Chapter 1

Pulping and Papermaking of Non-Wood Fibers

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Additional information is available at the end of the chapter

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Abstract

In general, the main raw materials of pulp and papermaking industry can be classified into three categories: wood, non-wood, and non-plant (mainly wastepaper), of which non-wood fiber material is an important fiber source in the areas where forest resources are scarce. Nowadays, in the total pulp consumption of the world, the proportions of wood pulp, wastepaper pulp, and non-wood pulp are 63, 34, and 3%, respectively. The effective use of non-wood fiber resources, especially grasses, cereal straws, corn stalks, bamboo, and bagasse, would play a major role in optimizing papermaking raw materials. On the other hand, there are non-wood fibers such as flax, hemp, jute, kenaf, cotton, sisal, and abaca with properties as good as or much better than softwood materials.

Keywords: non-wood fibers, pulping, bleaching, papermaking, cellulose, lignin

1. Introduction

In recent years, the three major problems that would continue to puzzle the development of the paper industry are the shortage of resources, contamination of environment and the level of technical equipment. The most dominating factor is the shortage of raw material resources, which is largely due to the contradiction between the structure of the raw material and the structure of the fiber resources [1]. Thereby, non-wood fibers possess a rich variety of excellent properties in physical and optical aspects, which could be used to improve their products [2]. However, throughout the world, non-wood fiber accounts for only a small fraction of the raw material of paper and paperboard [2]. However, in some developing countries, about 60% of the cellulose fiber comes from non-wood materials, such as bagasse, corn straw, bamboo, reed, grass, jute, flax, sisal, and so on. Particularly, in China and India, 70% of the raw materials used in the pulp industry come from non-wood plants including cereal straw and bagasse [3], and these two countries own 80% of the total non-wood pulp production [4].

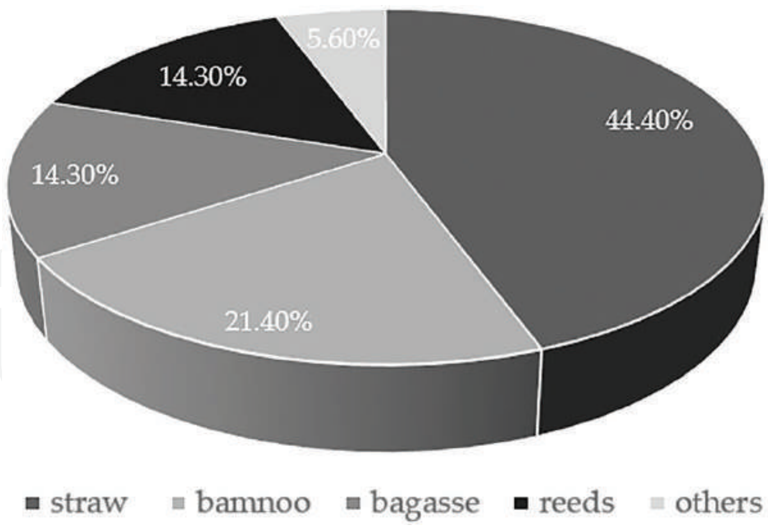

Figure 1. The ratio of non-wood pulp in paper production [5].

Around the world, multitudinous non-wood fibers are used in the field of pulp and papermaking, which include annual agricultural waste and natural growth or artificial cultivation grass and so on. In China, because of the increasing productions of wastepaper pulp and wood pulp, the structure of non-wood pulp had changed in recent years, of which the percentage of straw pulp was decreased from 77.2% in 2004 to 44.4% in 2015. However, the bamboo pulp showed a dramatic upward trend from 2.7% in 2000 to 21.4% in 2015 [5, 6]. The ratio of non-wood pulp in paper production is presented in **Figure 1**.

2. Categories of non-wood raw materials

The non-wood fiber materials used in papermaking can be divided into the following four categories:

2.1. Gramineous fiber materials

The gramineae fiber material is composed of several sections, each of which consists of nodes and internodes (**Figure 2**). This kind of raw materials include bamboo, bagasse, rice straw, wheat straw, sorghum residue, corn straw, reed, and so on, in which the cellulose content is generally around 50%, closing to wood. However, with the heterogeneity of cellulose, the utilization of this kind of plant in pulping is far less than that of wood.

2.2. Bast fiber materials

Bast fiber material usually refers to the materials whose phloem is highly developed. This material includes two types, one of which is the bark which is proved to be of great value in pulp and papermaking because of the abundant fibers in the cortex, such as mulberry, tan skin, skin structure, cotton stalk bark; the other one of which is the hemp, including kenaf, jute, hemp, flax, and so on.

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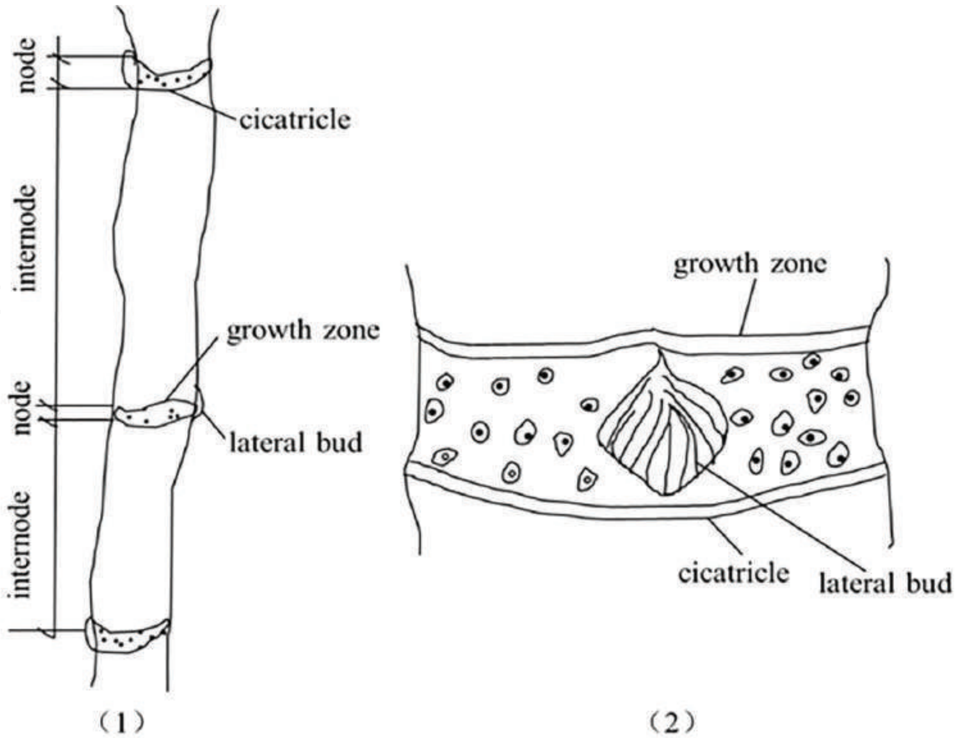

Figure 2. The structure of straw: (1) the composition of straw and (2) the structure of node.

2.3. Seed hull fiber materials

This kind of raw materials consists of cotton and cotton linters, and so on. With cellulose content as high as 95%, cotton fiber is the highest cellulose fiber in nature, so it is an advanced papermaking raw material. Besides, cotton linters are also high-end fibrous raw materials, which can be used in the production of vulcanized base paper, paper napkins, and other senior products.

2.4. Leaf fiber materials

The leaves of certain plants are valuable for pulp and papermaking because of the ample cellulose, such as banana leaves, sisal, abaca, sugarcane leaves, and so on. In recent years, the most commonly used non-wood fiber is straw, accounting for 46%, followed by bagasse (14%) and bamboo (6%). Other non-wood fibers, for instance cotton, hemp, sisal, and kenaf, are also becoming increasingly important in pulp and papermaking industry.

3. The pulping properties of non-wood raw materials

Pulping property refers to the characteristics that present in pulping process, the fiber features and the degree of difficulty of pulping. The performance of fiber material can be estimated by the following factors: (1) whether the fiber contents and forms are of economically viable in pulping or not; (2) difficulty on the degree of delignification and fiber dissociation in pulping process; (3) the adaptability of pulping methods, and the conveniences of stock preparation; (4) the color, degree of bleaching difficulty, drainability, and beating performance of pulp.

The non-wood fiber materials have the following advantages as pulp and papermaking raw material [7, 8]: (1) it is the fast annual growing fiber resource, and it has smaller content of lignin than wood; (2) non-wood pulp can be produced at low temperatures with lower dosage of chemicals; (3) a smaller factory can be feasible in manufacturing processes, giving a simplified process; (4) the beating of non-wood pulp fibers is easy to implement; (5) from the agricultural point of view, the non-wood fiber materials pulping can bring additional economic benefits from the food crops.

