential, since they directly impact the properties of the pulps and the quality of the produced papers. Most of the non-wood pulps except eggplant stalks contain many fines, which is generated from nonfibrous parenchymatic cells (Figures 3.2-3.5). Bamboo had the highest amount of fines 75.2% followed by corn stalks, 58.6% and eggplant stalks pulp showed the lowest amount of fines. The lowest amount of fines in eggplant stalks pulp can be explained by wood like anatomical structure (sclerenchyma). The high fines content may correspond to the fibers that are more flexible. The length weight fiber length of okra plant pulp was longest. Fines and fiber length have large effect on paper formation. Reducing fibre length has little direct effect on the sheet structural and optical properties, but does reduce papermaking properties. [8]. The coarseness of these non-wood plants fibre had a lot of variation (3.4–14.3 mg/100 m). This parameter is related to the fiber wall thickness and influences the fiber collapse degree and development of bulk [9]. Curl and kinks index of okra plant pulp were higher. Curl and kinks are fiber deformations that contribute to a more developed network, generating less inter-fiber bonds and leading to a potential develop bulk, porosity, and smoothness in the final product.

Table 5.1. Fiber quality of Soda-AQ pulps from crops residues.

Raw materials	Fines (%)	Length Weighted (mm)	Mean Curl Index	Mean Kink Index (mm^{-1})	Mean Width (µm)	Degree of External Fibrillation (%)	Coarseness (mg/m)
Bagasse	29.4	1.035	0.125	1.94	19.8	1.36	0.131
Bamboo	75.8	0.778	1.852	1.66	14.5	1.11	0.081
Banana pseudo stem	54.35	1.166	0.191	2.74	16.75	2.02	0.081
Banana leaf	51.5	1.597	0.194	2.485	15.6	1.265	0.11
Banana peduncle	33.05	1.551	0.103	1.59	21.7	1.995	0.097
Cassava stalks	53.2	0.436	0.040	0.938	26.9	1.0	0.034
Chia stalks	31.3	0.651	0.093	1.72	16.2	1.17	0.149
Corn stalks	58.6	0.601	0.126	1.92	17.4	1.12	0.081
Cotton stalks	28.9	0.758	0.138	2.11	18.0	1.43	0.089
Dhaincha stalks	18.8	0.792	0.059	1.22	24.1	1.14	0.079
Eggplant stalks	18.2	0.449	0.067	1.4	16.4	1.7	0.058
Jute	27.7	1.756	0.166	1.20	15.8	1.03	0.080
Jute Stick	73.4	0.309	0.077	1.39	24.4	2.57	0.051
Kash stalks	42.7	1.604	0.149	1.69	15.1	1.53	0.136
Kaun straw	51.5	0.602	0.138	2.37	12.8	0.78	0.106
Mulberry stalks	36.7	0.434	0.101	1.75	21	1.4	0.143
Mustard stalks	48.2	0.485	0.105	1.83	19.8	2.07	0.167
Okra stalks	31.6	1.236	0.101	1.75	21	1.4	0.143
Pineapple leaves	47.4	0.783	0.071	1.50	11.3	0.96	0.069
Red Lentil stalks	37.7	0.470	0.138	2.15	16.3	2.62	0.128
Rice straw	47.3	0.575	0.176	2.71	11.0	1.90	0.083
Wheat straw	29.8	1.003	0.151	2.44	16.1	1.77	0.096

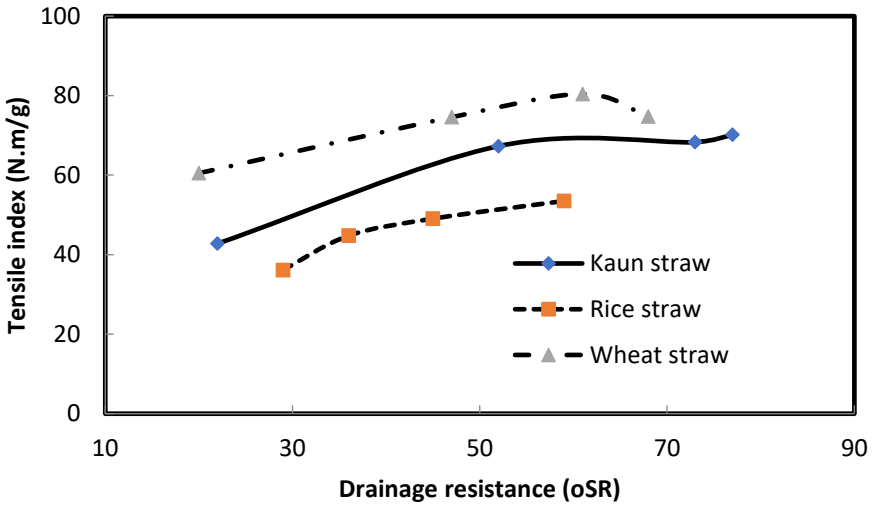
5.5. Physical properties of paper sheets

To improve the papermaking properties, soda-AQ pulps from twenty-two crops residues were beaten in a Valley beater to various drainage resistance and strength properties were measured. The basic strength properties of pulps from non-wood raw materials are shown in Appendix II. It was observed that beating of straw pulps (wheat straw, rice straw, kaun straw) increased drainage resistance rapidly and improved the strength properties. These pulps had higher unbeaten drainage resistance than the hardwood pulp available in the market. The drainage resistance of kaun straw, wheat straw and rice straw pulps were 22, 20 and 29 ^{o}SR respectively, which can be explained by the presence of the parenchyma cells in the pulp (Figures 3.4 and 3.5). Mild beating with the non-wood pulps resulted in large increase of drainage resistance. Crushed parenchyma cells are probably the cause of these drainage impairments.

As can be seen from the SEM and micrograph images, most of the crops residues are very high in parenchyma cells (Figures 3.2-3.5). These parenchyma cells have thin cell walls, which, in small quantities, can aid in fiber bonding. However, in larger percentages, thin walled parenchyma cells can plug the sheet reducing paper machine drainage. With mild mechanical action, these cells crush, further reducing the ability to remove water from the sheet.

The highly swollen hemicelluloses and the increased content of fines with beating cause a high drainage resistance of pulps [6]. In the unbeaten state the tensile index of non-wood pulps was lower than pulp pulps after beating. Similar behavior was observed for burst index. The high selectivity and consequently high-hemicelluloses content of this pulp resulted in good fiber bonding ability and hence high tensile and burst strength (Appendix II). Figure 5.3 (c) shows that refining had negative impact on tear index of pulps. The non-wood pulps showed decreasing trend with increasing ^{o}SR value.

(a)



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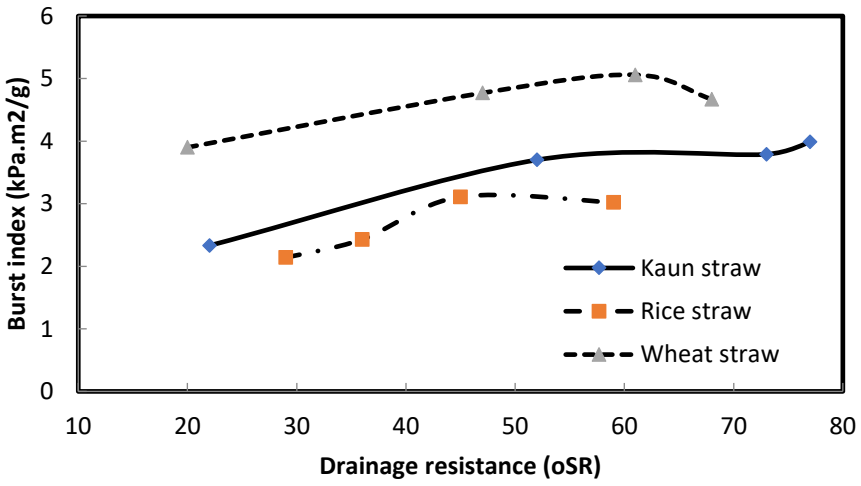

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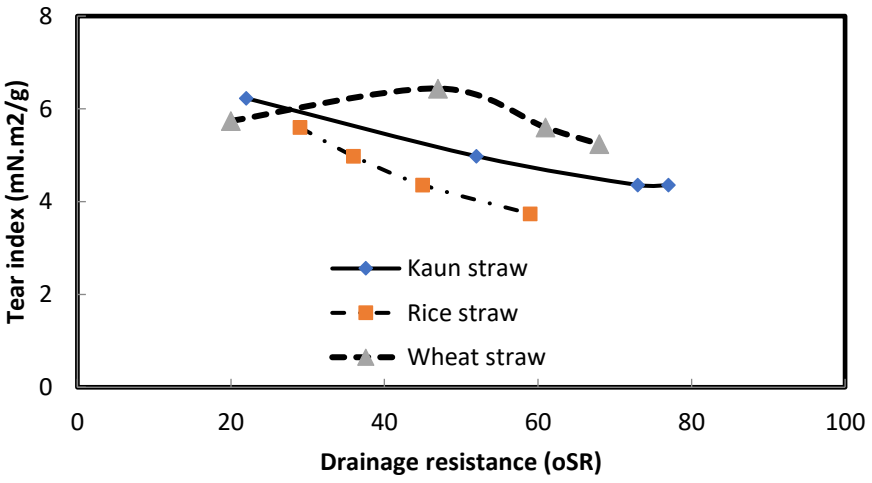
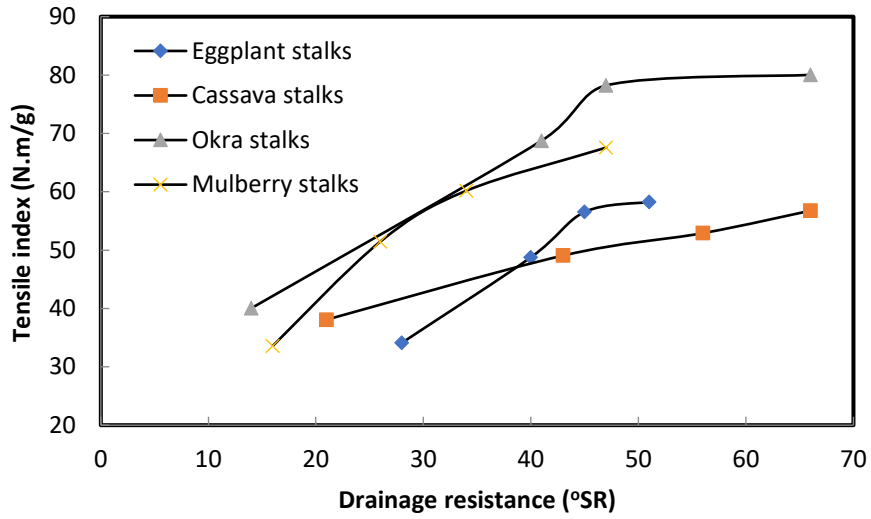


Figure 5.3. Relationship of drainage resistance of kaun straw, wheat straw and rice straw pulps with (a) Tensile index, (b) Burst index, and (c) Tear index.

Similar results were observed in case of cassava, eggplant, mulberry and okra stalks pulp (Figure 5.3) and for bagasse, kash and corn stalks pulps (Figures. 5.4). The papermaking properties were significantly improved by the refining operation for these non-woods. It is interesting to note that the unbleached okra plant pulp exhibited very good properties in terms of tensile, bursting and tearing strengths. This can be explained by longer fiber length of okra plant pulp (Table 3.3).

It is observed from these data that the tensile and burst index of produced papers increased with increasing beating degree, while tear index decreased. Dhaincha stalks pulp exhibited the highest tensile index at any ^{o}SR followed by bagasse pulp (Appendix II). A good tensile index of these pulps in the unbeaten state can be explained by higher external degree of fibrillation, which facilitates fiber bonding (Table 5.1). Similar behavior of tensile, tear and burst index relationship with ^{o}SR was observed for all other non-wood raw materials also.

(a)



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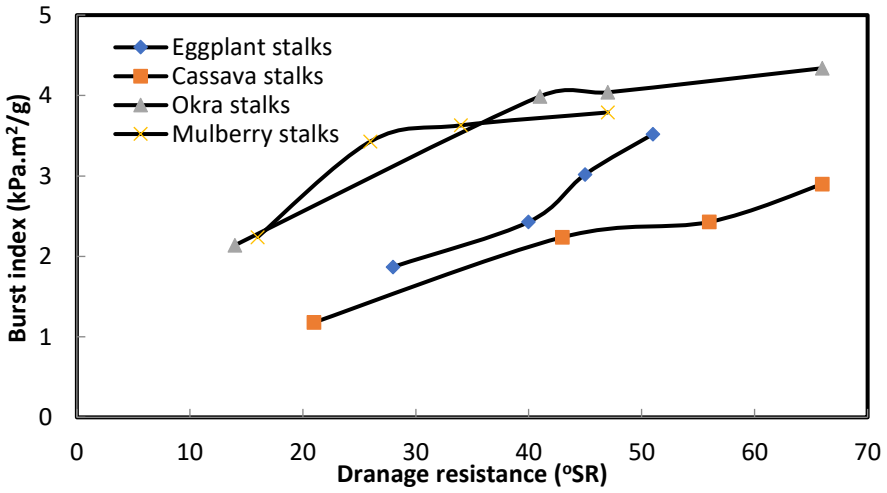

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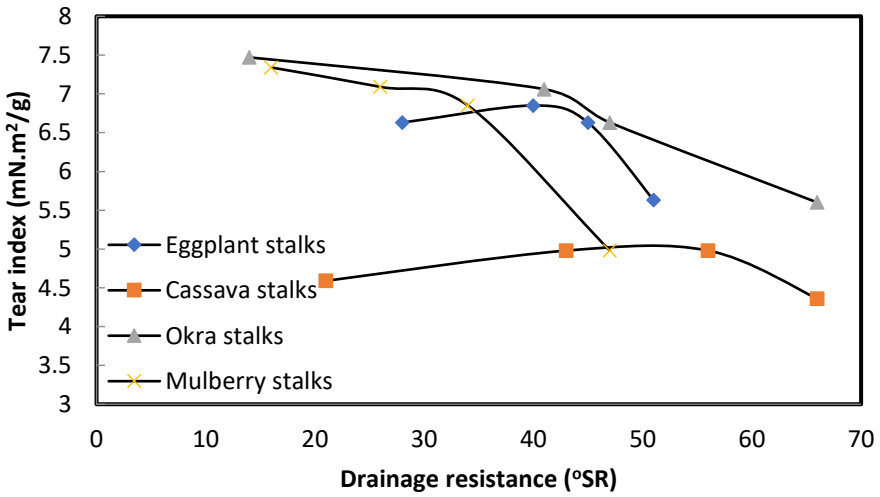
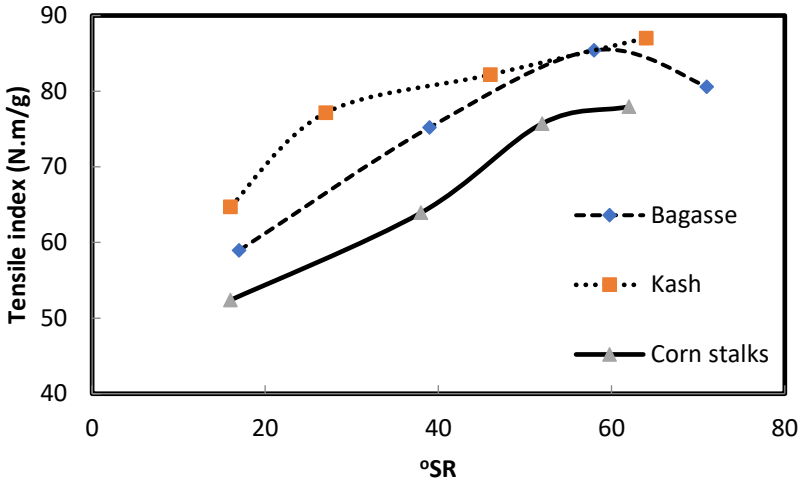


Figure 5.4. Relationship of drainage resistance of cassava, eggplant, mulberry and okra stalks pulps with (a) Tensile index, (b) Burst index, and (c) Tear index.