3.1. Gramineous fiber materials

The delignification process of gramineous fiber materials can also be divided into three stages: the main stage of lignin removal, the supplementary stage of lignin removal, and the stage of residual lignin removal. Compared with wood fiber, the delignification process is different with gramineous straw materials, which is shown in **Table 1**. As shown in **Table 1**, the lignin of gramineous straw materials is easier to soluble than that of softwood materials

Items	Softwood	Straw	
		Sodium-hydroxide method	AQ-sodium-hydroxide method
The first stage of lignin removal	The initial stage of lignin removal	The main stage of lignin removal	
Temperature/°C	<140	<100	<100
The removal rate of lignin/%	20–25	60	61–62
The dissolution rate of hemicellulose/%	—	45	45
The second stage of lignin removal	The main stage of lignin removal	The supplementary stage of lignin removal	
Temperature/°C	140–170°C and the earlier stage of heat preservation	100–160	100–160
The removal rate of lignin/%	60–70	25–28	28
The dissolution rate of hemicellulose/%	—	9	9
The third stage of lignin removal	The stage of residual lignin removal	The stage of residual lignin removal	
Temperature/°C	The later stage of heat preservation (170°C)	Heat preservation at 160°C	Heat preservation at 160°C
The removal rate of lignin/%	10–15	5–10	5–10
The dissolution rate of hemicellulose/%	—	2–3	1–2

Table 1. The comparisons of delignification stages between softwood and straw [9].

in alkaline pulping process. The main reasons are as follows: (1) the fibrous structure of this kind of fiber is loose, lignin content is low and hemicellulose content is high. (2) The rapid cooking process of gramineous straw fiber is also closely related to the structure of lignin. Containing high percentage of phenolic hydroxyl and acid groups which can be easily ionized in alkaline medium, the gramineous straw lignin is lyophilic and readily soluble. Besides, this lignin possesses the characteristics of low molecular weight and high dispersity, which can account for why the lignin can be easily removed. (3) With a small molecular weight and low polymerization degree, the hemicellulose in gramineous straw material, of which the main ingredient is alkali soluble xylan, is easy to be degraded and dissolved during cooking process with temperature increasing to 100°C, which is accompanied by the decrease of the content of lignin-carbohydrate complex (LCC). The dissolution of hemicellulose can also open the channel for the penetration of the cooking liquor and the digestion of lignin, thereby promoting the removal of lignin from the cell wall.

In addition, the reasons for the distinction between grass and wood are not only the biological composition of grass, but also the cell types that constitute grass.

1. **Fiber cell**: Accounting for 40–60% of total cell mass, fiber cell is the foremost cell of gramineous fiber, of which fiber length is 1.0–2.0 mm (except for bamboo), and the diameter is generally 10–20 μm. The fiber properties of common grass fiber materials are shown in **Table 2**.

2. **Parenchymal cell**: Parenchyma cell is another kind of main cells in the raw material, whose shape and size are variable. The cell wall is thin and the cell cavity is large, and the water absorption is 15 times higher than that of the fiber cells, which would increase the liquid ratio in cooking process. Moreover, the length of the parenchyma cell is small, which would affect the strength and stability of the paper [14]. Therefore, the higher the content of the parenchyma cells is, the lower the pulping value would be.

3. **Vessel**: The vessel is the main channel for the transportation of nutrients and water by the plant, consisting of many vessel elements. In the cooking process, the vessel is the main path for penetrating the cooking liquid. The liquid chemicals pass into the vessel from one side of the material firstly, followed by entering the other cell through the pits. In particular, unlike ordinary straw pulp, the vessel elements of bamboo are usually relatively large.

4. **Epidermis cell** [15]: The types of epidermal cell are long cell and short cell. The function of long cell is to improve the binding strength between cells; moreover, the silicon cell of short cell is the major source of silica. During alkaline pulping process, silica cells are dissolved by alkali, which can increase the content of sodium silicate in the waste liquor, increase the viscosity of the black liquor, and increase the hazard of "Silicon Interference" in alkali recovery process. When acid pulping method is adopted, epidermal cell would be found in the pulp, which may cause paper disease.

5. **Sclereid**: Sclereid, a sclerenchyma cell with supportive effect, is characterized with thick and lignification secondary walls, and a common single pit. Furthermore, Sclereid belongs to non-fibrous cells, and it is found mainly in the cortex and pith, especially in bamboo fiber.

Raw material	Fiber length (mm)	Fiber diameter (μm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Bamboo [10]	2.7–4	15	52–68	15–26	21–31
Reed [11]	1.5–2.5	20	42–50	20–23	22–25
Giant reed [12]	1.2	15	49.8	24–25	—
Bagasse [11]	1.0–1.7	20	55	27–32	18–24
Rice straw [13]	0.5–1.4	8–10	28–36	23–28	12–16
Wheat straw [13]	1.0–1.5	13	29–35	26–32	16–21
Cornstalk [11]	1.0–1.5	16–20	36–38	23–25	18–19

Table 2. The fiber properties of grass fiber materials.

3.2. Bast fiber materials

Bast fiber, a powerful mechanical tissue in the phloem, is one kind of excellent fiber materials, which consist mainly of hemp and bark. Bast materials are characterized by their thin and long fibers, such as hemp, flax, jute, kenaf and so on. The relative performances are described in **Table 2**.

The kenaf bast fiber has the advantages of long length, large length-width ratio which is beneficial to pulping, and the lower energy consumption and chemicals dosages. However, the feature of large wall thickness lumen ratio (1.73) may impose negative impacts on pulping and beating.

The average length of 20 mm can illustrate that flax fiber is substantially long, of which the length of the longest fiber is up to 47 mm. In addition, with respect to the flax fiber, the outer wall is smooth, the cell cavity is tiny, both ends are gradually pointed, the tube wall has extremely few pits, and the transverse knot is obvious. It can be seen from **Table 2** that flax fiber has the advantages of higher cellulose content and lower lignin content, which would ultimately lead to the results that in chemical pulping process, the chemical dosage is low, the pulping process is mild, the pulp yield is high, and the strength is good [16].

Hemp fiber is similar to flax fiber, but shortens in length. The features of hemp fiber are the existence of transverse knots, thick fibrous cell wall, and smooth surface. Conversely, hemp fiber is long and the degree of lignification is higher than that of flax fiber. It is apparent from **Table 3** that hemp fiber is also an excellent raw material for pulping.

Raw material	Fiber length (mm)	Fiber diameter (μm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Kenaf [11]	2.6	20	53	21–23	15–18
Flax [11]	25–30	20–22	70	6–17	10–25
Hemp [17]	20	22	57–77	9–14	5–9
Jute [11]	2.0–2.5	20	57	15–26	16–26

Table 3. The fiber properties of bast fiber materials.

Raw material	Fiber length (mm)	Fiber diameter (μm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Cotton	20–30	20	95–97	—	—
Cotton linter	0.6–3.0	20	90–91	—	3

Table 4. The fiber properties of seed hull fiber materials.

Raw material	Fiber length (mm)	Fiber diameter (μm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Sisal [11]	3.0–3.5	17–20	43–56	21–24	8–9
Abaca [11]	6.0	20–24	61	11	9

Table 5. The fiber properties of leaf fiber materials [11].

Jute fiber is characterized by its smooth and shiny surface and uneven thickness of cell wall. Owing to its high lignified degree and lignin content, its pulping properties are inferior to hemp and flax.

3.3. Seed hull fiber materials

In all kinds of natural fibers, cotton fiber has the highest cellulose content, with the merits of excellent flexibility, good elasticity, high strength, and strong resistance to dilute acids and dilute alkalis. In other words, this kind of materials is an excellent fiber of pulp and papermaking. Its relative properties are shown in **Table 4**.

3.4. Leaf fiber materials

With the rich content of holocellulose (the total content of cellulose and hemicellulose) and poor content of lignin, the chemical pulping process of leaf fiber materials has the strengths of moderate cooking conditions, low chemical consumption, and high pulp yield. The properties of this kind of fibers are presented in **Table 5**.

4. Non-wood raw materials pulping

The technology of pulp and papermaking originated in China almost 2000 years ago when the raw material was non-wood pulp, especially the textile rags. With the development of pulp and papermaking industry, many kinds of non-wood raw materials, such as cereal straw, reeds, grasses and sugar cane bagasse have been used in pulping and papermaking, particularly in Asia [3]. Nowadays, although the utilization of wood is increasingly widespread, non-wood pulp production is also crucial in countries that do not have enough trees for pulp industry such as China, India, Pakistan, Egypt, and Columbia [2]. As the pulping materials are ushered in a new era, the pulping methods also present a high-speed development.

4.1. Pulping method of non-wood raw material

Nowadays, the delignification technology in alkaline pulping process of wood materials has been applied in non-wood fiber cooking process. In general, alkaline cooking requires adding some cooking agents, such as NaOH, Na_2CO_3, and so on. This section provides an overview of alkaline pulping, sulfite pulping, organic solvent pulping, and biological pulping.

4.1.1. Alkaline pulping

In the procedure of alkaline pulping, the aqueous solution of alkaline chemical agent would be utilized to treat fiber materials to dissolve most of the lignin and separate the fibers from the material into pulp. According to the diversity of cooking agents, the alkaline pulping process of non-wood can be divided into oxygen alkali method, sulfate method, caustic soda method, lime method, and so on.

After the preparation of raw material, the digester would be used to hold the qualified material, which is followed by feeding cooking liquor (made from white liquor, black liquor, and water at a given concentration) into digester. After that, in order to make the cooking reaction uniform, the digester can be idled firstly, which precedes the indirect heating or direct steam heating to the required temperature for cooking (general 150–170°C). Then this temperature should stay for a period to remove the lignin and separate the fibers. When the cooking end point is reached, the pulp in digester should be blown or pumped into the blow tank. **Figure 3** illustrates the above process in a simplified flowchart.

4.1.1.1. Caustic soda pulping

The caustic soda pulping process has been widely used in the pulping of non-wood raw material [18–20]. The main component of the cooking liquor is NaOH, sometimes Na_2CO_3, the dosage of which depends on the fiber properties. Cooking temperature is, essentially, cooking time and alkali charge which refers to the amount of the active alkali dosage. Generally, the alkali charge is around 16%, and the cooking temperature is 140–170°C.

The addition of anthraquinone (AQ) would provide the possibilities for the improvement of caustic soda pulping effect. Due to the fact that AQ can accelerate the cooking rate and

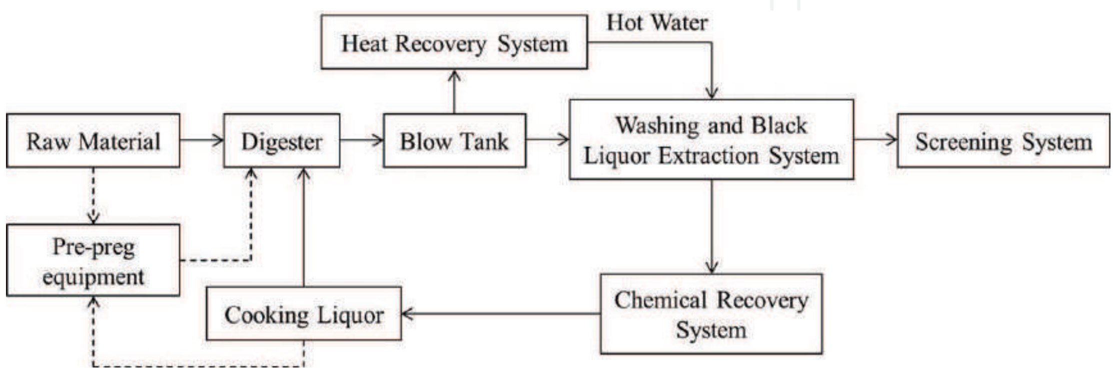

Figure 3. The flowchart of alkaline pulping.

protect the carbohydrates, in the same conditions of cooking, the slurry with AQ has lower kappa number and higher yield as compared with slurry without AQ. According to relevant research, adding AQ in Kenaf pulping process, the removal of lignin would be accelerated, the consumption of alkali would be reduced, the kappa number of pulp would be decreased, the whiteness of pulp would be improved, and the pulp yield and viscosity would be increased, which declare that the slurry has better performance. As added to the digester, anthraquinone will oxidize the terminal group of carbohydrate to form the carboxyl group to avoid the occurrence of peeling reaction, and at the same time, the anthraquinone itself is reduced to anthrahydroquinone (AHQ). In an alkaline solution, anthrahydroquinone would be ionized to anthrahydroquinone ion, and then oxanthrone ion would be formed to react with the methylene quinone structure of lignin. After the reaction, oxanthrone ion could convert back into anthraquinone which can sequentially oxidize carbohydrates. The reaction of anthraquinone with carbohydrates and lignin is shown in **Figure 4**.

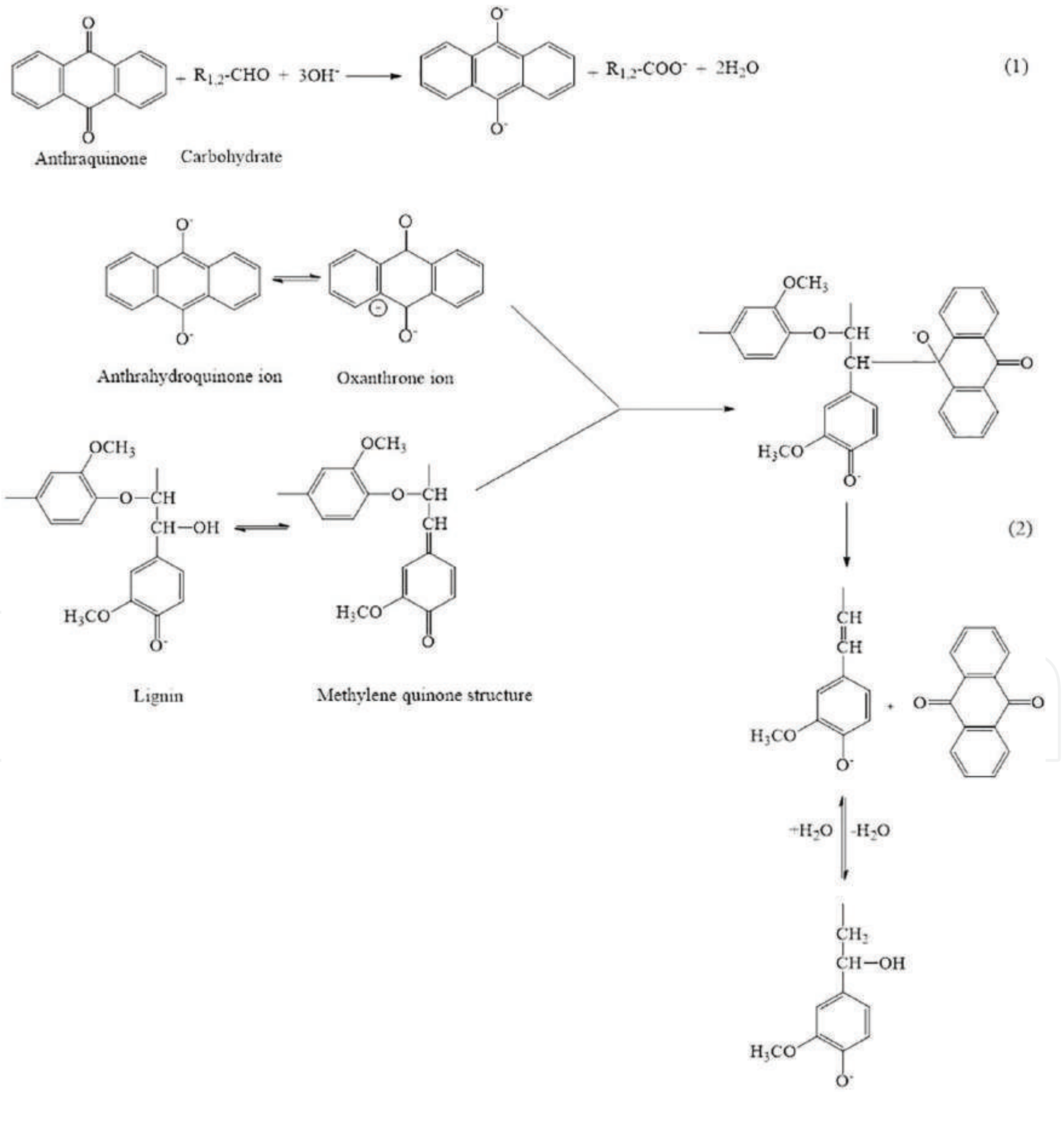

Figure 4. The reaction mechanism of anthraquinone with carbohydrates and lignin: (1) the reaction of anthraquinone with carbohydrates; (2) the reaction of anthraquinone with lignin.

In addition, O_2 also can be added to alkaline pulping to improve the removal rate of lignin, namely, alkaline-oxygen pulping. The pulping method is a new type of non-polluting pulping technology, which is mostly used in the straw pulping process. This technology exploits the synergistic action of oxygen and alkali to eliminate the contaminated exhaust gases during cooking process. Result from the loose structure of the grass material, oxygen can be fully penetrated. If straw material is pretreated before cooking, the structure will be much looser, the transfer channel will be enlarged, and the surface tension will be increased, which would ultimately lead to the results that the cooking liquid and oxygen may be more easily penetrated into the raw materials, and the removal of lignin can be more easily available. This method can effectively reduce the alkaline hydrolysis of raw materials and increase the yield of pulping. Moreover, through oxygen-alkaline pulping, the pulp with high brightness, high yield and excellent physical properties is obtained. Therefore, the oxygen-alkaline pulping method is a very promising clean pulping technology.

The mechanism of oxygen alkali cooking is the dissolution of lignin and the breakage of chains. In alkaline condition, through ionization, the free phenolic hydroxyl groups turn into negative ions that can react with oxygen to generate peroxide intermediates of cyclohexadienone, followed by oxidative degradation which can change lignin structure and generate the side chain cleavage. This series of changes in lignin structure (**Figure 5**) can raise hydrophilicity of lignin molecular, which would contribute to the degradation and dissolution of lignin.

However, when lignin is oxidized, the cellulose is also subjected to alkaline hydrolysis and oxidation reaction. In alkaline-oxygen pulping process, the reducing end group of cellulose is easy-to-reach by oxygen and then produces uronic acid end groups. These terminal groups are unstable under oxygen and high-temperature condition, which leads to rapid decomposition.