(a)



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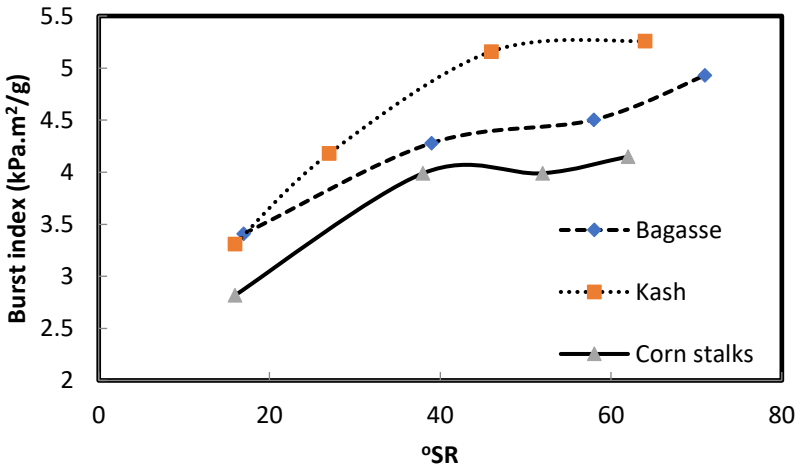

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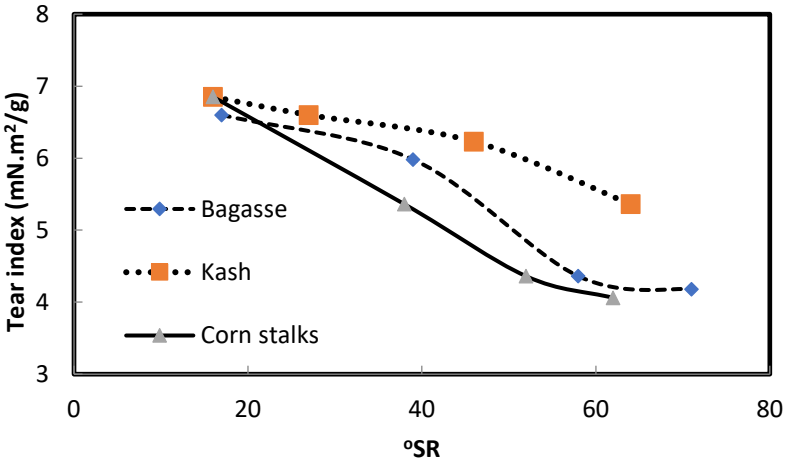

Figure 5.5. Relationship of drainage resistance of bagasse, kash and corn stalk pulps with (a) Tensile index, (b) Burst index, and (c) Tear index.

5.6. Conclusions

In this chapter, soda-anthraquinone pulping of twenty-two crops residues were evaluated. The α-cellulose contents were found to be quite acceptable to consider these samples as pulping raw materials. It was found that at very low alkali charge (~12-16%), the kappa value of the individual non-wood pulp was lowered which indicted high delignification of the pulps. The pulp yield reached upto 64.4% for jute pulp, followed by dhaincha 48.9% and bamboo 46.3%. It was observed that the tensile and burst index of produced papers increased with increasing beating degree, while tear index decreased. Dhaincha stalks pulp exhibited the highest tensile index at any ^{o}SR followed by bagasse pulp (Appendix II). A good tensile index of these pulps in the unbeaten state can be explained by higher external degree of fibrillation, which facilitates fiber bonding (Table 3.3). Similar behavior of tensile, tear and burst index relationship with ^{o}SR was observed for all other non-wood raw materials also.

5.7. References

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CHAPTER 6

HIGH TEMPERATURE CHLORINE DIOXIDE BLEACHING OF SODA-AQ PULP, PROPERTIES OF BLEACHED PULP AND ENVIRONMENTAL IMPACT

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6.1. INTRODUCTION

Pulp bleaching is a chemical process to brighten the pulp through the removal of lignin. The major part of delignification occurs during the pulping process and rest is removed further in bleaching stages. It is the most expensive and polluting step in pulp industry as extensive bleaching is required by pulps produced by chemical pulping. It is accomplished with various compounds containing chlorine or oxygen and alkali extractions in several stages. During bleaching lignin is reacted with elemental chlorine and its derivatives to produce fragmented chlorolignins [1]. Alkali used in extraction stage dissolves these fragmented non-cellulosic chlorolignin compounds. The major groups of chlorolignin compounds found in pulp mill effluent are chlorophenols, chlorocatechols, chlorotannins, chlorinated resin and fatty acids etc. [2]. The reduction of chlorine compounds in pulp bleaching reduces chlorinated organics in the effluent [2-5]. Many attempts have been studied in reducing ClO_2 consumption [6-10]. Hot acid treatment and high temperature chlorine dioxide delignification (D_{HT}) bleaching were thoroughly investigated by Ragnar and Lindström, and showed that the D_{HT} had superior results of the investigated parameters [11].

The basic concept for the high temperature ClO_2 delignification (D_{HT}) stage is that the reaction rate of chlorine dioxide with remaining pulp lignin is faster at high temperature than that with hexeneuronic acid (HexA). Thus, at the early stage of the reaction most of the chlorine dioxide reacts with lignin, but the HexA remains in the pulp and are eliminated later through pulp acid hydrolysis stages [12]. Ventorim et al. revealed that a partial acid hydrolysis of HexA occurred in D_{HT} treatment resulting into decrease in generation of chlorinated organic halides [13]. Ventorim et al. (2005) also found that at a similar ClO_2 dose (kappa factor 0.20 at pH 3.0) in D_{HT} bleaching produced 46.3% less AOX in the filtrate in relation to the D_0 [13]. Brogdon (2009) stated is his review that hot A-stage removed 30 to 90% of HexA entering into the bleach plant and some lignin as well [14]. Most applications of hot A-stages are combined with

the D_0 into a single operation, (A/D_0) or "hot D_0-Stage". Such processes can be very effective at reducing the total ClO_2 needed for ECF bleaching of hardwood pulps (20 to 50%). The delignification during pulping occurs exclusively due to nucleophilic reactions [15-17], whereas delignification during bleaching is primarily initiated by electrophilic reactions, which may be followed by nucleophilic processes [18-21].

In this study, chlorine dioxide bleaching (ClO_2) of unbleached and oxygen delignified pulps of non-wood plants was carried out with varying ClO_2 charge (kappa factor 0.15, 0.2 and 0.25) and temperature (70 and 85^{o}C). The final pulp properties as well as the effluent quality were also studied.

6.2. EXPERIMENTAL

6.2.1. Oxygen Pre-bleaching

Oxygen pre-bleaching was conducted in a 1000 mL rotary digester. The reactor was then charged with 500g o.d. pulp, 0.5% $MgSO_4$ and 2% NaOH. The consistency was maintained 10% using deionized water. After sealing the reactor, the vessel was pressurized with O_2 (276 kPa) and rapidly heated to the desired temperature (76^o-105^{o}C). The reaction was terminated after 1 h; the reactor was cooled and the O_2 pressure was released. The pulp was then washed, dried, and applied for subsequent bleaching stages.

6.2.2. $D_0(EP)D_1$ and $D_{HT}(EP)D_1$ bleaching

Unbleached and oxygen delignified pulps were bleached by $D_0(EP)D_1$ and $D_{HT}(EP)D_1$ bleaching sequences (where D represents chlorine dioxide and EP represents peroxide reinforced alkaline extraction). The chlorine dioxide charge in D_0 and D_{HT} stages were varied by kappa factors 0.15, 0.2 and 0.25. The temperature was 70^{o}C in D_0 stage for 45 min. Pulp consistency was 10%. The pH was adjusted to 2.5 by adding dilute H_2SO_4. In the D_{HT} stage, bleaching temperature was 85^{o}C and all other parameters remained same. In the alkaline

extraction stage, temperature was 70 °C for 60 min in a water solution of 2 % NaOH and 0.5 % H_2O_2 (on o.d. pulp) were used. After (EP) stage, kappa number, viscosity and brightness were determined in accordance with Tappi Test Methods as above.

In the D_1 stage, pH was adjusted to get end pH 4.5. The ClO_2 charge in the D_1 stage was fixed to 1%. The brightness, viscosity and HexA of the bleached pulp and COD in the mixed effluent collected from D_0, EP and D_1 stages were determined in accordance with PAPTAC Methods H.3.

6.2.3. Viscosity of pulp

Viscosity of a pulp gives an estimation of the average degree of polymerization of the cellulose fiber. So, the viscosity indicates the relative degradation of cellulose fiber during pulping or bleaching process.

0.125 gram (OD) pulp was taken and then 12.5 ml water and 12.5 ml CED solution was added to the flask and continuous shaking was performed until the pulp was dissolved. 10 ml sample solution was taken into viscosity tube by pipette and time was counted with a stop watch.

Calculation

Viscosity (v) = c×t×d

Here, c= Viscosity constant (0.09654)

t= Average reflux time

d= Density of the pulp solution

6.2.4. Hexeneuronic acid content of chemical pulp

The main uronic acid groups in chemical pulps is 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid (hexenuronic acid, HexA). This acid does not exist in native wood but is formed in chemical (alkaline) pulping through β-elimination of methoxyl groups from 4-

methylglucuronic acid (MeGlcA). Hexeneuronic acid (HexA) affects the kappa number determination by reaction with permanganate. The presence of the HexA increases chlorine dioxide consumption in chlorine dioxide bleaching. It also causes overestimation of the residual lignin in pulps, which could lead to over dosage of peroxide in peroxide bleaching. Even a small amount of HexA can bond with transition metals and reduce pulp brightness stability.

Procedure

0.05 gram (oven dried) pulp sample was weighed accurately and it was transferred to a 20 ml vial containing 10 ml of hydrolysis solution and was sealed by a septum. The vial was shaked and heated in a water bath at 60-70ºC for 30 minutes. A 3ml plastic syringe was used to retrieve the resulting solution form the vial. A 0.2 µm syringe filter was used on the plastic syringe to filter fines and fines before dispensing the filtrate into a silica sampling cell for UV absorption measurements. The absorption signals were recorded at 260nm and 290 nm.

Calculation

HexA content determination,

$$C_{HexA}\,(\mu mol/g) = 0.287 \times \frac{(A_{260} - 1.2A_{290}).V(ml)}{w(g)}$$

Where, 0.287 = calibration constant obtained using a standard pulp (2). This calibration constant can be universally used to calculate HexA content in any pulps. There is no need to conduct calibration.

1.2 = ratio between lignin absorption at 260 nm and 290 nm that is used to correct lignin absorption on HexA determination

6.2.5. Chemical Oxygen Demand (COD) of bleached pulp liquor

The chemical oxygen demand (COD) is defined as the milligrams of oxygen consumed by 1 L of sample under the conditions of the test. The COD of water and waste water is determined by reaction with a measured excess of potassium dichromate under reflux conditions.

Calculation

$$\text{COD, mg/L} = \frac{(A-B)\times M\times 8000}{V}$$

Where,

A= volume of ferrous ammonium sulphate used for titration of the blank, mL

B= volume of ferrous ammonium sulphate used for titration of the test specimen, mL

M= molarity of ferrous ammonium sulphate as standardized against standard dichromate sol^{n}

V= volume of test specimen

8000 = titrimetric factor ton convert from moles oxygen per litre to miligrams oxygen per litre.

6.2.6. Evaluation of pulp

The kappa number (T 236 om-99), viscosity (T 230 om-99), brightness (T 452 om-92) and HexA (T282 pm-07) of the resulting pulps from the unbleached and oxygen delignified state were determined in accordance with Tappi Test Methods. Three replicates of all experiments were done, and average reading was taken.

6.3. RESULTS AND DISCUSSION

Pulps from twenty-two non-wood plants were prebleached by oxygen delignification under identical conditions. Entering kappa number was varied from 10.1 in kaun straw pulp to 33.3 banana leaf pulp. The oxygen delignification degree varied among the raw material from 21.5% to 72.7%. The lowest and highest delignification degrees on oxygen delignification were observed for banana peduncle and bamboo pulps, where entering kappa number was 28.8 and 26.8, respectively. The oxygen delignification should be limited up to 50% delignification to maintain pulp viscosity. Oxygen delignification increased pulp brightness from 6% to 28% depending on non-wood pulps. Unbleached brightness of jute fiber pulp was 28.95%, which increased to 56.99% on oxygen delignification. On the other hand, oxygen delignification of wheat straw pulp increased to 35.7% for 29.37% in the unbleached state.

Pulp viscosity loss during oxygen delignification is caused by cellulose chain cleavage resulting from attack by oxygen-based radicals generated through reactions with lignin. As shown in Table 6.1, there were no significant changes of pulp viscosities after oxygen prebleaching. The pulp viscosities decreased by 2% to 12%. The maximum viscosity drop was 12% for mulberry stalks pulp, where delignification degree was 67%. The HexA content in twenty-two non-wood plants pulps was varied from 7.66% to 79.41 μmole/g pulp. The lowest HexA content was in rice straw pulp and the highest in jute fiber pulp. Oxygen delignification did not change HexA content (Table 6.1).

In alkaline pulping process, 4-O-methyl-α-D-glucuronic acid groups react with alkali and form hexenuronic acids through beta elimination of the methoxyl [22]. Thus, HexA is a product of alkaline cooking, and their amount in the pulp depends on the amount of 4-O-methyl-α-D-glucuronic acid originally present in the raw material and alkaline cooking condition. Oxygen delignification is a part of extended alkaline cooking. Therefore, HexA content in oxygen delignified pulp did not decrease, even in some cases increase.

Table 6.1. Pulp properties of unbleached and oxygen delignified pulps of non-wood plants

Raw material	Kappa number		Viscosity (mPa.s)		Brightness (%)		HexA (µmole/g)	
	Unbleached	O_2-delignified	Unbleached	O_2-delignified	Unbleached	O_2-delignified	Unbleached	O_2-delignified
Bagasse	14.34	8.51	15.12	15.52	27.86	52.45	10.52	10.07
Bamboo	26.82	7.31	16.13	14.98	19.81	45.74	13.11	13.34
Banana pseudo stem	23.57	12.03	19.08	18.51	11.32	15.93	10.91	10.67
Banana leaf	33.28	17.41	20.89	20.79	16.09	23.66	28.32	28.65
Banana peduncle	28.8	22.6	21.39	19.59	14.32	27.86	20.34	20.76
Cassava stalks	31.4	10.32	12.81	12.56	16.22	24.78	24.28	24.76
Chia stalks	27.65	12.11	10.96	10.22	15.62	22.55	53.65	53.24
Corn stalks	35.0	12.23	33.64	32.34	21.44	28.64	9.21	9.08
Cotton stalks	31.19	8.01	11.78	11.61	11.15	30.57	76.73	61.23
Dhaincha	14.1	6.9	14.69	13.26	29.59	53.42	53.32	53.14
Eggplant stalks	28.79	13.68	12.81	12.56	21.71	30.5	26.64	27.22
Jute	11.98	7.62	13.21	12.48	28.95	56.99	79.41	67.34
Jute Stick	18.26	6.26	14.85	13.13	27.47	47.69	77.60	70.36
Kaun straw	10.07	6.56	15.49	14.23	32.26	41.51	32.32	33.43
Kash stalks	14.84	7.23	10.85	10.21	21.08	51.41	12.92	12.07
Mulberry stalks	21.35	6.86	12.65	11.09	22.86	44.92	60.65	61.04
Mustard stalks	18.6	10.45	13.51	12.73	23.12	41.59	37.03	38.22
Okra stalks	30.68	22.31	21.57	21.01	13.02	15.28	22.00	25.32
Pineapple leaves	19.3	6.1	12.65	11.79	19.44	32.25	8.87	8.23
Red Lentil stalks	18.26	5.42	12.69	11.55	24.75	39.50	21.90	22.23
Rice straw	13.16	5.17	16.04	15.31	37.93	50.05	7.66	7.67
Wheat straw	12.32	5.56	16.75	16.05	29.37	35.70	10.66	10.33

6.3.1. D_{HT}(EP) and D_0(EP) pulp properties

The effect of kappa factor on (EP) kappa number, brightness and viscosity of twenty-two non-wood pulps are shown in Table (Appendix III). First ClO_2 stage is denoted as D_0 and D_{HT} at 70°C and 85°C, respectively. As expected, increasing kappa factor resulted in decrease kappa number and viscosity and increase brightness regardless D_0 or D_{HT} processes. D_{HT} bleaching is more efficient than D_0 and support chlorine dioxide dose reduction during bleaching (Appendix III). The delignification to a lower kappa number is one of the factors to get high pulp brightness. The oxygen delignified pulp showed lower kappa number after (EP) stage.