4.1.1.2. Kraft pulping

The main components of kraft cooking liquor are NaOH and Na_2S. During the cooking process, except for the strong base NaOH, the S^{2-} and HS^- also play an important role in cooking, which would be generated by the ionization of Na_2S and the hydrolysis of S^{2-}, respectively.

It is well known that unlike wood raw materials, the kraft pulping method is not common for non-wood raw materials. The most immediate factor is that the strength of non-wood kraft pulping is inferior to that of alkaline pulping. Therefore, in this section, this method is no longer introduced.

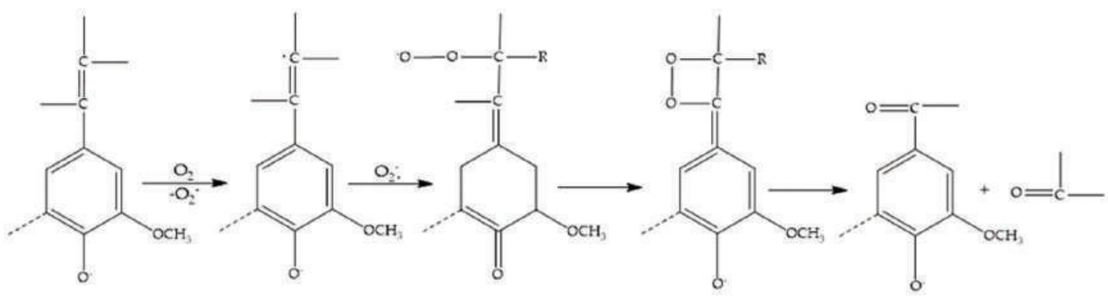

Figure 5. The reaction between oxygen and phenol-type lignin.

4.1.1.3. Other alkaline pulping methods

4.1.1.3.1. NACO pulping

NACO method is developed from alkaline-oxygen pulping. At present, some pulp and papermaking mills have used NACO to produce straw pulp. The main principle of the NACO method is to remove the lignin in the Na_2CO_3 solution, with NaOH as a supplementary chemical to reduce the Kappa number.

The NACO process involves the pretreatment of raw materials, delignification, pulp bleaching, combustion of waste liquid, and recovery of chemicals. First, the mechanical pretreatment of raw materials was carried out under the condition of 1–2% of NaOH dosage and temperature 50°C. The primary purpose of pretreatment is to remove heavy impurities in the material to reduce the silicon content and remove wax which will affect the infiltration of medicine during delignification.

4.1.1.3.2. SAICA pulping

SAICA is a semi-chemical pulping process, using NaOH as a chemical agent. Initially, the crushed and clean wheat straw is obtained by hammering and air drying, followed by dipping in a bucket with black liquid. Under the conditions of normal atmospheric pressure and temperature 94–97°C, the impregnated wheat straw was transferred into the digester for continuous heating. Preimpregnation with waste cooking liquid has positive influences of wheat straw on the absorption of fresh cooking liquid. Preimpregnation can contribute to an effective utilization of the residual active chemicals in the waste liquid.

To achieve the purpose of washing, NaOH should be added in the middle of the digester, while water ought to be added in the slurry discharge area. The black liquor flows continuously from the bottom of the digester, while the washed straw pulp is drawn from the top of the digester. After washing and grinding, the semi-chemical pulp can be empowered to produce corrugated board.

4.1.2. Sulfite pulping

In sulfite pulping process, the raw material is cooked with sulfite as cooking liquid, and most of the lignin in the raw material is dissolved, along with the separation of fibers. **Figure 6** depicts the process of sulfite pulping in a simplified flowchart.

4.1.2.1. Neutral sulfite pulping

The active chemical of neutral sulfite process (NS) is Na_2SO_3 prepared by dissolving SO_2 in Na_2CO_3 solution. With buffer function, the Na_2CO_3 left in cooking liquor can let the pH value of the cooking liquor keep at 7–8. It is reported that the pulping conditions of bleached wheat straw pulp are 10–15% of Na_2SO_3 and cooking temperature 165°C. Compared with alkaline pulping, the yield of neutral sulfite pulping is 8–10% higher, and the pulp is easier to bleach.

In neutral sulfite pulping process, anthraquinone (AQ) also can be used as additive, namely, NS-AQ. The application of NS-AQ method reduces the organic content in the waste liquor, and the yield of the slurry is higher, which indicates that neutral sulfite pulp can compete

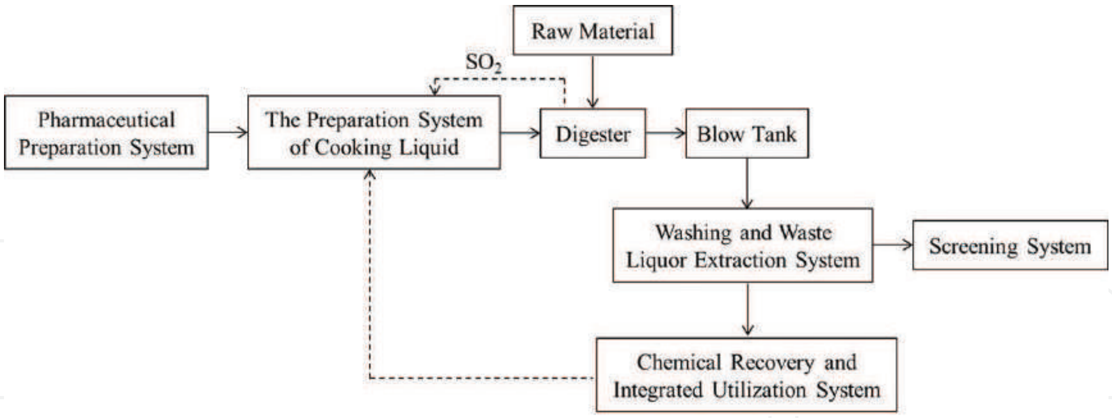

Figure 6. The flowchart of sulfite pulping.

with the kraft pulp. However, the recycling of waste liquid would reduce the removal rate of lignin, and the yield and quality of the slurry may be reduced.

As to straw raw materials, the neutral sulfite semi-chemical pulping (NSSC) method can endow high yield pulp with the characteristics of low kappa number and excellent opacity and strength, except the poor tearing properties.

4.1.2.2. Alkaline sulfite pulping

In alkaline sulfite pulping process, the raw materials are cooked in the cooking liquid consisting of NaOH and Na_2SO_3 at pH 10–13.5. Compared with kraft pulping process, one of the advantages of alkaline sulfite process is that the gas produced is odorless. With the addition of anthraquinone in alkaline sulfite process (AS-AQ), the pulp yield and viscosity can be established to improve.

Many studies have shown that in the same cooking condition, the selectivity of lignin removal will be increased by increasing the concentration of sulfite. For wheat straw, the optimum concentration of sulfite in the cooking liquor is 0.3–0.5%.

4.1.3. Organosolv pulping

In the procedure of organosolv pulping, the organic solvents are utilized as cooking liquor to dissolve most of the lignin and separate the fibers from the composite material into pulp. According to the diversity of cooking agents, the organosolv pulping process of non-wood can be divided into the following categories:

1. Alcohols solvents: methanol, ethanol, n-butanol, amyl alcohol, ethylene glycol, propylene glycol and so on;
2. Organic acids solvent: formic acid, acetic acid, and formic acid + acetic acid, and so on.
3. Ester organic solvent: ethyl acetate;
4. Compound organic solvent: methanol + acetic acid, ethyl acetate + ethanol + acetic acid, and so on.

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5. Phenol organic solvents: phenol, cresol and mixed cresol;
6. Active organic solvents: dimethyl sulfoxide, dioxane, diethanol amine, and so on.

Among the above six solvents, organic alcohols and organic acids are the most commonly used organic solvents in the study.

Similar to the corresponding sulfate pulping and alkaline sulfite pulping, in the alkaline organic solvent cooking reactions, the fracture of β-ether bond is more important than that of α-ether bond. In contrast, in the alkaline organic solvent cooking process, the cleavage ofα-ether bond in lignin is the most important reaction, but the cleavage of β-ether bonds also plays a part.

4.1.3.1. Methanol pulping

At present, methanol has been used in a variety of pulping methods, and the addition of methanol can promote the dissolution of lignin and protect carbohydrates, among which alkaline sulfite AQ-methanol process (ASAM) is considered to be a reformative sulfite cooking method [21]. The active chemicals used in ASAM are NaOH, Na_2CO_3 and Na_2SO_3. Compared with the Kraft process, the addition of methanol in alkaline sulfite cooking liquor can significantly improve the delignification rate, which can also result in obtaining the pulp with excellent strength, fine bleaching properties, and high yield.

The cooking liquid of ASAM contains 10% (volume fraction) of methanol and 0.05–0.1% (relative to the quality of raw materials) of AQ, with the cooking temperature 175°C and cooking time 60–150 min. **Figure 7** illustrates the process of methanol pulping in a simplified flowchart.

4.1.3.2. Ethanol pulping

Because of the high boiling point of ethanol, ethanol pulping whose main cooking agent is ethanol which can be cooked at lower pressure [22].

1. **ASAE pulping**: Alkaline sulfite AQ-ethanol process (ASAE) was improved on the basis of alkaline sulfite AQ-methanol pulping. However, the amount of ethanol required for alkaline sulfite AQ-ethanol cooking is much greater than that of methanol needed for alkaline sulfite AQ-methanol cooking. Nevertheless, the pulp produced by ASAE is characterized by low lignin content, favorable physical properties, high yield, and good beatability, which manifests that this method can save a large amount of energy, compared with the sulfate process.
2. **ALCELL pulping**: Under the cooking temperature 190–200°C, with the ethanol solution as the only delignification agent, the cooking liquor of ALCELL is an aqueous solution of 50% ethanol fraction, of which the pH is about 4 due to the effect of acetyl groups. In addition, to maintain a slight overpressure during cooking, nitrogen is injected into the digester. The whole process can be regarded as three independent processes: lignin removal; ethanol recycle from cooking liquid; the recovery of lignin, furfural and polysaccharide. The main production process is provided in **Figure 8**.

3. **IDE pulping**: IDE pulping method is a nonsulfur alkaline pulping technology. Because of the addition of ethanol and AQ, the rate of delignification can be accelerated in IDE pulping process. The IDE method consists of three successive steps: impregnation by Na_2CO_3 solution; lignin degradation; extraction of pulp with ethanol aqueous solution to remove the degraded lignin. When the IDE method is carried out in the pulping process of wheat straw, the yield of pulp would be more than 50%, and lignin residue would be less than 2.5%.

4. **Punec pulping**: The active chemicals of Punec pulping are ethanol, AQ and caustic soda. The raw material is pretreated with ethanol water solution, which precedes high pressure cooking to remove lignin. During cooking process, lignin and hemicellulose dissolve into the cooking liquid, followed by the ejection of black liquor to the flash tank. Then the black liquor is treated by acid to separate the lignin. To recycle the residual ethanol solution, the hemicellulose rich black liquor should be distilled. Since this method is considered to be pollution-free pulping technology, it deserves further study.

4.1.3.3. Organic acids pulping

Formic acid and acetic acid are commonly used in organic acid pulping, which can react with lignocellulose to produce the corresponding esters in delignification process [13, 18, 23, 24]. It is clear that formic acid and acetic acid can be obtained in acid treatment process of lignocellulose, which is a major advantage of formic acid and acetic acid pulping. Furthermore, the organic acids used in the organic acid pulping process can be recovered by distillation. However, organic acids, especially formic acid, are highly corrosive, so serious equipment corrosion may be caused during pulping.

1. **Milox pulping**: The chemicals used for cooking in Milox pulping process are performic acid or peracetic acid, which are produced by the reactions of hydrogen peroxide with formic acid and acetic acid. Milox, a kind of sulfur free pulping technology, which can realize total chlorine free bleaching, but there are also problems in chemical recovery, due to the productions of acetic acid and formic acid in recovery process. If the mixed solution of formic acid and acetic acid can be used as solvent, the Milox method will be a more economical way of pulping, but this is the feasibility of technology with the worth for further exploring.

2. **Acetosolv pulping**: Acetosolv method is one of the acetic acid pulping technologies using hydrochloric acid as a catalyst. This pulping process should be carried out at atmospheric pressure, with cooking temperature of 110°C.

3. **Acetocell pulping**: The Acetocell pulping, developed from the Acetosolv pulping, should be taken place in the presence of acetic acid at high temperature (170–190°C) without additional catalyst.

4. **Formacell pulping**: Formacell pulping is developed from Acetocell pulping method. At the temperature of 160–180°C, the raw materials are cooked in the cooking liquid, the mixed solution of formic acid (75%), acetic acid (10%) and water.

5. **CIMV pulping**: CIMV pulping is developed from Formacell pulping method, which can be used to produce the bleaching pulp of straw and bagasse. The cooking liquid of CIMV pulping is the compound of acetic acid (20–30%), formic acid (50–60%) and water (20%).

4.1.4. Chemi-mechanical pulping

In recent years, the use of chemi-mechanical pulping in non-wood pulping has attracted a great deal of interest. Chemi-mechanical pulping has the advantages of high pulp yield

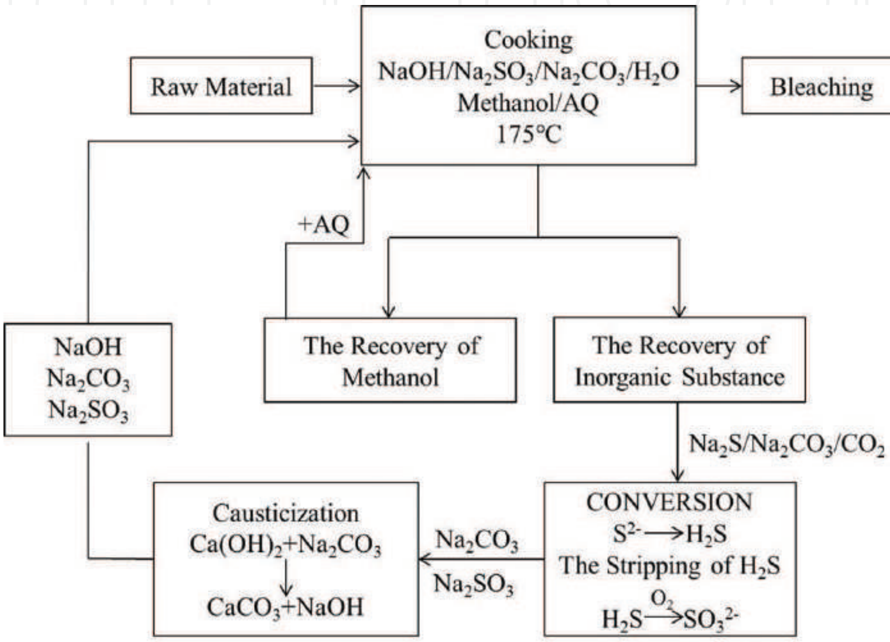

Figure 7. The flowchart of methanol pulping.

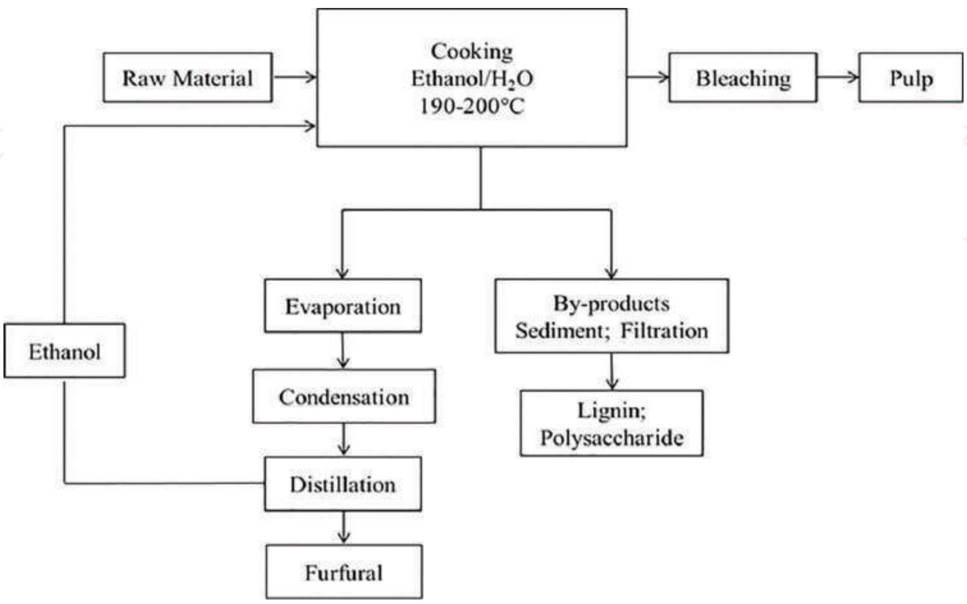

Figure 8. The flowchart of ALCELL pulping.

and no need for chemical recovery systems. **Table 6** shows the chemical pretreatment conditions and slurry properties of certain non-wood materials [18].

4.1.4.1. CMP and CTMP

Unlike CMP pulp obtained by grinding at atmospheric pressure, CTMP is grinded under pressure, so the chemical dosage required in the chemical pretreatment stage is relatively low.

For CMP and CTMP, the cooking temperature is 100–160°C, and the cooking time is 10–30 min. The reason why fibers are softened and the energy consumption is decreased is chemical pretreatment by Na_2SO_3 and NaOH. Therefore, the amount of Na_2SO_3 and the maximum temperature of pretreatment would affect sulfonation degree and swelling of lignin; the dosage of NaOH and the pretreatment time may influence the brightness and yield of pulp. For unbleached reed pulps, if the amount of NaOH is increased from 1–4%, the degree of sulfonation will rise, but the whiteness and yield of the pulp will reduce.

4.1.4.2. APMP

APMP method is the pulping technology which adopts H_2O_2 to bleach in the process of dipping and grinding, by which the darkening phenomenon can be eliminated, along with the increase of the pulp brightness. The chemicals used in the APMP process are NaOH and H_2O_2, with the addition of DTPA, magnesium salts or silicates as inhibitors to reduce the decomposition of H_2O_2.