The kappa numbers after (EP) stage in D_{HT} bleaching were always lower than the corresponding D_0 bleaching. This is related to the acid leaching of lignin as described and reported by [23-24]. The highest and lowest (EP) kappa numbers were observed for okra plant and wheat straw, respectively. As shown in Figure 6.1, for the pulp bleaching with kappa factor 0.2, (EP) kappa number were 11.76 and 7.78 in D_0 bleaching, which decreased to 9.61 and 5.15 in D_{HT} for unbleached and oxygen delignified pulp, respectively. The (EP) kappa number for wheat straw pulps decreased from 1.83 and 0.98 in D_0 bleaching to 1.38 and 0.63 in D_{HT} bleaching. The higher kappa number decreased in the D_{HT}(EP) stage as compared to the D_0(EP) can be explained by the higher removal of HexA [25]. This can also be explained by the degradation of hemicellulose during D_{HT} treatment, which breaks down the bonds of the lignin-carbohydrate complex (LCC) and increases the extraction of the lignin from the surface of the fiber, which is described by [26]. But according to Ikeda et al., the temperatures were not high enough to cleave the C-O or C-C bonds that link lignin to carbohydrates in LCC [23]. McDonough and co-workers speculated that that proportion of HexA contributing to the pulp's kappa number entering the D_0 stage affected bleachability of a red oak pulp that underwent a hot acid hydrolysis [27].

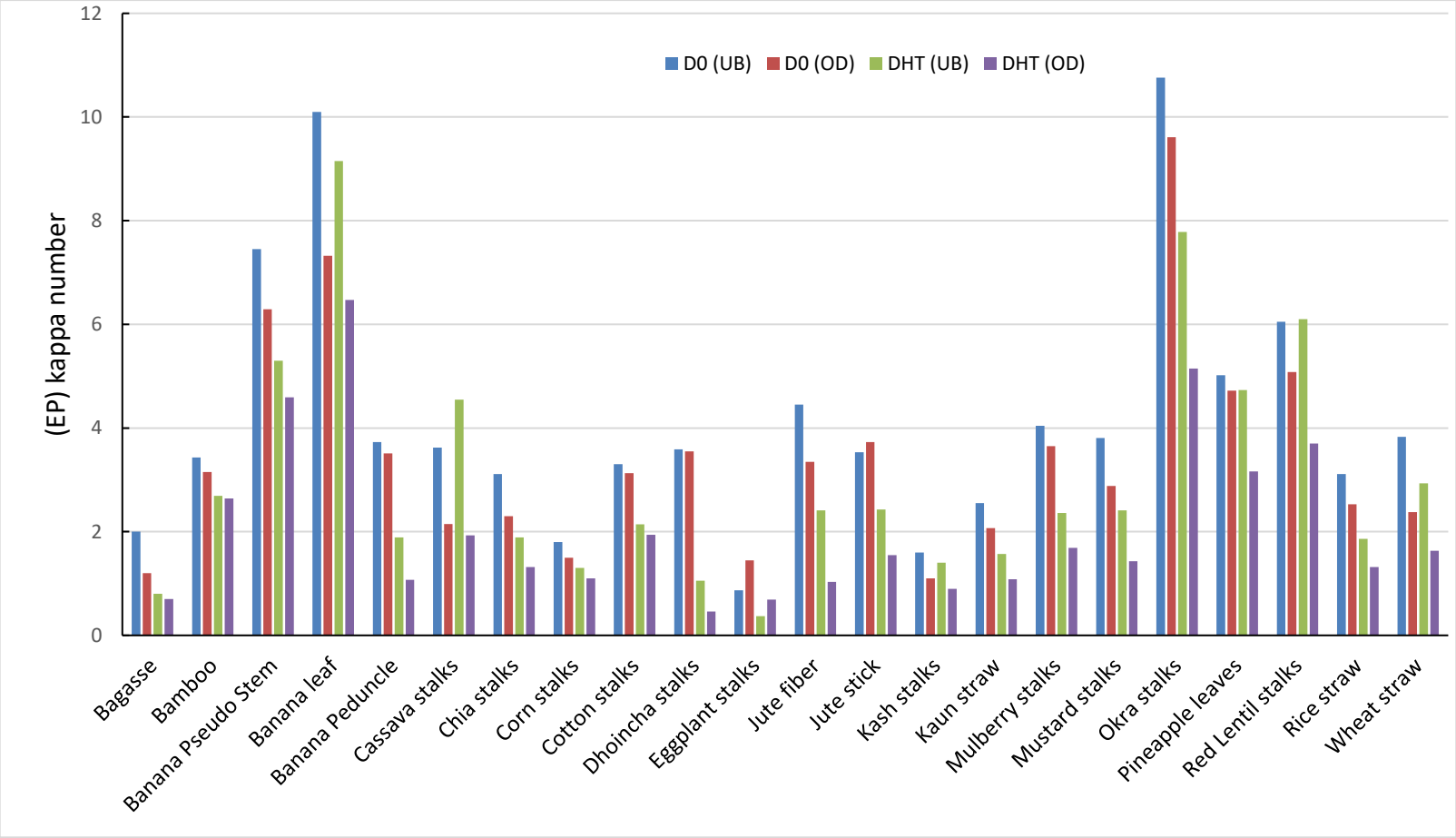

Figure 6.1. Effect of high temperature (D_{HT}) delignification on kappa number after EP stage

Pulp brightness after D_0(EP)/D_{HT}(EP) stage is also shown in Table (Appendix IV). Oxygen delignified pulp showed better pulp brightness than the unbleached pulp regardless D_0 or D_{HT} bleaching. The (EP) brightness of D_{HT} treated pulps was better than those treated by D_0 process using an identical kappa factor. Bamboo, dhaincha, jute fiber and jute fiber pulps showed improved brightness, while banana pseudo stem pulp showed the worst brightness. Initial pulp brightness is indicator pulp bleachability. At the staring, banana pseudo stem pulp brightness of was 11.32% and 15.93% for unbleached and oxygen delignified pulps, respectively (Table 6.2). Only (EP) brightness data of a few non-wood plant pulps are shown in Figure 6.2.

The highest brightness advantage in D_{HT} stage than D_0 stage after (EP) stage was 3% for dhaincha oxygen delignified pulp. Ventorim et al. found the first chlorine dioxide stage at high temperature (D_{HT}) decreased the brightness by 2.5% ISO and kappa number by 46% (1.9 units) after extraction stage as compared to the conventional D stage [28]. Their results were also supported by others [11,29]. The target of this study was to improve brightness and kappa number reduction at 85^{o}C for shorter bleaching time, which was achieved in this study.

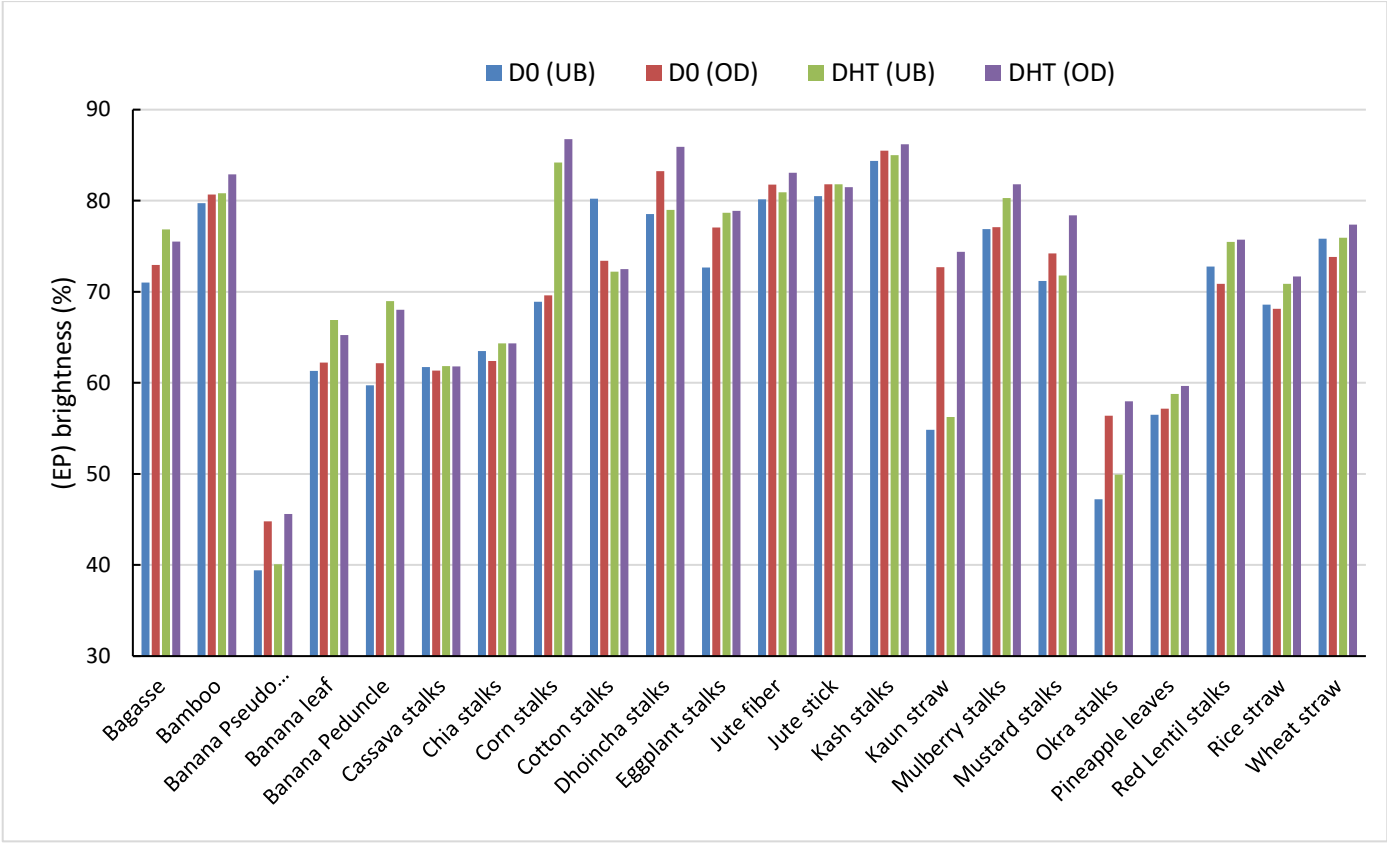

Figure 6.2. Effect of D_{HT} delignification on brightness after EP stage of bleaching

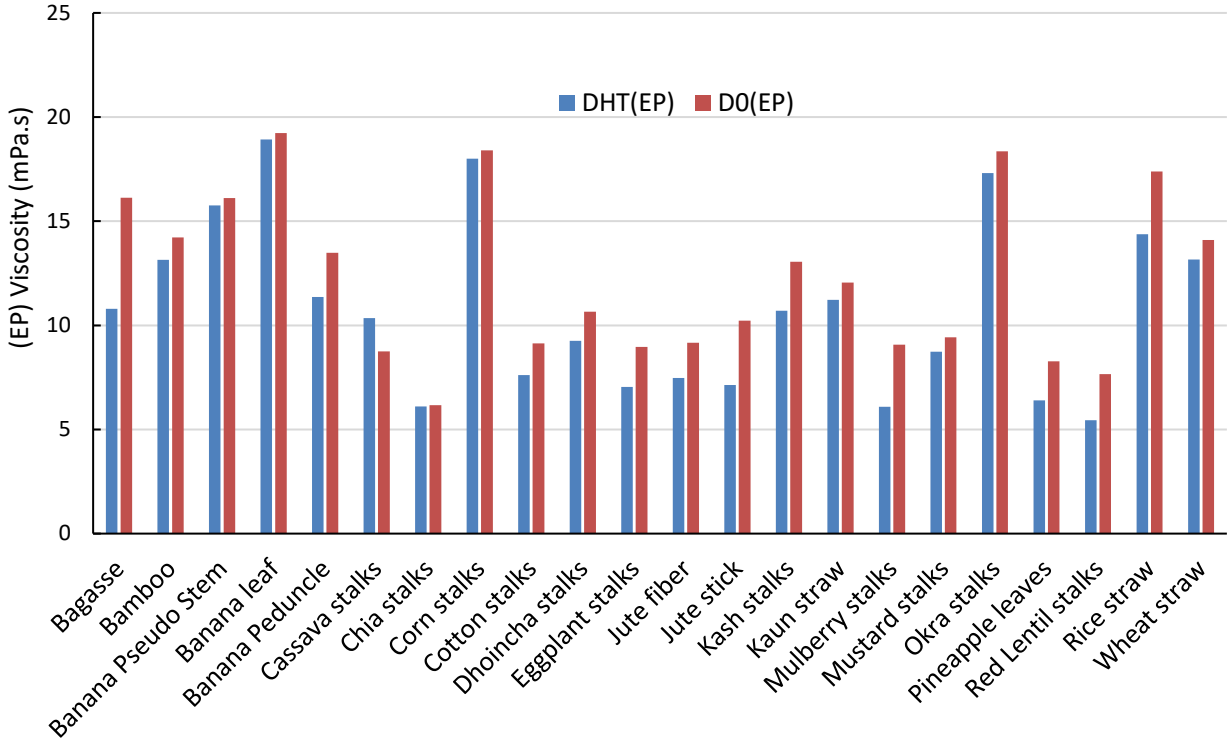

Figure 6.3. Effect of high temperature (D_{HT}) delignification on viscosity after EP stage

As shown in Table (Appendix III), oxygen delignification reduced pulp viscosity insignificantly. The highest and lowest (EP) pulp viscosity was for banana leaf and chia pulp, respectively. There was no significant change in post extraction pulp viscosity after D_{HT} bleaching. As for example, Figure 6.3 shows that the pulp viscosity of oxygen delignified banana leaf pulp decreased from 19.23 mPa.s in D_0 process to 18.93 mPa.s in D_{HT} process only. No change of pulp viscosity was observed for chia pulp. But other studied showed that the $D_{HT}E$ treatment at 95°C for resulted in significant drop in post extraction pulp viscosity as compared to the DE one [11,28]. Pulp exposed to high time/temperature reaction and acid pH may undergo slight carbohydrate hydrolysis. The significant viscosity loss is related to the hot acid hydrolysis of the carbohydrates with the 2.5 pH conditions [28].

6.3.2. $D_{HT}(EP)D_1$ and $D_0(EP)D_1$ pulp properties

The impact of D_0 and D_{HT} process on the final pulp brightness and viscosity of twenty-two non-wood plant pulps are shown in Table (Appendix IV). A lot of variation of bleachability among these twenty-two non-wood plant pulps was observed. Wheat straw pulp showed the highest final pulp brightness. At kappa factor 0.15, final pulp brightness of oxygen delignified was 90.17% in D_0 process, which increased to 91.30% in D_{HT} process. As in initial and $D_0/D_{HT}(EP)$ low brightness, there was no improvement of final pulp brightness for banana pseudo stem pulp. The final brightness reached to 44% only at the highest ClO_2 charge. Dhaincha, eggplant plant, jute fiber and jute tick pulps also showed good bleachability. The oxygen delignified eggplant stalks pulp also showed good beachability. At kappa factor 0.25, the final brightness of eggplant stalks oxygen delignified pulp reached to 82.24% in D_0 process, while the same brightness was obtained at kappa factor of 0.15 in D_{HT} process and saved 40% ClO_2 in the first stage. Kumar et al. showed that the use of D_{HT} reduced 15% ClO_2 requirement and improved the brightness and brightness stability in comparison with the reference sequences D_0 [1].