The typical APMP pulping consists of two segments: (1) steaming of raw materials after impregnation by chelating agent, residual alkali and H_2O_2; (2) impregnation by alkali, H_2O_2 and chelating agent to remove the metal impurities in raw materials.

Pulping methods	**Extrusion pulping**	**explosion pulping**	**APMP**	**APMP**	**APMP**
Raw materials	**Wheat straw**	**Bagasse**	**Wheat straw**	**Kenaf**	**Bagasse**
Dosage of Na_2SO_4/%	-	8	-	-	-
Dosage of NaOH/%	3	1	3	3	10
Dosage of H_2O_2/%	-	-	3	3	3
Temperature/°C	140	190–210	-	90	-
Reaction time/min	120	1–4	-	50	-
Fine pulping yield/%	-	60	84	-	71
Beating degree/°SR	35	-	-	56	20
Tensile index /$N \cdot m \cdot g^{-1}$	-	56	-		
Burst index /$kPa \cdot m^2 \cdot g^{-1}$	2.41	3.00	-		2.38
Tear index /$mN \cdot m^2 \cdot g^{-1}$	3.2	5.7	-	4.2	3.0
Brightness /%	-	-	50.0	53.2	72.1

Table 6. The conditions of chemical pretreatment and the properties of chemi-mechanical pulp.

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4.1.4.3. Steam explosion pulping

After chemical impregnation, steam explosion (SEP) is a process of short time cooking of raw material in saturated steam, which is followed by rapid relief-pressure and grinding at atmospheric pressure. The impregnating solutions include Na_2SO_3, NaOH, $MgCl_2$, $NaHCO_3$ and $MgCO_3$, which have positive influences on reducing the refining energy.

Steam explosion is suitable for pulping of non-wood raw materials. The performances of the obtained pulp are almost the same as that of the CMP and CTMP, even better, except for the lower yield.

4.1.5. Biological pulping

In biological pulping process, microorganisms or enzymes are adopted to pretreat raw material, which precedes the combination with the corresponding mechanical, chemical and organic solvent methods. Because of its unique advantages in terms of environment and energy saving, it represents the future direction of clean pulping technology development [25].

Biological pulping includes biochemical pulping and biomechanical pulping. The basic principle is to selectively decompose lignin by microorganisms or biological enzymes.

There are many microorganisms that can degrade lignin, the most important of which is the basidiomycete, such as white rot fungus. With the existence of oxygen, after the treatment of microorganisms, the lignin would be degraded, and at the same time, the carboxyl group and conjugated carbonyl group increased significantly, while the methoxy content reduced. Therefore, the biodegradation of lignin is mainly oxidation reaction.

Biological enzyme pulping method is derived from microbiological method. In general, the species of biological enzymes mainly include cellulose enzyme, hemicellulose enzyme, and lignin enzyme. With the pretreatment of these biological enzymes, the kappa number would decrease and the whiteness of unbleached pulp would increase. Besides, under the same bleaching condition, the whiteness of the enzyme chemical pulp is higher than that of the chemical pulp.

Unlike lengthy fermentation (about dozens of hours) by microorganisms, only dozens of minutes does the biological enzyme pulping need. In addition, the biological enzyme pulping can also overcome destructive effects of temperature and pH on polymerization degree of cellulose. However, the disadvantage is that the biological enzyme preparations need to be added continuously in the system, so the cost of production is high.

4.1.6. Washing, screening and purification of non-wood pulp

4.1.6.1. Washing of non-wood pulp

The main purpose of pulp washing is possibly to purify the pulp and increase the extraction rate of waste liquor with a certain concentration at the same time, so the maximum amount of waste liquid should be extracted with the least amount of water.

The frequently used pulp washing methods include single stage washing and multistage washing, of which multistage washing can be divided into multistage unidirectional washing and multistage countercurrent washing. However, in order to clean the pulp as much as possible and get high temperature and high concentration black liquid, multistage countercurrent washing method is adopted. Multistage countercurrent washing usually adopts three-stage or four-stage washing process, as shown in **Figure 9**.

The washing of pulp is affected by temperature, pressure difference or vacuum degree, thickness of slurry layer, concentration of sizing and output slurry, cooking method, hardness of pulp and pulp species, washing water consumption and washing times.

Generally, with satisfactory water filtration properties, long fiber pulp is easy to wash, such as bast fiber and cotton fiber. In contrast, with heavy parenchyma cells, small slurry layer gap, high hemicellulose contents, and high content of silicon, the straw pulp is hard to wash. However, the neutral sulfite pulp of straw is easy to wash.

The washing difficult order of some kinds of straw pulp is: rice straw pulp >wheat straw pulp > bagasse pulp> reed pulp > bamboo pulp > cotton pulp.

4.1.6.2. Screening and purification of non-wood pulp

The purpose of screening and purification is to remove the crude fiber bundle, straw knots and non-fibrous constituent in the pulp, in order to meet the needs of product quality and normal production.

The bases of screening are the distinctions in size and shape of fibers, with fine pulp through the sieve plate and pulp residue intercepted. The frequently used screening instruments include Johnson Screen, centrifugal screen, and selectifier screen. According to the size of slurry and the desired results, the process conditions will be selected and determined. Taking centrifugal screen as an example, the screen conditions for non-wood pulp are shown in **Table 7**.

To sum up, the washing, screening and purification systems of pulp are advanced technologies, which can realize the comprehensive utilization of the material and energy cycle to the utmost extent. **Figure 10** is the flowchart of washing, screening and purification process of wheat straw pulp.

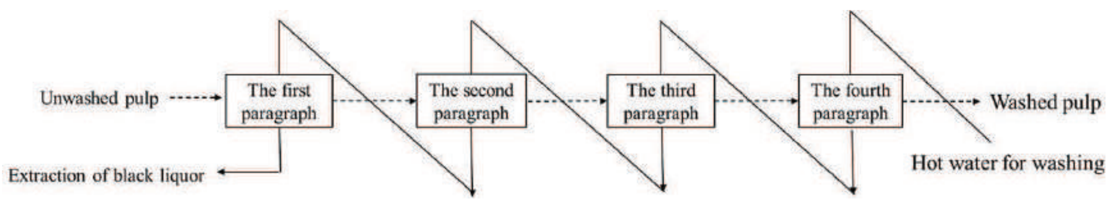

Figure 9. Four-stage washing process of multistage countercurrent washing method.

Pulp species	Sieve diameter /mm	Feeding concentration /%	Fine pulp concentration/%	Pulp residue concentration/%	The rate of rejects /%
Reed pulp	1.0~2.0	0.8~2.0	0.6~1.5	1.0~2.0	2~4
Wheat straw pulp	1.0~1.8	0.6~1.6	0.5~1.0	1.0~1.8	4~6
Bagasse pulp	1.0~1.6	0.6~1.2	0.5~1.0	1.0~1.8	4~6

Table 7. The screen conditions of centrifugal screen.

4.1.7. Bleaching of non-wood pulp

Through chemical action, bleaching can be achieved by the removal of lignin in pulp or changing the structure of chromophoric group. Chemicals used for bleaching cover oxidizing bleach, reductive bleach, sodium hydroxide, chelating agents and enzymes, which can be used alone or in combination. The CEH three-stage bleaching process is mainly adopted in traditional non-wood pulping. However, this bleaching method not only has large drainage capacity, but also has heavy waste water pollution. Besides, the generated AOX is toxic and harmful substances with the property of difficult degradation. Since the 1980s, researchers found that most of the organic compounds in AOX were of highly toxic and highly mutagenic,

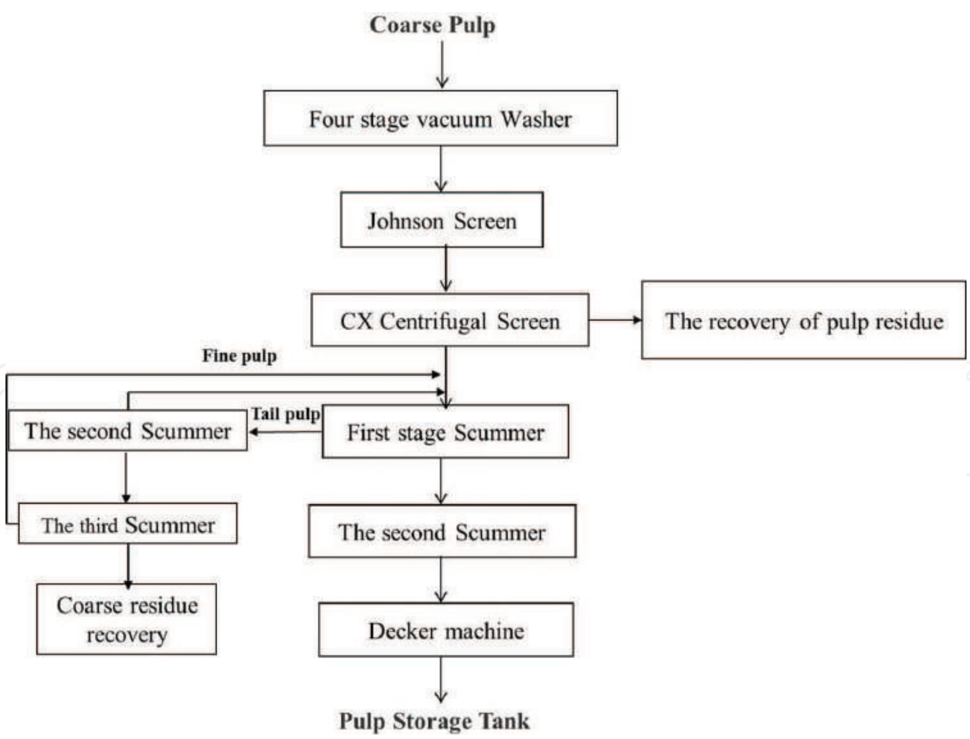

Figure 10. The flowchart of washing, screening and purification process of wheat straw pulp.

and some compounds also had carcinogenic properties. Therefore, the emission of AOX in bleaching wastewater is more and more stringent. In Canada, the AOX emissions should be lower than 2.5 kg/t (pulp) during the 1990–1991 year period, and it was reduced to 1.5 kg/t (pulp) after 1993. In British Columbia, the AOX emission is forbidden. In China, the discharge standard of wastewater from pulp and papermaking industry stipulates that AOX emission should be lower than 12 mg/L (relative to wastewater) [26].