Final pulp viscosity was also shown in Table (Appendix IV). The final pulp viscosity was related to the entering viscosity of pulp of unbleached. Chia plant and lentil stalks showed the lowest final pulp viscosity of 5-7 mPa.s, where pulp viscosity entering into the bleaching system was 10-12 mPa.s. The viscosity loss represented pulp cellulose degradation, which represents papermaking properties.

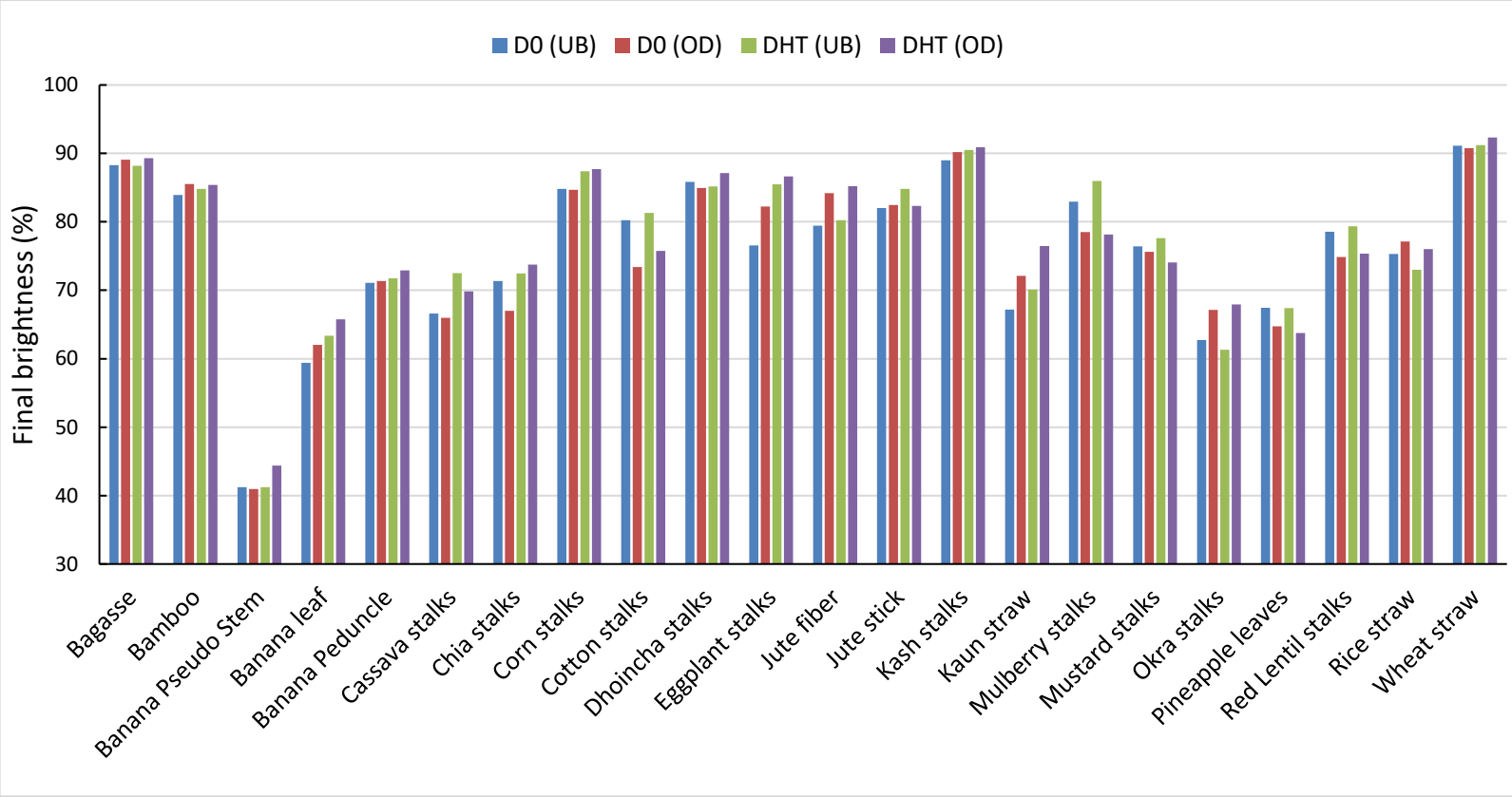

Figure 6.4. Effect of D_{HT} delignification on brightness after final stage of bleaching

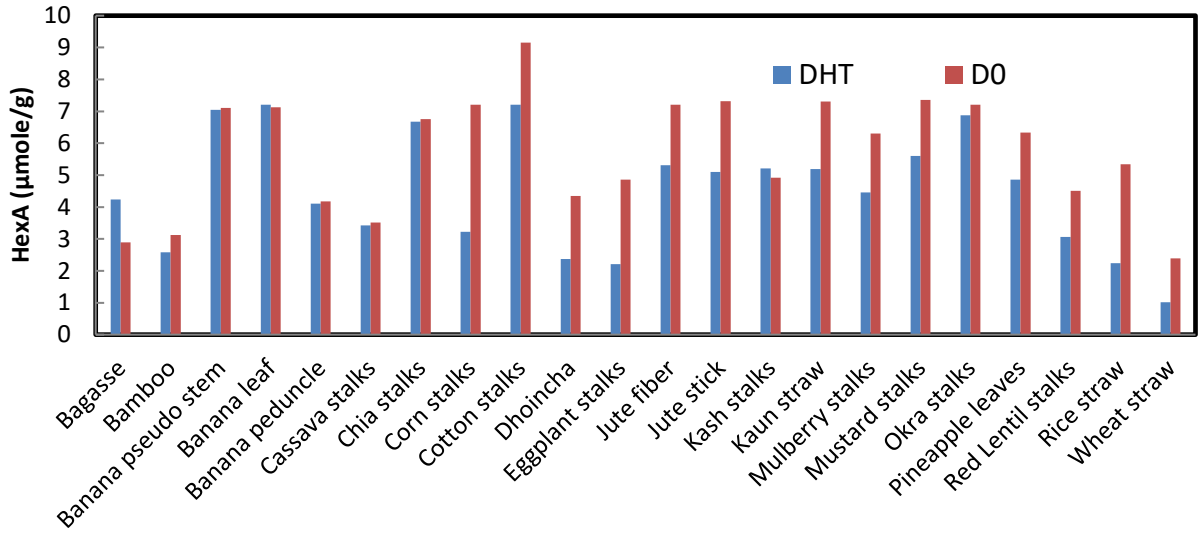

Figure 6.5. Effect of D_{HT} delignification on HexA content in final bleached pulp

The effect of the D_{HT} on the residual HexA of final pulps (oxygen delignified) was also studied and shown Figure 6.5. The residual HexA content in most of the D_{HT} bleached pulps was much less than the D_0 pulps. Banana pseudo stem, banana leaf, banana peduncle, chia plant and cassava plant pulps did not show significant differences in HexA contents between D_0 and D_{HT} in final pulps. This result reflected in final pulp brightness. At kappa factor, 0.2, the residual HexA contents were 1.02, 2.37, and 5.31 µmol/g for D_{HT} pulps and 2.39, 4.34 and 7.21 µmol/g for D_0 pulps from wheat straw, dhaincha and jute fiber pulps, respectively. This is cause of degradation of HexA in D_{HT} process [30]. HexA could not react with chlorine dioxide, but react with its intermediates such as hypochlorous acid and molecular chlorine, thereby influencing the bleachability and enhancing the consumption of chlorine dioxide [31-32]. Percentage of HexA removal in D_{HT} process showed a linear relationship with final pulp brightness (Figure 6.6). The HexA removal in banana pseudo stem pulp was only 35%, consequently showed the lowest pulp brightness (44%) among these twenty-two non-wood pulps. On the other hand, the highest HexA removal was 96% for dhaincha pulp, where final pulp brightness was 86%.

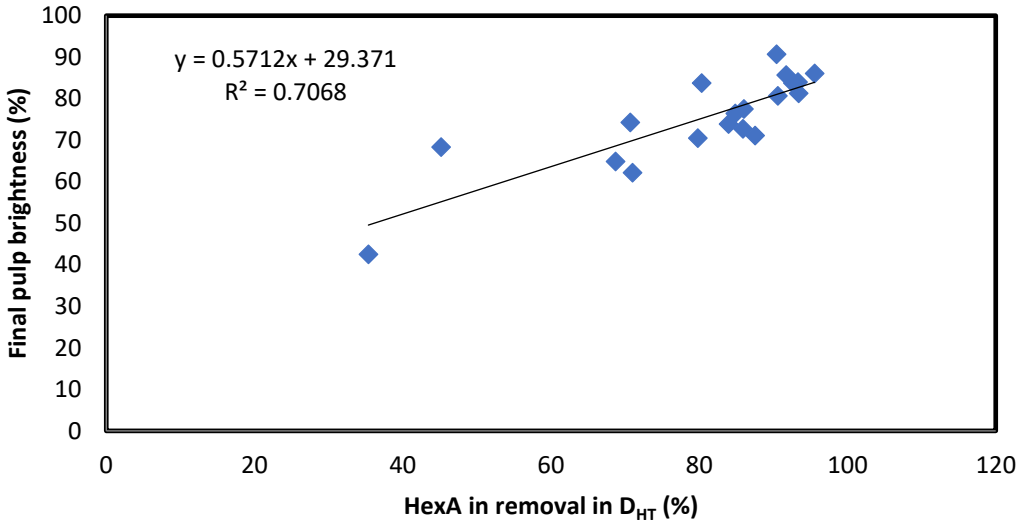

Figure 6.6. Removal of HexA content in D_{HT} delignification and final pulp brightness

6.3.3. COD in bleach effluent

The environmental impact of twenty-two non-wood plants pulps bleaching by D_0 and D_{HT} processes were investigated. As shown in Figure 6.7, the COD value of combined effluent from D_0, (EP) and D_1 stage in $D_{HT}(EP)D_1$ bleaching was lower than $D_0(EP)D_1$. Oxygen delignified pulp had always lower COD load in effluent. The ClO_2 charge in D_0/D_{HT} stage of oxygen delignified was certainly lower as kappa number was lower, thus released less organic material from the pulp to the filtrate and resulted lower COD load. Similar results were also observed in ECF bleaching by [23]. As an example of bamboo pulp, the D_{HT} process at kappa factor 0.2 decreased COD value from 652.92 mg/l to 443.9 mg/l for unbleached pulp and from 479.04 mg/l to 323.72 mg/l for oxygen delignified pulp. Similar COD value reduction in other reported data are available [2,33]. Rolf et al. showed that the amount of dissolved organics, represented by COD was proportional to kappa number of unbleached pulp for wood and non-wood pulps [34]. But at a given kappa number, the amount of COD was much higher for the non-wood pulp.

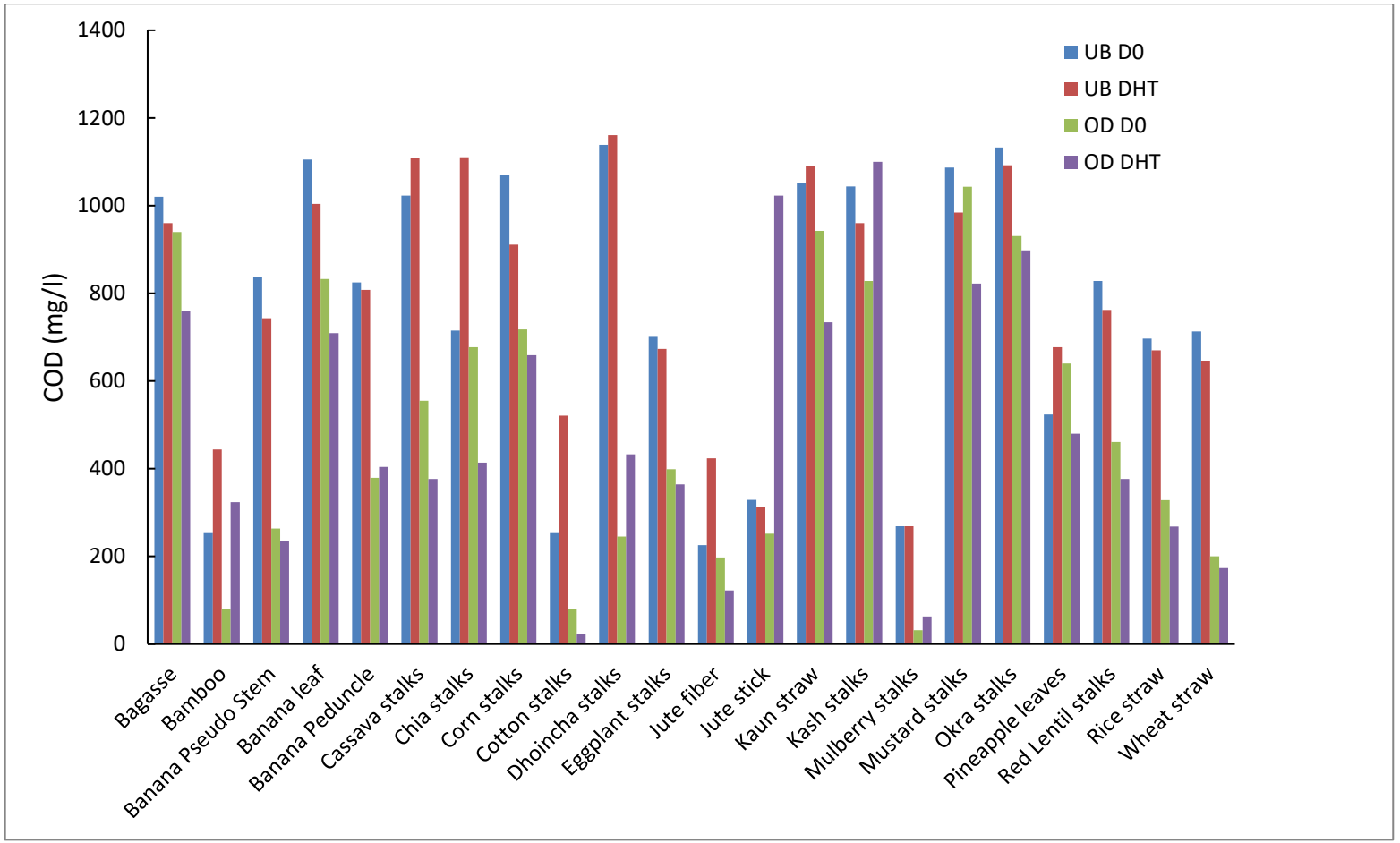

Figure 6.7. COD values (mg/l) of bleach effluents from twenty-two non-wood plant pulps

6.4. Conclusions

A lot of variation of bleachability among these twenty-two non-wood plant pulps was observed. Bleaching of soda-AQ pulps at high temperature (D_{HT}) produced pulp of lower kappa number and higher brightness than D_0 after the extraction stage. Brightness reached upto 90% for wheat straw, corn stalks, kash stalks and bagasse after D_{HT} delignification. HexA content in the final bleached pulp in D_{HT} delignification was lower than those of D_0 which resulted higher final brightness. Percentage of HexA removal in D_{HT} process showed a linear relationship with final pulp brightness. The oxygen delignified pulp and D_{HT} delignification discharged lower COD bleaching effluent water.

6.5. References

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CHAPTER 7

MATHEMATICAL MODELLING

7.1. Introduction
7.2. Materials and Methods
7.3. Results and discussion
7.3.1. Relationship of pulp yield and kappa number with chemical properties
7.3.2. Relationship of papermaking properties with morphological properties
7.4. Conclusions
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7.1. Introduction

Pulp yield is the one of the most important factor for the selection of a pulping raw material. Pulp yield has also been related to the lignin and polysaccharide contents of eucalypt woods [1]. Many studies have been carried out to correlate cellulose content of woods with pulp yields. Dillner et al. found that kraft pulp yields of *E. globulus* wood were well correlated with cellulose contents [2]. Wallis et al showed that wood samples with high cellulose content gave higher pulp yield [1].

Cohen and Mackney established significant correlations between wood chemical properties and the properties of pulps derived from the woods under fixed conditions [3]. Holocellulose gives a weak positive correlation with pulp yield [4]. Stewart et al showed that the kraft pulp yields of *E. regnans* samples were dependent on their lignin and pentosan contents [5]. Batchelor et al observed that kraft pulp yields of mixed eucalypt woods were well correlated with a combination of lignin, pentosan, and extractives [6].

The successful conversion of pulp into paper of required quality depends on the original fibre characteristics and the response of the fibre to the processing variables. Pulp fibers are the basic network in the paper sheet. It contributes to the basic strength of the paper. Fibers are long narrow cells with tapering ends and central canals known as lumen. The fibers depending upon origin differ significantly. The physical properties of paper differ from one species to another due to great variety of wood types. To evaluate the quality of raw materials, morphological characteristics of fibers and their derived values are of great importance. Such characteristics are length, diameter, cell wall thickness, lumen size, and the derived morphological values are runkel ratio, flexibility coefficient, slenderness ratio etc. [7]. Oluwafemi and Sotannde found that the cell-wall thickness and fibre length had the greatest influence on the strength properties of the unbeaten pulp [7]. Dinwoodie summarized that the principal fiber factors, such as fiber density, fiber length, and fiber strength controlled the strength properties of paper [8].

Wangaard and Woodson observed a positive influence on both breaking length and burst at a given level of sheet density fiber strength and fiber length [9].

All these studies were carried out on hardwood and softwood species. There is no report available on non-wood from multiple species.

Therefore, the present study seeks to correlate the chemical composition and morphological properties of 22 non-wood samples with the yields and papermaking properties. The correlation of papermaking properties with fiber quality of chemical pulps was also established.

The successful prediction of pulp yield and papermaking properties provides an opportunity of selecting raw material. No need to undertake time consuming and expensive pulping trials of many samples may be significantly reduced.

7.2. Materials and Methods

7.2.1. Raw materials

The twenty-two samples were cooked by soda-AQ process and the chemical and morphological characterization data (Table 3.1 and 3.3), the pulp yield and kappa number data (Figures 5.1 and 5.2.), and the prepared paper sheet evaluation data (Appendix II) were used for mathematical correlation**.**

7.2.2. Model development method

Pearson Correlation coefficients among Klason Lignin (%), acid soluble lignin (%), holocellulose (%), α-cellulose (%), kappa number and yield were computed first to assess the association between these parameters. The significance of correction coefficients was tested with 2-tailed t-test at 1% and 5% level of significance.

Next, linear regression models have been developed keeping yield and kappa number as dependent variables and Klason lignin (%), acid soluble lignin (%), holocellulose (%), α-cellulose (%) as independent variables. Coefficients of multiple determination (R^2) have been

calculated for each model which express how much the independent variables can express the total variation in the dependent variable in the model. R^2 varies from 0 to 100%.

For calculation of correlation coefficients and developing linear regression models, Statistical software, SPSS of its version 22.0 has been used.

7.3. Results and discussion

7.3.1. Relationship of pulp yield and kappa number with chemical properties

Table. 7.1. Correlation between pulp yield and kappa number with chemical characteristics

	Klason Lignin (KL) (%)	Acid Soluble Lignin (ASL) (%)	Holocellulose (%)	α- cellulose (%)	Kappa Number (KN)	Pulp yield (PY)
Klason Lignin (%)	1	-.206	.153	.038	.167	-.106
Acid Soluble Lignin (%)	-.206	1	-.376	-.420	.178	-.133
Holocellulose (%)	.153	-.376	1	.505*	-.378	.775**
α-cellulose (%)	.038	-.420	.505*	1	-.267	.359
Kappa Number (KN)	.167	.178	-.378	-.267	1	-.404
Pulp yield (PY)	-.106	-.133	.775**	.359	-.404	1

*. Correlation is significant at the 0.05 level (2-tailed)
**. Correlation is significant at the 0.01 level (2-tailed)

PY= -39.462-0.614* KL (%) +1.985*ASL (%) + 1.340*Holocellulose (%)-0.008*αcellulose (%)

……(1)

(R^2=0.819, Adjusted R^2=0.671)

KN= 44.129+054* KL (%) +1.895*ASL (%)-0.591*Holocellulose (%)-0.032*α-cellulose (%)

……(2)

(R^2=0.427, Adjusted R^2=0.183)

Cellulose content is strongly correlated with pulp yield and can therefore be used as an indirect measure of it. The chemical characteristics of twenty-two non-woods were determined and used these data to determine correlation with pulp yield and kappa number by multiple

regression analysis [1,9]. Equation 1 shows the relationship between unbleached pulp yield and chemical characteristics. Holocellulose shows a positive correlation with pulp yield and klason lignin was negatively correlated with the pulp yield (Eq 1). Similarly, Wallis et al. showed that the total carbohydrates of E. globulus wood samples were positively well correlated with pulp yield and lignin was negatively correlated [1]. Figures 7.1 and 7.2 show correlation of pulp yield with holocllulose and α-cellulose, respectively. The R^2 was 74.5% for holocellulose and 56.9% for α-cellulose. Kien et al. studied on the effectiveness of cellulose content, as a selection criterion in breeding programs for kraft pulp yield in *Eucalyptus urophylla* [10]. The regression of pulp yield of disk samples on cellulose content was strong. A lower correlation can be explained by heterogeneous non-woods with a lot of variation in anatomical properties (Table 3.3).

Equation 2 shows the multiple linear regression of KL (%), ASL (%), holocellulose (%) and α-cellulose (%) on kappa number, and the independent variables express 42.7% of the total variation on the dependent variable. Klason lignin and acid soluble lignin was a positive influence on kappa number. The predictive efficiency of the linear regression of kappa number involving klason lignin was accounted 31% only (Figure 7.3).

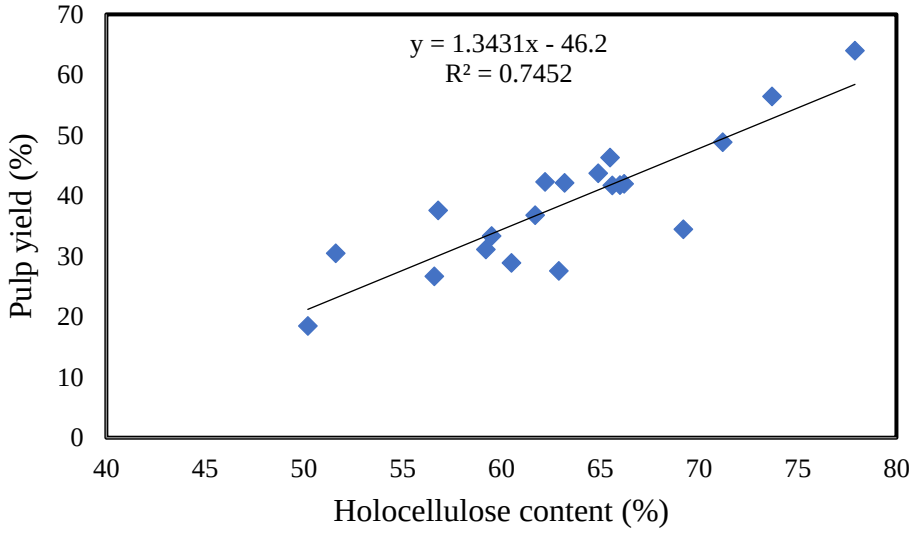

Figure 7.1. Relationship between holocellulose and pulp yield

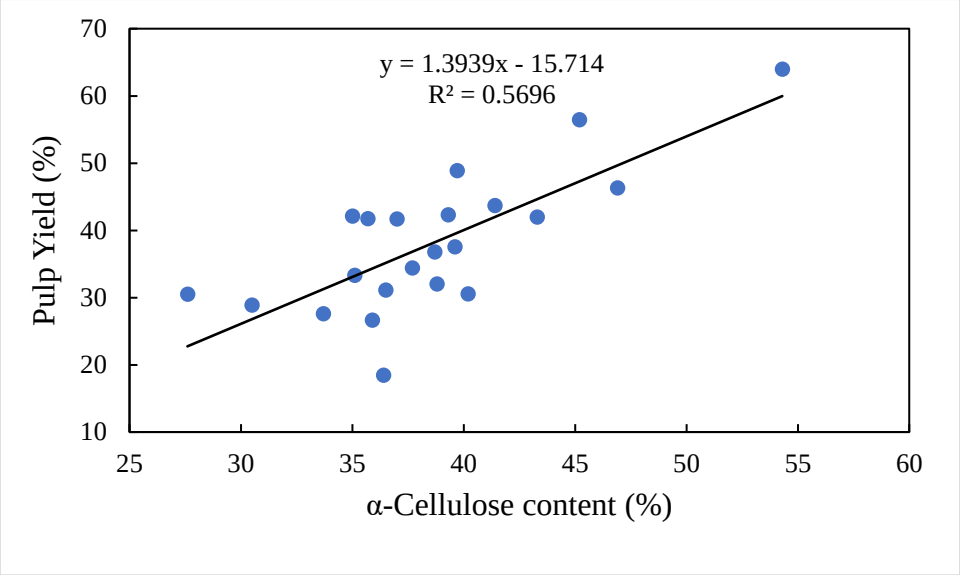

Figure 7.2. Relationship between α-cellulose and pulp yield

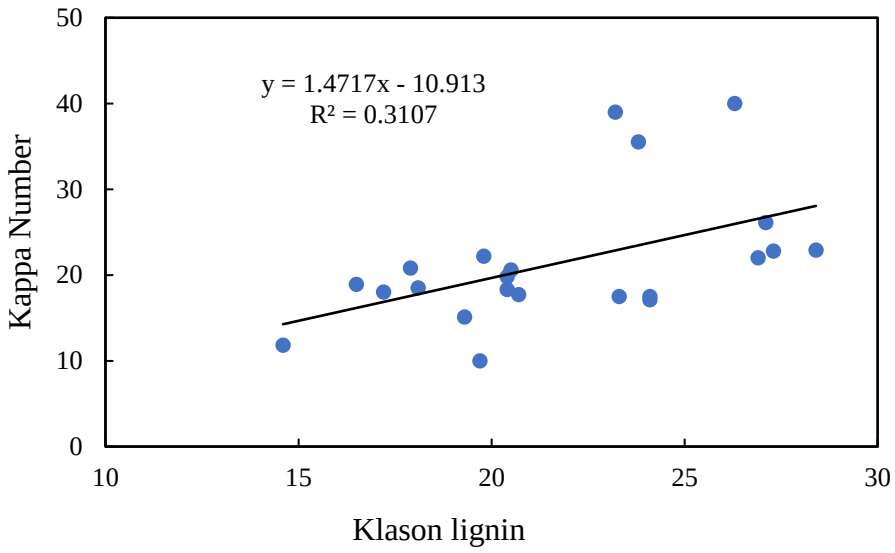

Figure 7.3. Relationship between Klason lignin and kappa number

7.3.2. Relationship of papermaking properties with morphological properties

Table 7.2: Correlation between papermaking properties and morphological properties

	FL	FW	WT	SR	RR	FC	UTenI	TenI	UBI	BI	UTI	TI
FL	1	.116	-.247	.806**	-.160	.254	.267	.407	.668**	.574*	.612**	.399
FW	.116	1	-.430	-.429	-.650**	.739**	-.171	-.205	-.192	-.243	-.022	.124
WT	-.247	-.430	1	.024	.856**	-.814**	-.294	-.251	-.330	-.284	-.198	-.254
SR	.806**	-.429	.024	1	.217	-.196	.375	.461	.694**	.660**	.548*	.310
RR	-.160	-.650**	.856**	.217	1	-.954**	-.101	-.152	-.072	-.112	-.115	-.174
FC	.254	.739**	-.814**	-.196	-.954**	1	.113	.191	.120	.177	.191	.266
UTenI	.267	-.171	-.294	.375	-.101	.113	1	.776**	.712**	.728**	.265	.356
TenI	.407	-.205	-.251	.461	-.152	.191	.776**	1	.666**	.860**	.563*	.577*
UBI	.668**	-.192	-.330	.694**	-.072	.120	.712**	.666**	1	.836**	.740**	.618**
BI	.574*	-.243	-.284	.660**	-.112	.177	.728**	.860**	.836**	1	.699**	.680**
UTI	.612**	-.022	-.198	.548*	-.115	.191	.265	.563*	.740**	.699**	1	.822**
TI	.399	.124	-.254	.310	-.174	.266	.356	.577*	.618**	.680**	.822**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

UTenI- Unrefined tensile index, TenI-Refined tensile index, UBI-Unrefined burst index, BI-Burst index, UTI-Unrefined tear index, TI-Refined tear index, WT-Wall thickness, FL-Fiber length, FW-Fiber width, SR-Slender ratio, RR-Runkel ratio, FC-Flexibility Coefficient

UTenI = -16.344 - 20.721*FL + 0.020 *FW - 11.593*WT + 0.389*SR + 42.524*RR + 0.918*FC

…..……(3)

(R^2=0.570, Adjusted R^2=0.325)

TenI = - 26.920 - 0.862*FL - 1.772*FW + 0.773*WT + 0.144*SR + 33.193*RR + 1.53*FC

…..……(4)

(R^2=0.659, Adjusted R^2=0.435)

UBI = -0.512 + 0.7162*FL - 0.056*FW - 1.117*WT + 0.010*SR + 3.271*RR + 0 .049*FC

…..……(5)

(R^2=0.811, Adjusted R^2=0.658)

BI = -7.603 - 0.895*FL - 0.102*FW - 0.310*WT + 0.032*SR + 4.862*RR + 0.159*FC

…..……(6)

(R^2=0.822, Adjusted R^2=0.675)

UTI = -7.499 + 1.659*FL - 0.104*FW + 0.030*WT + 0.019*SR + 4.725*RR + 0.160*FC

…..……(7)

(R^2=0.655, Adjusted R^2=0.428)

TI = - 8.242 - 1.248*FL + 0.050*FW - 0.594*WT + 0.034*SR + 6.603*RR + 0.159*FC

…..……(8)

(R^2=0.526, Adjusted R^2=0.277)