As far as environmental protection is concerned, the bleaching technology has been unable to meet the requirements. Currently, the main clean bleaching technologies are elemental chlorine free bleaching (ECF) and total chlorine free bleaching (TCF).

4.1.7.1. ECF

The main chemical in ECF bleaching is chlorine dioxide, which is a favorable bleaching agent with strong oxidation capacity [27]. The bleached pulp has high brightness and strong pulp strength. Nonetheless, chlorine dioxide must be compounded when it is in need, with high production cost and high corrosion. It is widely accepted that the main difficulty of chlorine dioxide bleaching is its preparation. As shown in **Figure 11**, chlorine dioxide, a kind of free radical, can easily attack phenol-type lignin to make it become free radical, followed by a series of free radical reactions, which are the main reactions in chlorine dioxide bleaching process. Besides, this reaction can also increase the water solubility and alkali solubility of residual lignin. Another important step is the oxidation demethylation reaction. In reaction, the o-quinone derivatives are formed, and the double bonds of quinone ring are attacked by chlorine dioxide or chlorite. In addition, chlorine dioxide can also react with non-phenolic structures and form the corresponding chlorides and oxidation products, but the reaction rate is very slow.

Table 8 presents the results of ECF bleaching of four non-wood pulps, wheat straw, bamboo, reed and sugarcane.

Annotation: C- chlorination (Cl_2); E- alkali extraction (NaOH); H- hypochlorite bleaching; D- chlorine dioxide bleaching; P- hydrogen peroxide bleaching (H_2O_2 + NaOH); O- oxygen bleaching (O_2 + NaOH); Q- chelating treatment (EDTA,DTPA,STPP).

As can be seen from **Table 8**, the brightness of the four bleached pulps can be equal to, even higher than, the traditional three stage bleaching, which shows that ECF bleaching technology is very mature in non-wood pulp bleaching.

4.1.7.2. TCF

Bleach used in TCF bleaching consists mainly of oxygen, hydrogen peroxide and ozone. Because of the property of non-chlorine, this kind of bleaching agent will not produce toxic and harmful substances after bleaching [28–30].

Molecular oxygen is an excellent oxidant, which has the tendency to react with organic substances and trigger a chain reaction of free radicals. Molecular oxygen, as a delignification agent, can react strongly with organic compounds through two unpaired electrons. Lignin oxidation is carried out through a series of electron transfer, and at the same time,

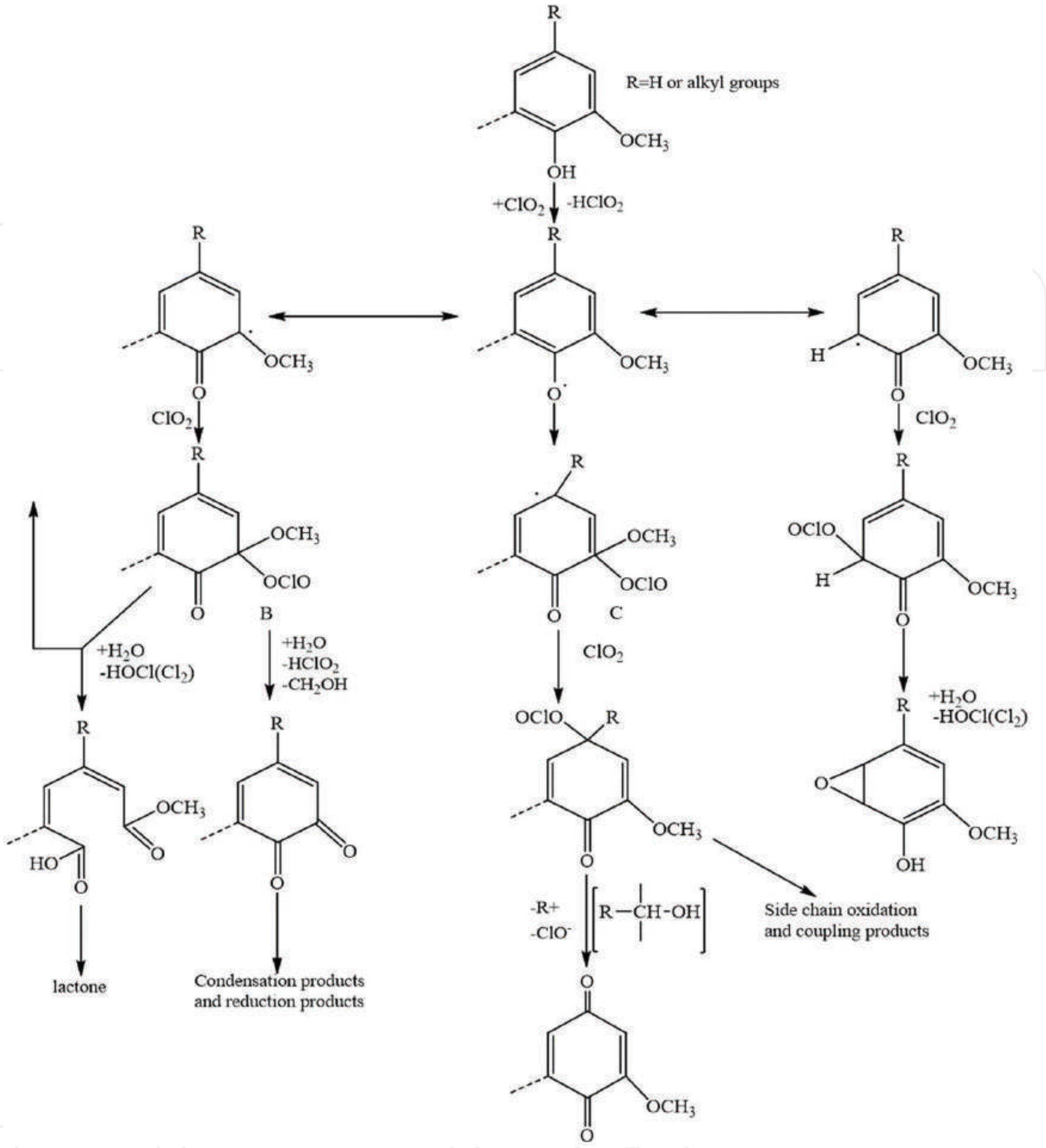

Figure 11. The reactions between phenol-type lignin and chlorine dioxide.

oxygen is gradually reduced and generates a variety of free radicals and ions, which varies with the pH values. These free radical and ionic groups play an important role in lignin degradation.

Hydrogen peroxide is a weak oxidizing agent. It can react with lignin through. There are complex series of reactions of lignin and hydrogen peroxide, including reactions with side chain carbonyl groups and double bonds, to oxide lignin and change the structure of chromophoric group to be of colorless. To a certain extent, the various free radicals generated in bleaching process can also react with lignin. Hydrogen peroxide is a non-volatile water solution, in which hydrogen peroxide anion is the main reactant. Therefore, in hydrogen peroxide bleaching process, sufficient ion concentration should be ensured to reduce the decomposition of hydrogen peroxide and improve the bleaching effect.

Raw materrials	Bleaching process	Brightness (ISO%)	Viscosity (mL/g)
Wheat straw	HD/H	78.6 ISO%	—
	ODQ(PO)	85.47	813
	CEH	85.1	538
Bamboo	D0(EOP)D1	87	—
	DEpDD	85.11	—
Reed	ODQ(PO)	84.31	821
	CEH	83.2	583
Bagasse	ODQ(PO)	86.38	807
	CEH	86.5	543
	DEpDD	85.98	

Table 8. The results of ECF bleaching.

Ozone is a non-selective oxidant. When ozone is used to remove lignin, the carbohydrate would be subjected to significant degradation. Ozone, as a bleaching agent, has the same reaction properties with elemental chlorine in reaction behavior with lignin. In acidic conditions, ozone is an oxidizing electrophilic reagent, which can oxidize the free phenolic hydroxyl, etherified phenolic hydroxyl and conjugated double bond. After that, the lignin molecular will diminish and dissolve in water or alkali to achieve bleaching purpose.