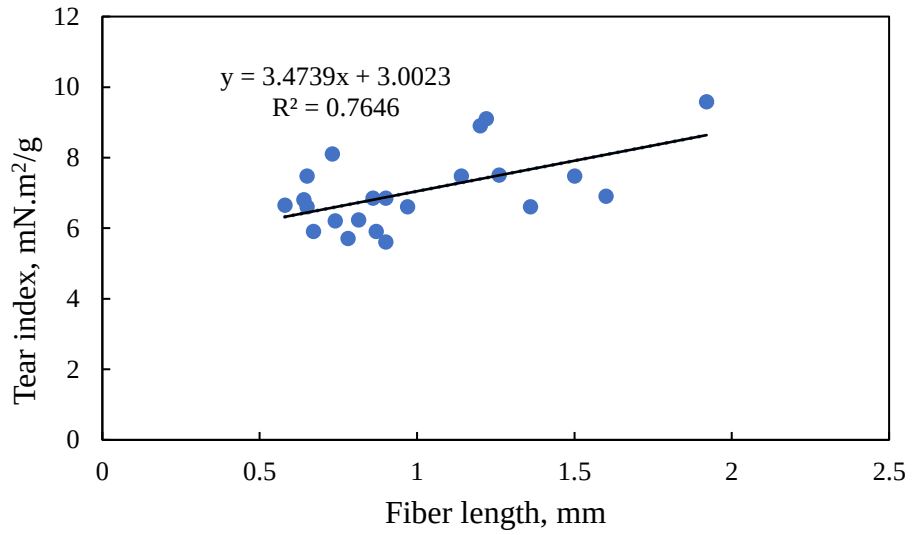

Figure 7.4. Relationship between fiber length and tear index of unrefined pulp

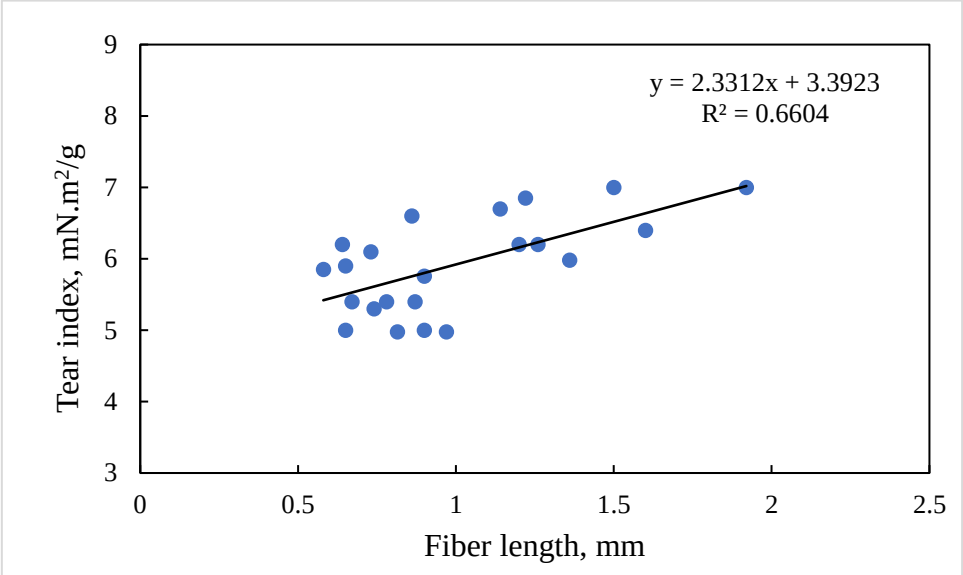

Figure 7.5. Relationship between fiber length and tear index of refined pulp

The papermaking properties of final products depend on the original fibre characteristics and the response of the fibre to the processing variables. The slenderness of the fiber is obtained by the length to width ratio. Solid mass of fiber depends on fiber cell wall. The central cavity in the fiber is known as fiber lumen which is void. Pulp refining depends on the fiber wall thickness and lumen. Fibers with thin cell walls collapse readily. Therefore, importance of the fiber wall on properties of paper had been recognized. The pulps obtained from thin-walled and wide lumen fibers give dense and well bonded sheets and those from thick wall give bulky sheets with high tearing resistance [12].

Tensile and bursting strengths of pulps are two properties highly dependent upon fiber-to-fiber bonding [13]. The tensile index of the unrefined pulp had no correlation with fiber length, while the tensile index of refined pulp showed positive correlation (Figure 7.3). Fiber length was the dominant factor for burst and tensile strength in the unbeaten state [14]. Wangaard and Woodson obtained positive influence on both breaking length and burst pulp from slash pine at a given level of sheet density with fiber strength and fiber length. Regressions for breaking length and burst factor accounted for 88 and 90%, respectively [9]. As shown in Eq 3, the multiple regression analysis of tensile index involving these variables accounted for 57% and 66% for unrefined and refined pulps, respectively. Slender ratio, runkel ratio and flexibility coefficient had a positive influence on tensile index of both refined and unrefined pulps.

Tear index of both refined and unrefined pulp was shown to be related directly to fiber length. The predictive efficiency of the regression model was 76.5% (Figure 7.4) and 66% (Figure 7.5) for unrefined and refined pulps, respectively. Horn (1978) showed that tearing strength of sheets made from either unbeaten ($r = 0.817$) or beaten ($r = 0.832$) hardwood fiber was principally dependent upon fiber length. Labosky and Ifju (2007) also found that tear factor was highly correlated with the relative position of loblolly pine wood, which varied fiber length [15]. The lower correlation in present experiment can be explained by different non-wood

species, which are heterogeneous in anatomical properties. Therefore, multiple factors affect in strength properties.

Early research belief that paper desirable strength properties could only be made from long-flbered wood species-i.e., softwood pulps [16-18]. Some research results shown that fiber length possibly were not the dominant factor in producing paper with acceptable strength [14,19-20].

Generally, bursting and tensile strengths of hand sheets made from hardwoods respond to the same fiber morphological effects as do softwoods. But non-wood pulp behaves differently. As for example, straws, banana waste fibers corn stalks etc. contains high amounts of fines, consequently, increased bonding potential at the unrefined state and exhibited higher tensile and burst index. Therefore, multiple factors affect bond depended paper properties in different non-wood pulps.

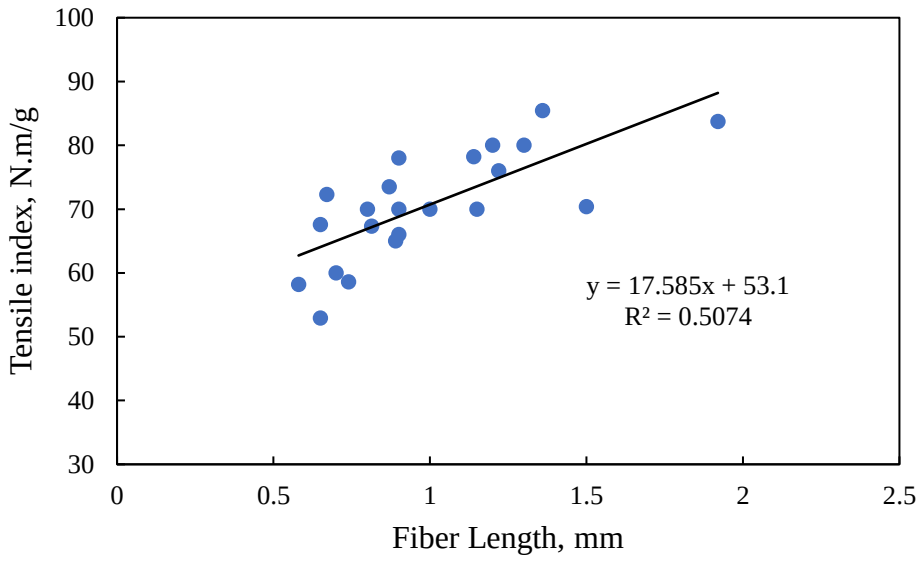

Figure 7.6. Relationship between tensile index (N.m/g) and fiber length (mm)

Table 7.3. Correlation between papermaking properties with pulp fiber quality

	Fines	Curl Index	Kink Index	Fibrillation	Coarseness	UTenI	TenI	UBI	BI	UTI	TI
Fines	1	.486*	.559*	-.069	-.005	.248	-.134	.384	-.009	.336	-.380
Curl Index	.486*	1	.858**	.114	.222	.234	.258	.492*	.465*	.188	.068
Kink Index	.559*	.858**	1	.236	.252	.146	-.049	.365	.168	.255	-.330
Fibrillation	-.069	.114	.236	1	.251	-.034	-.285	-.121	-.234	-.233	-.340
Coarseness	-.005	.222	.252	.251	1	.255	.252	.018	.026	-.091	-.244
UTenI	.248	.234	.146	-.034	.255	1	.616**	.715**	.626**	.368	-.077
TenI	-.134	.258	-.049	-.285	.252	.616**	1	.539*	.873**	.322	.551*
UBI	.384	.492*	.365	-.121	.018	.715**	.539*	1	.749**	.721**	.136
BI	-.009	.465*	.168	-.234	.026	.626**	.873**	.749**	1	.496*	.520*
UTI	.336	.188	.255	-.233	-.091	.368	.322	.721**	.496*	1	-.077
TI	-.380	.068	-.330	-.340	-.244	-.077	.551*	.136	.520*	-.077	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).
UTenI-Unrefined tensile index, TenI-Refined tensile index, UBI-Unrefined burst index, BI-Burst index, UTI-Unrefined tear index, TI-Refined tear index

UTenI = 32.170 + 0 .215* Fines + 93.994* Curl Index - 8.199* Kink Index - 0.690* Fibrillation +85.978*Coarseness……..(9)

(R^2 = 0.419, Adjusted R^2 = 0.175)

TenI = 80.868 - 0.156* Fines + 283.637* Curl Index - 18.985* Kink Index -7.237* Fibrillation +105.937* Coarseness……..(10)

(R^2 = 0.704, Adjusted R^2 = 0.495)

UBI = 1.478-0.013* Fines + 12.249* Curl Index - 0.431* Kink Index -0.186* Fibrillation - 0.632* Coarseness……(11)

(R^2 = 0.558, Adjusted R^2 = 0.311)

BI = 4.620-0.016* Fines + 25.591* Curl Index - 1.157* Kink Index - 0.457* Fibrillation - 0.38* Coarseness……..(12)

(R^2 = 0.695, Adjusted R^2 = 0.483)

UTI = 5.732 + 0.027* Fines - 9.984* Curl Index + 1.620* Kink Index - 1.167 * Fibrillation - 4.710* Coarseness…….(13)

(R^2 = 0.447, Adjusted R^2 = 0.20)

TI = 13.814 -.077* Fines + 80.615* Curl Index - 5.743* Kink Index - 1.138* Fibrillation - 15.95* Coarseness……..…….(14)

(R^2 = 0.849, Adjusted R^2 = 0.702)

Pulp fines, curl and kink index, external fibrillation and coarseness were measured in unrefined pulp and developed a multiple regression with papermaking properties. As shown from Eq. 9, multiple regressions of tensile index of unrefined with pulp fines, curl and kink index, external fibrillation, coarseness have the predictive efficiency of 41.9%, while the same for refined pulp was 70.4% (Eq 10). Similarly, multiple regression for burst index were 55.8% (Eq 11) and 69.5% (Eq 12) and for tear index were 44.7% (Eq 13) and 84.9% (Eq 14) for unrefined and refined pulps respectively. Equations 11-14 show that the fiber coarseness had negative effect on tear and burst index in both refined and unrefined pulps.

Pulp fines increase wet web strength, leading to denser and better bonded sheet [21]. These 22 non-wood pulps contain a wide variation of fines, 16.1% in dhaincha to 66.8% in banana leaf pulp. Fines consist mainly of cellulosics such as ray cells, vessel fragments, and broken cell wall material. Fines can play a determining role in many surface related interactions before sheet consolidation and they also affect final sheet properties. Eq. 9 showed positive influence of tensile index of unrefined pulp with pulp fines, while refined pulp showed negative influence. There is general agreement in the literature that primary fines contribute negligibly to sheet bonding [22-24]. Fines from kraft and recycled paper are quite effective, while those from TMP are ineffective in increasing hand sheet density, breaking length, and burst index.

Different non-wood fines behave quite differently, some of them facilitated fiber bonding and some of them were not. Therefore, the fibre coarseness influence virtually all pulp properties — drainage, wet-web strength, and the structural, strength, and optical properties of the dry sheets. Equations 11-14 show that fiber coarseness had a positive impact on tensile index and negative impact on burst and tear indexes. Seth (1990) explained on the basis that coarser fibres have thicker walls, are fewer per unit pulp mass, and have smaller specific surface area [25]. Retulainen (1996) observed a strong dependence of light scattering coefficient of paper on fibre coarseness [26].

7.4. Conclusions

A mathematical correlation of the chemical composition and morphological properties of twenty-two non-wood samples with the yields and papermaking properties for soda-AQ pulps was evaluated. The correlation of papermaking properties with fiber quality of chemical pulps was also established. Multiple regression equations involving non-wood characteristics and their morphological indices were determined to predict the pulp-sheet properties of non-wood at unrefined and refined state. Holocellulose and α-cellulose had a positive and lignin had a negative effect on pulp yield. Lignin content showed positive effect on kappa number. The fibre length had the greatest influence on the strength properties of the unbeaten pulp. Pulp fiber quality from a multiple heterogeneous raw material could not predict papermaking properties.

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CONCLUSIONS

In this study twenty-two crops residues were evaluated in organic acid and soda anthraquinone pulping. The α-cellulose contents in these samples were acceptable to consider these as pulping raw materials. Most of the crops residues was high in ash content, which was challenging to use those as pulping raw material. The morphological and anatomical characterization showed that all of the non-woods contain fibrous as well as non-fibrous components. The non-fibrous components included parenchyma, vessel and epidermal cells. The presence of non-fibrous components directly affected the quality and recovery of cooking chemicals. The ground tissue consisted of parenchyma cells, which are large, barrel-shaped and thin-walled leading to create problems in drainage. When the thin wall and poorly lignified parenchyma cells were plugged into sheets, they impaired drainage and easily flattened during refining causing further drainage problems.

Considering the high silica content in crops residue, formic acid pulping was assessed in this study. The formic acid concentration had a remarkable effect on the delignification of crops residues. Peroxyformic acid treatment reduced the residual lignin remarkably. Pulp yield after peroxyformic acid treatment was better than the soda-AQ pulp. Organic acid pulps from bagasse, bamboo, rice straw, wheat straw, banana peduncle, okra plant and corn stalks showed comparatively good bleachability in two stages alkaline peroxide bleaching. Crops residues generated very high amount of fines in organic pulping. A good tensile index of most of the bleached pulp was observed, while tear and burst index suffered. Considering all parameters, especially pulp yield, delignification, papermaking properties and bleachability, kash and banana peduncle showed the best raw materials for organic acid pulping.

In the soda-anthraquinone pulping of twenty-two crops residues, it was found that at very low alkali charge (~12-16%), the pulping operation lowered the kappa value of the individual non-

wood pulp which indicted high delignification of the pulps. The pulp yield reached upto 64.4% for jute pulp, followed by dhaincha 48.9% and bamboo 46.3%, while the kappa values were 4.9 for jute, 7.4 for dhaincha and 7.5 for rice straw. It was observed that the tensile and burst index of produced papers increased with increasing beating degree, while tear index decreased. Dhaincha stalks pulp exhibited the highest tensile index at any ^{o}SR followed by bagasse pulp. A good tensile index of these pulps in the unbeaten state can be explained by higher external degree of fibrillation, which facilitates fiber bonding. Similar behavior of tensile, tear and burst index relationship with ^{o}SR was observed for all other non-wood raw materials also.

A lot of variation of bleachability among these twenty-two non-wood plant pulps was observed. High temperature (D_{HT}) delignification produced pulp of lower kappa number and higher brightness than normal temperature (D_0) after extraction stage. Hexenuronic acid (HexA) content in the final bleached pulp in D_{HT} delignification was lower than those of D_0, resulted higher final brightness. Percentage of HexA removal in D_{HT} process showed a linear relationship with final pulp brightness. The oxygen delignified pulp and D_{HT} delignification discharged lower COD.

Considering all parameters, especially pulp yield, delignification, papermaking properties and bleachability, dhaincha, kash and banana peduncle showed the best raw materials for organic acid pulping. For soda-AQ pulping, the beast results were found for jute, dhaincha, bamboo, kash and bagasse.

Finally, a mathematical correlation of the chemical composition and morphological properties of 22 non-wood samples with the pulp yields and papermaking properties for soda-AQ pulps was evaluated. The correlation of papermaking properties with fiber quality of chemical pulps was also established. Multiple regression equations involving non-wood characteristics and their morphological indices were determined to predict the pulp-sheet properties of non-wood at unrefined and refined state. Holocellulose and α-cellulose had a positive and lignin had a

negative effect on pulp yield. Lignin content showed positive effect on kappa number. The fibre length had the greatest influence on the strength properties of the unbeaten pulp. Pulp fiber quality from a multiple heterogeneous raw material could not predict papermaking properties.

APPENDIX I

Table. Soda-AQ pulping of crops residue.

SL	Raw materials	NaOH charge (%)	Yield (%)			Kappa number	SL	Raw materials	NaOH charge (%)	Yield (%)			Kappa number
			Screened	Reject	Total					Screened	Reject	Total	
1.	Bagasse	14	36.11	9.83	45.94	33.43	7.	Chia plant	14	15.61	18.33	33.94	69.9
		16	40.65	4.17	44.82	26.22			16	9.21	34.17	43.38	83.29
		18	31.69	0.83	32.52	19.84			18	29.2	3.83	33.03	55.16
		20	40.55	0.33	40.88	14.44			20	28.57	0.33	28.9	38.96
2.	Bamboo	12	54.97	26.17	81.14	45.48	8.	Corn stalks	12	32.82	0.5	33.32	9.95
		14	52.54	16.0	68.54	33.45			14	31.84	0.33	32.17	4.32
		16	46.29	7.83	55.12	24.68			16	32.1	0.17	32.27	8.67
		18	48.62	6.67	55.29	20.79			18	27.61	0.08	27.69	7.61
3.	Banana pseudo stem	12	33.17	1.67	34.84	42.6	9.	Cotton plant	14	12.56	42.33	54.89	73
		14	33.33	0.83	34.16	33.99			16	17.29	31.67	48.96	72.86
		16	30.22	0.33	30.55	17.06			18	21.36	24.0	45.36	62.79
		18	29.99	0.83	30.82	17.06			20	32.74	9.0	41.74	50.15
4.	Banana leaf	14	39.84	11.05	50.89	37.68	10.	Dhaincha	12	21.78	38.0	59.78	47.7
		16	36.79	20.78	57.57	45.4			14	36.05	18.33	54.38	24.31
		18	35.77	11.85	47.62	31.29			16	49.10	0.83	49.93	25.31
		20	34.55	9.15	43.7	17.74			18	48.86	0	48.86	7.50
5.	Banana peduncle	14	-	-	-	-	11.	Eggplant stalks	12	18.49	29.7	48.19	8.0
		16	-	-	-	-			14	29.56	14.4	43.96	11
		18	35.67	11.8	47.47	38.13			16	33.21	8.9	42.11	17.5
		20	40.44	16.0	56.44	36.56			18	27.77	11.6	39.37	6.8
6.	Cassava stalks	14	-	-	-	-	12.	Jute	12	64.24	0	64.24	11.82
		16	-	-	-	-			14	63.97	0	63.97	7.32
		18	17.38	1.33	18.71	36.57			16	64.39	0	64.39	4.92
		20	17.68	0.78	18.46	30.32			18	62.82	0	62.82	6.94

Table. Soda-AQ pulping of crops residue (continuation)

SL	Raw materials	NaOH charge (%)	Yield (%)			Kappa number	SL	Raw materials	NaOH charge (%)	Yield (%)			Kappa number
			Screened	Reject	Total					Screened	Reject	Total	
13.	Jute Stick	14	13.85	41.0	54.85	127.62	18.	Okra plant	14	8.18	39.83	48.01	71.0
		16	26.19	17.67	43.86	62.04			16	9.25	36.33	45.58	66.85
		18	32.86	3.83	36.69	56.30			18	13.11	28.00	41.11	55.0
		20	30.93	0.50	31.43	32.0			20	21.55	16.00	37.55	47.43
14.	Kash	12	43.77	5.0	48.77	41.61	19.	Pineapple plant	12	30.32	0.17	30.49	22.41
		14	44.47	1.16	45.63	25.39			14	26.76	0.33	27.09	23.0
		16	41.31	0.67	41.98	20.44			16	21.64	0.33	21.97	15.44
		18	41.93	0.16	42.09	10.82			18	20.91	0.10	21.01	9.7
15.	Kaun straw	12	29.8	0.8	30.6	18.4	20.	Red Lentil stalks	14	10.60	31.67	42.27	39.29
		14	29.7	0.3	30.0	15.1			16	15.84	20.5	36.34	37.64
		16	28.5	0	28.5	14.2			18	22.15	11.67	33.82	39.12
		18	27.9	0	27.9	9.8			20	27.29	3.83	31.12	35.46
16.	Mulberry stalks	14	15.73	34.0	49.73	35.24	21.	Rice straw	12	31.8	0	31.8	8.5
		16	23.06	24.0	47.06	36.64			14	29.8	0	29.8	7.8
		18	26.66	10.83	37.49	36.64			16	28.1	0	28.1	7.3
		20	27.84	4.17	32.01	40.0			18	27.8	0	27.8	7.4
17.	Mustard stalks	14	14.21	30.17	44.38	80.41	22.	Wheat straw	12	41.4	0.5	41.9	19.9
		16	17.99	32.0	49.99	70.15			14	38.9	0.5	39.4	14.6
		18	28.07	2.83	30.9	46.20			16	38.3	0.2	38.5	13.2
		20	27.09	0.5	27.59	18.52			18	37.4	0	37.4	11.3

APPENDIX II

Table. Paper quality evaluation with beating of soda-AQ pulp

Sample	Beating (Min)	^{0}SR	Tensile index (N.m/g)	Tear index (mN.m^2/g)	Burst index (kPa.m^2/g)	Elongation (%)	TEA (J/m^2)
Bagasse	0	17	59.167±2.471	5.60±0.43	3.41±0.12	3.185±0.289	78.79±11.448
	10	39	75.913±5.983	4.98±1.20	4.28±0.19	3.683±0.584	117.395±25.174
	20	58	83.556±0.72	4.36±0.83	0.504±0.21	4.051±0.242	143.427±10.26
	30	71	80.658±6.409	4.98±0.47	4.93±0.54	3.988±0.584	140.411±32.281
Bamboo	0	10	34.842±1.654	13.69±0.32	0.973±0.	1.348±0.093	17.652±2.198
	20	31	66.799±5.19	14.94±0.25	4.67±1.06	3.384±0.169	91.854±10.557
	30	39	76.489±1.34	14.32±1.04	5.64±5.19	3.374±0.176	104.13±8.768
	45	57	84.48±2.548	14.32±0.29	6.62±0.52	3.879±0.248	133.474±16.936
Banana Pseudo Stem	0	25	44.64±2.685	10.58±0.51	3.59±1.03	3.916±0.313	77.491±9.97
	10	67	71.365±3.312	6.85±0.25	4.93±0.32	4.502±6.350	135.811±15.89
	13	72	76.004±6.366	6.63±0.44	5.16±0.17	5.406±0.732	175.082±36.668
Banana Leaves	0	28	48.74±4.83	8.09±5.19	3.69±5.19	4.66±0.471	99.77±18.765
	10	69	83.704±5.114	6.63±0.61	5.93±0.20	4.959±0.173	166.145±13.445
	15	78	80.78±2.587	4.98±0.74	5.64±0.12	4.862±0.223	158.866±12.368
Banana Peduncle	0	24	48.52±1.903	7.47±0.71	3.11±0.48	3.17±0.419	65.704±12.063
	10	56	69.37±3.022	4.98±0.43	4.54±5.19	4.818±0.402	146.474±17.872
	15	64	70.361±3.679	5.6±0. 0.88	4.23±0.59	4.326±0.693	132.873±28.785
Cassava	0	21	31.758±1.043	4.59±5.19	1.18±1.206	1.832±0.07	23.424±1.510
	10	43	47.705±1.702	4.98±0.21	2.24±0.71	2.596±0.246	52.321±7.808
	15	56	46.623±1.757	4.98±1.206	2.43±0.92	2.688±0.358	53.669±10.655
	20	66	46.963±2.092	4.36±0.712	2.14±1.03	2.929±0.312	58.952±9.312
Chia	0	20	42.695±2.173	5.915±0.514	1.65±0.84	2.084±0.233	36.066±5.671
	10	45	64.795±4.257	4.36±1.043	3.41±0.22	2.696±0.484	72.467±18.831
	15	52	70.681±2.682	3.74±0.49	3.31±1.20	2.961±0.205	85.147±10.036
	20	64	72.619±7.613	3.74±0.32	3.79±0.71	2.891±0.49	86.017±23.97
Corn	0	16	47.233±1.206	6.85±5.19	2.82±0.54	3.249±0.46	64.264±2.82
	10	38	67.189±0.712	4.36±1.20	3.99±1.04	4.268±0.164	119.66±4.898
	15	52	72.787±3.578	4.36±1.20	3.99±1.04	4.379±0.078	133.463±8.346
	20	62	77.958±2.958	4.36±1.20	3.99±1.04	4.467±0.262	146.891±12.522

Table. Paper quality evaluation with beating of soda-AQ pulp (continuation)

Sample	Beating (Min)	^{0}SR	Tensile index	Tear index	Burst index	Elongation	TEA
Cotton	0	14	23.93±0.453	5.6±0.21	0.876±0.14	1.787±0.098	17.59±1.115
	10	31	41.971±3.858	4.98±0.25	2.53±0.82	2.83±0.621	50.483±15.616
	20	47	48.787±2.167	3.74±0.46	3.06±1.01	3.567±0.166	75.218±7.619
	25	57	53.209±4.768	4.39±0.43	3.33±0.35	3.066±0.768	69.766±24.162
Dhaincha	0	18	48.548±2.685	8.09±0.52	2.24±0.73	2.013±0.113	39.148±3.663
	10	31	81.634±7.321	8.09±0.61	4.89±0.69	3.618±0.231	121.359±19.322
	20	42	84.92±3.921	6.63±1.26	5.35±0.14	4.382±0.308	153.41±17.121
	30	53	92.068±4.857	6.63±0.43	5.64±0.36	4.792±0.09	182.135±11.786
Eggplant	0	28	27.99±3.119	6.63±0.62	1.87±0.52	2.801±0.593	27.467±5.82
	10	40	41.188±0.761	6.85±0.11	2.43±0.11	3.362±0.188	61.236±4.109
	15	45	45.492±1.338	6.63±0.47	3.02±0.72	3.803±0.099	77.494±3.665
	20	51	48.569±2.736	6.63±0.514	2.92±0.31	3.509±0.665	75.634±19.975
Jute	0	12	32.246±0.404	2.49±0.21	0.78±1.15	1.091±0.062	12.482±0.761
	10	17	60.282±3.121	16.81±0.38	2.82±0.23	2.077±0.17	48.014±6.917
	20	39	73.742±4.071	14.32±1.35	4.86±0.40	2.492±0.732	75.045±32.736
	40	62	89.902±5.615	14.32±0.77	5.16±0.71	2.832±0.3	100.937±18.179
Jute Stick	0	27	53.383±2.39	1.25±0.62	2.33±0.92	2.145±0.147	45.62±5.586
	10	41	75.631±4.446	4.36±0.28	3.99±0.51	3.154±0.19	96.783±11.801
	15	46	66.918±12.918	3.74±0.92	4.18±0.67	2.432±1.03	66.984±8.457
	20	52	72.919±7.438	4.98±0.74	4.77±0.55	3.142±0.856	96.70±37.155
Kash	0	16	61.958±3.23	6.85±0.51	3.31±0.92	3.214±0.269	81.053±12.247
	10	27	75.153±2.259	5.6±0.17	4.18±0.13	3.471±0.23	105.409±10.519
	20	46	83.201±2.515	6.23±0.17	5.16±0.44	4.022±0.065	137.64±5.241
	30	64	91.729±6.202	4.36±1.42	5.06±1.05	3.428±0.516	130.069±28.732
Kaun	0	22	41.80±1.082	6.23±0.28	2.33±0.56	2.917±.118	50.704±3.18
	10	52	69.59±2.09	4.98±0.32	3.70±0.14	3.317±.177	94.48±7.78
	20	73	84.94±27.27	4.36±0.712	3.79±0.66	3.14±.40	105.16±23.85
	25	77	71±9.44	4.36±0.68	3.99±0.43	3.38±1.63	104.58±43.97

Table. Paper quality evaluation with beating of soda-AQ pulp (continuation)

Sample	Beating (Min)	^{0}SR	Tensile index	Tear index	Burst index	Elongation	TEA
Mulberry	0	16	43.077±3.849	9.34±1.06	2.24±0.29	2.299±0.456	40.902±12.557
	10	26	57.107±2.672	8.09±0.32	3.43±0.42	3.499±0.312	86.655±12.718
	20	34	64.205±2.426	6.85±0.17	3.43±0.52	3.814±0.378	107.129±16.014
	30	47	56.772±1.565	4.98±0.18	3.79±0.19	4.56±0.335	116.396±12.367
Mustard	0	25	47.75±3.083	5.9±0.55	1.663±0.67	2.057±0.222	37.369±7.243
	5	39	64.558±1.015	4.36±0.36	2.62±0.16	2.686±0.110	70.652±4.495
	10	52	69.967±6.037	5.60±0.38	3.025±0.44	2.635±0.475	74.863±320.311
	15	62	72.377±7.329	4.36±0.25	4.98±1.015	2.45±0.721	72.411±29.952
Okra	0	14	35.732±0.1768	7.47±0.22	2.14±0.712	2.617±0.114	40.629±3.945
	10	41	63.175±3.661	4.36±0.46	3.99±0.54	3.359±0.159	92.878±9.247
	15	47	75.581±3.335	6.63±0.38	4.38±0.29	3.799±0.157	118.502±10.332
	25	66	77.501±8.206	5.60±0.712	3.60±0.16	2.579±0.415	79.233±21.343
Pineapple leaves	0	34	31.648±3.627	8.09±0.56	0.62±0.59	2.114±0.433	28.008±9.724
	10	64	38.703±2.246	6.85±0.18	2.29±0.77	2.182±0.317	33.541±7.579
	15	72	37.094±4.6166	6.85±0.38	2.24±1.015	2.102±0.495	37.781±13.181
Red Lentil	0	20	28.208±4.334	3.74±0.65	1.71±0.42	1.373±0.423	15.531±7.904
	10	33	43.845±1.552	3.74±0.75	2.96±0.58	2.188±0.119	30.301±3.993
	20	49	47.723±0.514	3.11±0.25	2.09±0.6	2.483±0.191	49.567±4.823
	25	55	47.563±4.136	3.11±0.52	2.24±0.73	2.179±0.433	42.56±13.475
Rice Straw	0	29	48.112±2.815	5.60±0.42	2.14±0.27	3.21±0.176	67.04±10.178
	5	36	44.79±1.015	4.98±1.08	2.43±0.48	3.88±0.289	75.94±8.768
	10	45	49.06±1.517	4.36±0.56	3.11±0.41	3.91±0.156	82.85±5.522
	20	59	56.51±1.38	3.74±0.29	3.02±0.12	4.67±.289	101.91±8.89
Wheat Straw	0	20	63.486±4.02	6.84±0.34	3.89±0.18	3.556±0.196	95.541±12.7
	10	47	77.575±1.083	4.98±0.32	4.77±0.29	4.208±0.131	136.777±6.434
	20	61	83.388±5.647	4.36±0.45	5.06±0.65	4.452±0.415	156.329±24.562
	25	68	79.807±4.257	3.74±1.10	4.77±0.40	4.393±0.315	149.137±18.651

APPENDIX III

Table. Effect of D_{HT} and D_0 bleaching on pulp properties after EP stage

RM	Kappa Factor	D_0 (70 ^{0}C)						D_{HT} (85 ^{0}C)					
		Kappa Number		Brightness (%)		Viscosity (mPa.s)		Kappa Number		Brightness (%)		Viscosity (mPa.s)	
		UB	OD	UB	OD	UB	OD	UB	OD	UB	OD	UB	OD
Bagasse	0.15	2.6	1.4	69.43	70.31	18.4	16.57	1. 8	1.2	70.10	72.41	18.7	14.50
	0.2	2.4	1.4	70.76	72.51	18.5	16.49	1.4	0.7	73.92	73.28	17.8	15.24
	0.25	2.0	1.2	71.00	72.96	18.9	16.12	0.8	0.7	76.85	75.51	16.5	10.79
Bamboo	0.15	3.49	3.31	75.95	70.75	14.67	14.32	3.37	2.75	79.65	81.79	14.91	14.33
	0.2	3.43	2.69	77.95	80.79	14.51	14.22	3.15	2.64	79.80	82.28	13.46	13.15
	0.25	2.84	2.63	79.73	80.67	14.26	13.86	2.55	2.42	80.82	82.89	12.88	11.98
Banana pseudo stem	0.15	7.45	6.29	27.31	35.29	17.23	17.02	5.81	5.13	28.61	37.88	17.24	16.47
	0.2	7.02	6.00	31.11	41.68	16.54	16.11	5.30	5.19	31.40	42.75	16..47	15.76
	0.25	6.33	5.87	39.42	44.78	16.05	15.76	5.08	4.81	40.09	45.59	15.08	14.51
Banana leaf	0.15	19.1	18.32	59.48	58.16	20.21	20.02	19.15	17.47	59.44	60.64	19.93	19.45
	0.2	18.2	17.43	61.62	63.42	19.38	19.23	18.12	16.55	65.72	61.38	19.14	18.93
	0.25	17.3	16.37	61.3	62.23	18.88	18.67	17.02	15.56	66.90	65.24	18.89	18.79
Banana peduncle	0.15	2.73	3.51	57.16	59.59	14.54	14.26	1.91	1.90	59.41	59.64	12.54	12.43
	0.2	2.23	2.20	58.97	60.47	13.36	13.48	1.54	1.56	61.69	63.24	11.55	11.36
	0.25	1.63	1.71	59.73	62.15	12.33	12.26	1.08	1.02	68.98	68.03	10.39	9.59
Cassava stalks	0.15	3.62	2.15	43.11	43.94	11.81	10.87	2.55	1.93	44.43	44.48	11.34	9.66
	0.2	3.03	2.04	51.54	52.44	11.03	10.34	1.98	1.43	51.85	53.70	10.65	8.75
	0.25	2.56	1.67	61.72	61.35	10.76	9.68	1.36	1.12	61.84	61.82	9.65	7.34
Chia stalks	0.15	4.57	3.2	45.77	52.8	7.65	6.30	2.87	2.51	49.82	55.17	7.33	6.94
	0.2	3.48	2.67	62.58	60.59	7.13	6.17	2.07	1.87	62.05	61.94	7.50	6.11
	0.25	3.11	2.3	63.51	62.42	6.84	5.78	1.89	1.32	64.35	64.33	6.72	5.61
Corn stalks	0.15	3.5	2.3	66.9	83.4	22.8	18.7	2.1	2.0	76.03	80.58	22.5	18.6
	0.2	2.5	2.1	82.29	85.2	22.6	18.2	1.8	1.6	83.1	83.4	22.1	18.2
	0.25	1.8	1.5	83.6	85.52	23.0	18.4	1.3	1.1	84.2	86.75	21.4	18.0

Table. Effect of D_{HT} and D_0 bleaching on pulp properties after EP stage (Continuation)

RM	Kappa Factor	D_0 (70 ^{0}C)						D_{HT} (85 ^{0}C)					
		Kappa Number		Brightness (%)		Viscosity (mPa.s)		Kappa Number		Brightness (%)		Viscosity (mPa.s)	
		UB	OD	UB	OD	UB	OD	UB	OD	UB	OD	UB	OD
Cotton stalks	0.15	3.30	3.13	66.7	65.8	10.76	10.31	2.14	1.94	67.1	66.6	9.56	9.21
	0.2	2.71	2.32	67.01	67.1	10.23	9.78	1.64	1.36	68.9	69.2	8.12	8.06
	0.25	1.85	1.14	68.9	69.6	9.36	9.14	1.01	0.88	72.2	72.5	7.78	7.61
Dhaincha	0.15	1.93	1.46	76.57	80.59	12.45	12.32	2.59	2.55	77.86	82.04	11.36	11.12
	0.2	2.34	2.22	77.06	81.79	11.65	11.34	1.97	2.02	78.84	84.76	10.56	10.48
	0.25	2.22	1.93	78.53	83.23	11.04	10.65	1.75	1.78	79.00	85.91	9.69	9.26
Jute	0.15	3.50	2.50	79.00	79.09	10.34	10.22	2.95	2.51	80.93	81.49	10.26	9.79
	0.2	2.98	2.02	79.58	80.52	10.21	9.69	2.71	2.11	81.76	81.59	9.25	8.86
	0.25	2.45	2.35	80.15	81.76	9.43	9.16	1.41	1.03	80.93	83.07	8.21	7.48
Jute Stick	0.15	2.53	2.73	75.4	76.99	12.67	12.14	2.43	1.55	79.9	77.36	10.86	10.74
	0.2	2.03	2.21	80.03	79.80	11.34	11.07	1.86	1.43	81.12	80.87	9.76	9.64
	0.25	1.86	1.65	80.50	81.79	10.48	10.23	1.31	1.15	81.80	81.49	7.85	7.13
Eggplant	0.15	3.17	3.14	63.81	70.85	10.35	10.02	2.90	1.94	67.09	69.58	9.59	9.69
	0.2	2.12	1.78	72.18	73.64	9.38	9.18	1.95	1.45	74.66	75.53	9.13	8.78
	0.25	1.87	1.45	72.67	77.05	9.55	8.97	1.37	1.69	78.68	78.90	8.29	7.04
Kash	0.15	1.6	1.1	66.0	84.20	14.4	11.07	1.4	0.9	81.09	83.10	14.4	10.8
	0.2	1.2	0.9	82.0	85.35	15.4	12.74	0.9	0.8	84.48	85.15	14.6	10.2
	0.25	0.7	0.7	84.38	85.5	13.5	13.05	0.8	0.7	85.02	86.2	13.9	10.7
Kaun straw	0.15	3.05	1.97	48.5	66.78	14.21	13.25	2.57	1.68	53.4	70.30	13.33	13.26
	0.2	1.89	1.59	50.58	72.55	13.26	12.74	1.58	1.23	55.68	71.63	12.98	12.27
	0.25	1.38	1.00	54.86	72.72	12.48	12.05	1.12	1.03	56.25	74.40	12.49	11.23
Mulberry stalks	0.15	3.04	2.65	69.60	71.50	10.87	10.32	2.36	1.69	71.57	74.20	8.89	8.72
	0.2	2.21	1.85	75.95	72.50	10.03	9.52	1.44	1.32	76.70	75.70	7.87	7.76
	0.25	1.78	1.47	76.90	77.09	9.66	9.07	1.21	0.95	80.30	81.80	6.65	6.09

Table. Effect of D_{HT} and D_0 bleaching on pulp properties after EP stage (Continuation)

RM	Kappa Factor	D_0 (70 ^{0}C)						D_{HT} (85 ^{0}C)					
		Kappa Number		Brightness (%)		Viscosity (mPa.s)		Kappa Number		Brightness (%)		Viscosity (mPa.s)	
		UB	OD	UB	OD	UB	OD	UB	OD	UB	OD	UB	OD
Mustard stalks	0.15	3.10	2.53	67.00	72.4	11.56	10.87	2.89	2.87	67.4	76.5	10.88	10.36
	0.2	2.76	2.20	69.9	73.3	10.78	10.18	2.72	1.63	70.1	77.87	9.79	9.34
	0.25	1.81	1.88	71.2	74.2	9.79	9.43	2.41	1.43	71.8	78.4	8.51	8.73
Okra stalks	0.15	13.96	8.95	28.94	44.68	20.68	19.87	11.38	6.05	30.83	45.48	19.66	19.14
	0.2	11.76	7.78	41.06	52.60	19.21	19.02	9.61	5.15	45.41	54.96	18.81	18.35
	0.25	11.23	6.62	47.21	56.41	18.34	18.36	8.59	4.03	49.92	57.99	17.57	17.31
Pineapple leaves	0.15	5.33	5.13	46.31	50.74	10.47	10.05	4.73	3.16	52.27	51.91	9.87	9.26
	0.2	4.35	4.32	52.51	52.56	9.56	9.07	3.40	3.30	56.68	58.81	8.36	8.07
	0.25	3.36	3.03	56.51	57.16	8.78	8.27	3.33	2.87	58.79	59.65	6.65	6.39
Red lentil stalks	0.15	6.20	5.59	62.98	61.60	10.22	9.78	6.1	5.7	68.02	68.28	9.54	8.85
	0.2	4.84	4.47	67.94	65.54	9.34	8.86	4.22	3.96	70.63	71.27	7.87	7.55
	0.25	3.23	3.08	72.76	70.89	7.87	7.65	3.15	3.03	75.49	75.73	6.69	5.45
Rice straw	0.15	2.43	1.85	66.64	67.34	16.65	18.473	1.32	0.95	67.7	68.33	16.25	15.87
	0.2	1.32	1.62	67.39	67.77	15.67	18.27	1.23	0.43	70.43	70.31	15.38	15.31
	0.25	1.11	0.79	68.59	68.14	14.91	17.38	0.86	0.33	70.86	71.67	14.96	14.37
Wheat straw	0.15	1.81	0.95	72.62	72.71	15.76	15.26	1.50	0.78	74.84	75.19	14.96	15.39
	0.2	1.83	0.93	74.51	73.46	14.98	14.32	1.38	0.63	75.93	76.78	14.69	14.52
	0.25	0.99	0.81	75.84	73.84	14.61	14.10	0.79	0.44	75.92	77.38	13.44	13.16

APPENDIX IV

Table. Effect of D_{HT} and D_0 bleaching on final pulp properties

RM	Kappa Factor	D_0 (70 ^{0}C)				D_{HT} (85 ^{0}C)			
		Brightness (%)		Viscosity (mPa.s)		Brightness (%)		Viscosity (mPa.s)	
		UB	OD	UB	OD	UB	OD	UB	OD
Bagasse	0.15	87.2	86.0	14.85	13.0	85.6	85.0	12.7	12.6
	0.2	89.1	87.1	14.2	12.5	89.3	88.6	12.5	11.1
	0.25	89.3	89.1	13.12	11.4	89.2	88.3	12.1	11.5
Bamboo	0.15	80.67	80.59	14.47	14.23	82.99	84.97	13.33	13.24
	0.2	82.55	82.93	13.53	13.14	83.76	85.15	12.75	12.45
	0.25	83.93	85.51	12.78	12.53	84.81	85.40	11.88	11.98
Banana pseudo stem	0.15	38.89	45.05	15.35	15.07	37.21	41.13	15.04	14.76
	0.2	43.72	44.51	14.75	14.46	42.49	43.30	14.56	14.55
	0.25	44.21	44.97	14.33	14.05	44.23	44.39	14.08	14.51
Banana leaf	0.15	65.41	56.97	18.23	17.22	60.25	61.90	17.87	17.14
	0.2	60.76	59.54	17.32	17.03	62.17	63.00	17.21	16.95
	0.25	59.41	65.02	16.26	16.32	63.35	62.75	16.89	15.79
Banana peduncle	0.15	68.64	69.33	17.12	16.76	69.06	66.65	16.76	15.05
	0.2	71.83	71.33	16.37	15.89	70.51	70.79	15.36	14.58
	0.25	73.10	73.35	15.34	15.21	78.76	78.91	14.39	12.59
Cassava stalks	0.15	62.46	62.55	10.43	9.87	63.74	64.35	9.87	9.15
	0.2	69.06	70.60	9.45	8.78	72.71	73.56	8.55	8.16
	0.25	72.58	75.98	8.44	7.52	75.50	75.83	7.65	7.34
Chia stalks	0.15	62.7	63.79	6.85	6.83	66.03	67.84	6.46	6.30
	0.2	70.72	73.30	5.99	5.92	71.11	74.62	6.01	5.69
	0.25	71.34	75.98	5.66	5.36	72.48	76.76	5.96	5.22
Corn stalks	0.15	83.5	83.8	15.3	14.5	87.2	87.8	13.7	12.5
	0.2	83.7	83.7	15.5	14.8	87.1	87.9	13.5	12.7
	0.25	84.8	84.7	15.2	14.2	87.4	87.7	13.5	12.4
Cotton stalks	0.15	76.56	76.07	9.66	9.20	77.19	78.21	9.30	9.26
	0.2	81.03	81.46	8.74	8.62	80.65	81.87	8.33	7.72
	0.25	80.22	80.41	7.85	7.23	81.29	82.76	6.78	6.61
Dhaincha	0.15	82.00	82.87	10.23	10.10	82.84	83.53	8.98	9.0
	0.2	83.16	83.46	9.24	9.05	86.05	85.61	8.34	8.65
	0.25	84.85	84.93	9.45	9.21	87.17	87.13	7.69	7.26
Jute	0.15	81.34	81.65	8.89	8.76	84.23	85.34	8.16	8.02
	0.2	83.25	84.04	7.76	7.85	85.67	86.78	7.21	6.87
	0.25	84.44	85.18	6.86	6.48	87.24	88.23	6.21	6.18

Table. Effect of D_{HT} and D_0 bleaching on final pulp properties

RM	Kappa Factor	D_0 (70 ^{0}C)				D_{HT} (85 ^{0}C)			
		Brightness (%)		Viscosity (mPa.s)		Brightness (%)		Viscosity (mPa.s)	
		UB	OD	UB	OD	UB	OD	UB	OD
Jute Stick	0.15	79.33	79.16	8.87	8.68	83.68	83.95	8.45	8.11
	0.2	81.83	81.92	8.24	8.12	84.02	84.87	7.63	7.42
	0.25	82.02	82.47	7.34	7.04	84.84	85.33	7.45	7.13
Eggplant	0.15	69.76	78.92	7.96	7.95	76.04	82.2	8.11	7.68
	0.2	73.33	80.06	7.23	7.08	81.34	87.97	6.88	6.79
	0.25	76.56	82.24	6.35	6.80	85.49	88.62	6.81	6.56
Kash	0.15	83.0	87.0	14.79	10.45	90.0	89.6	11.03	10.5
	0.2	88.6	90.4	14.2	10.49	90.2	90.0	10.8	10.2
	0.25	89.0	90.2	14.24	13.23	90.5	90.9	10.5	10.0
Kaun straw	0.15	64.09	65.64	12.23	11.87	67.92	69.27	11.23	10.87
	0.2	70.06	72.85	11.86	11.21	73.89	73.96	10.56	10.13
	0.25	71.16	72.13	11.23	10.76	75.11	76.46	10.49	9.23
Mulberry stalks	0.15	75.12	76.74	8.87	8.32	77.85	76.86	8.43	8.45
	0.2	76.75	77.83	7.76	7.21	83.79	82.93	7.74	7.12
	0.25	78.93	79.50	7.11	6.87	85.98	85.15	6.65	6.09
Mustard stalks	0.15	70.73	70.46	8.34	8.68	73.56	73.71	8.33	8.23
	0.2	74.07	74.50	8.16	8.33	76.45	76.70	8.03	7.67
	0.25	76.4	75.61	7.21	7.15	77.64	77.06	7.51	7.33
Okra stalks	0.15	54.75	54.41	18.76	18.54	59.62	59.36	18.86	18.35
	0.2	56.49	57.04	18.14	18.23	64.85	66.69	18.34	17.56
	0.25	62.75	67.12	17.67	17.78	65.30	67..94	17.57	17.32
Pineapple leaves	0.15	60.47	60.67	8.27	8.24	64.9	60.99	8.14	7.64
	0.2	62.50	63.58	7.85	7.38	68.37	68.40	7.24	7.11
	0.25	67.44	67.73	7.29	6.95	69.41	69.76	6.65	6.59
Red lentil stalks	0.15	40.57	68.86	6.88	6.79	73.58	70.45	6.38	6.28
	0.2	77.84	72.60	6.36	6.08	77.52	77.67	5.83	5.64
	0.25	78.55	74.88	5.86	5.45	79.34	79.37	5.69	5.55
Rice straw	0.15	73.27	75.82	16.39	15.91	76.61	76.01	16.09	14.76
	0.2	75.28	76.12	15.43	16.35	74.27	76.98	15.30	15.66
	0.25	75.3	77.12	14.96	16.25	75.02	77.08	15.05	15.31
Wheat straw	0.15	87.34	90.17	15.09	15.26	90.02	91.30	15.56	15.24
	0.2	88.86	90.24	14.62	14.32	90.72	91.67	14.14	14.39
	0.25	91.14	90.79	14.18	14.09	91.21	92.32	14.05	14.75

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