At present, as to TCF, there are an increasing number of researches on non-wood pulp. When TCF was used for bleaching wheat straw pulp, it was found that the brightness of bleached pulp was as high as 83.5% ISO, and the physical properties of the paper were admirable. This kind of bleached pulp could be used instead of high-quality pulp for the production of writing paper and printing paper. For reed pulp, the same effect was achieved with TCF, and the brightness was even higher, with a maximum 87.6% ISO. All these studies show that TCF bleaching technology has an eminent application effect and prospect in non-wood pulping.

4.1.8. The key contaminants of non-wood pulping

In recent years, with the increasingly stringent requirements of environmental protection, the contradiction between cleaner production level of pulp and papermaking and environmental requirements is increasingly prominent, especially straw pulping. Straw pulp production has become the main source of pollution in the paper industry.

It is well known that chemical components of the straw and the wood are different, so the pulping characteristics of these two kinds of raw materials are different. For straw materials, the pulp has poor filtration property, and the black liquor has high ash content and high sugar content, which is also the reason for the high viscosity of black liquor, so it is difficult

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for extraction, evaporation and combustion of black liquor. Viscosity, an important physical property of black liquor, has a great impact on the extraction of black liquor, flow, evaporation and combustion. There is a great difference in the viscosity of different black liquor. Generally, rice straw > wheat straw > bagasse > bamboo > wood.

Generally, the residual lignin content of straw chemical pulp is lower than that of wood pulp, and its molecular weight is small. Therefore, it is believed that the bleachability of straw pulp is better than that of wood pulp. Using traditional hypochlorite bleaching, the brightness can reach 70%, but the bleaching wastewater contains toxic organic chloride (AOX). Therefore, the abolition of hypochlorite bleaching method of straw pulp and the development of chlorine free bleaching agent are imperative for straw pulp bleaching.

4.2. Non-wood raw materials papermaking

4.2.1. Beating characteristics of non- wood pulp

Beating is an important link in the pulp and papermaking process, which has an important influence on the operation of paper machines and the strength properties of paper. Beating can make fiber transformative, swelling, and fibrotic and so on, so that the binding forces between the fibers are improved, and paper strength is enhanced [31].

4.2.1.1. The structure of cell wall of non-wood fiber

In order to sufficiently understand the beating characteristics of fiber, it is necessary to comprehend the structure of the fiber cell wall:

The cell walls of plant fiber are divided into middle lamella (M), primary wall (P) and secondary wall (S), and secondary wall is separated into, outer layer (S1), middle layer (S2) and inner layer (S3). Thereinto, the existence of the primary wall can impede the contacts between the secondary wall and the outside, besides the swelling and the fibrillation may also be influenced. Therefore, the primary wall needs to be broken in the beating process. In addition, although the S1 layer is the transition layer of the S2 and P layers, it may limit the swelling and fibrillation of the S2 layer, so S1 layer also need to be removed during the beating process. For the S2 layer, the main object of beating, it is the main body of the fiber cell wall. Beating which can cause displacement and deformation of S2 makes it possible to increase the interspace between the fine fibers, and permeate the water molecules easily. With respect to S3, it is usually not considered in the beating process.

In addition, for some non-wood fiber raw materials, since there are numerous parenchyma cells in the fibers, the function of beating is also slightly different to them. Generally, in the structure of straw fibers, the parenchyma cell with thin wall content is high and both ends of the catheter are flat, so both of them are easy to become debris in the beating process and exist in the pulp, which makes the pulp filter difficult. Sclereids, one kind of non-fibrous cell with thick wall, are easily washed away by washing. Epidermal cells are generally difficult to break in the beating process.

4.2.1.2. Beating characteristics of common non-wood pulp

4.2.1.2.1. Beating characteristics of gramineous fiber materials

Compared with wood raw materials, it is difficult to beat and achieve the external fibrillation for gramineous fiber materials.

Take wheat straw as an example, in the initial stage of beating, the fiber starts to fluff and the thin secondary wall breaks and falls, so the beating degree would rise rapidly. When the secondary wall was completely detached, with the beating continuing, the morphology of the fiber would change little. With the improvement of beating degree, the fiber is cut off gradually. The fiber will have obviously longitudinal devillicate until the beating degree is 80–90°SR, but at this time, degree of disconnecting is powerful, which shows that wheat straw fiber is difficult to fibrillate. The main reasons are as follows:

The gramineous fiber materials feature with small cell cavity and thick S1 layer which is difficult to break during beating process. Furthermore, the close connection of S1 and S2 would limit the swelling of S2 layer. In addition, the secondary wall of some grasses is made up of multilayer structure, and the arrangements of micro fibers in different layer are often diverse. As to bamboo, the arrangements of micro fibers are mostly horizontal, which may restrict the devillicate of longitudinal micro fibers.

4.2.1.2.2. The beating properties of bast fiber raw materials

With thin and long fibers, bast fiber raw materials generally are excellently advanced raw material of pulp and papermaking. This section will take flax and Kenaf as examples.

Due to the constraint of the primary wall and S1 layer, the flax long fibers have difficulty to beat. However, once the primary wall and S1 layer are removed, the beating degree will rise rapidly, and the fiber diameter will gradually become thin, accompanied by longitudinal devillicate.

The S1 layer of kenaf fiber is thin, and the structure is not obvious. The S2 layer is the main portion of the cell wall, and the internal structure of S2 layer is loose, which may result in dislocation of micro fibers, so the inner of fibers is prone to be fibrillated. Therefore, the beating degree in preliminary stage rise rapidly, and the consumption of beating energy is low. However, due to the large winding angle of micro fiber of S2 layer, longitudinal devillicate is difficult to generate. Only in the case of more power consumption, the micro fiber can produce more dislocation [32].

4.2.2. The papermaking performance of non-wood pulp

The papermaking performance of pulp mainly includes three aspects, the strength of wet paper, the adhesive properties of wet paper and the water filtering performance of the pulp [33, 34]. For pulping, non-wood fiber has advantages of wide source, low price, easy pulping, and smooth surface of paper. However, the non-wood fiber pulp has lower strength of paper, poor water filtering and papermaking performance.

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4.2.2.1. The strength properties of wet paper

It is accustomed to indicate the wet paper strength only with the tensile strength of the wet paper, which is feasible to some certain degree, but does not apply to non-wood pulps. The tensile strength of some non-wood fiber pulps is often higher than that of wood chemical (mechanical) pulps, but non-wood fiber pulps often are broken into actual papermaking process. The reason, affecting the wet strength, is not only related to the wet tensile strength, but also the elongation of the wet paper. Therefore, to measure the wet paper strength of non-wood fiber paper, every aspect should be considered comprehensively. For example, although the kenaf chemical pulp has higher tensile strength of wet paper, the elongation of wet paper is low and its comprehensive strength is low, so it is prone to break in production. The wet strength of some non-wood fiber pulps is shown in **Table 9**.

The basic of wet tensile strength is the length of fibers. The tensile strength of wet paper increases with the fiber length growing. The elongation of wet paper depends on the synergistic action of all fiber components. In addition, beating can increase the elongation of wet paper, which is result from the increase of fiber crimp index. For the same pulping, proper beating can make the fiber swelling and fibrillating, increase the contact area between fibers and promote the function of Van der Waals force, so as to obtain larger wet paper strength.

4.2.2.2. The adhesion properties of wet paper

Non-wood pulp has higher adhesion force, which is attributed to higher hemicellulose, shorter average fiber length, more detailed groups and higher content of parenchyma cell, among which, the pentosan content has the greatest influence on the adhesive force.

Compared with wood pulp and cotton pulp, the adhesion of wheat straw pulp is much higher, mainly because of the higher content of hemicellulose in wheat straw pulp, especially pentosan and Arabia, rather than the difference in fiber shape.

Pulp	Wet paper tensile index(N·m/g)	Wet paper elongation (%)
Bagasse CMP	0.695	6.09
Bagasse chemical pulp	0.636	9.67
Kenaf xylem CMP	0.648	5.07
Kenaf stalk CMP	0.521	10.31
Sulfite reed pulp	0.683	17.51
Kraft reed pulp	0.676	17.50
Bamboo kraft pulp	0.601	9.663

Table 9. The wet strength properties of several pulps.

4.2.2.3. Water filtration properties of non-wood fiber pulps

The filtration property of pulp is a key factor in the production of paper, which may affect the production effective of paper machine. There are many factors affecting filtration property, such as fiber fines content, beating degree and water retention value.

For example, straw pulp has poor water filtration properties, which results from the high content of fine fibers and parenchyma cell in the structure of straw fibers. In addition, after squeezing, the dryness of pulp is lower than that of wood pulp because the water filtration of the straw pulp is seriously damaged during the beating process. Moreover, the water filtration of straw pulp is affected by water retention.

As for bagasse pulp, the fibers have the features of short fiber length and the difficulty of fibrillation. Since parenchyma cell, with a high content, can only be swelled and smashed in beating process, the connections of parenchyma cell and fiber are weak. These properties can usually bring about the difficulty of filtering water at wet end, low wet strength and strong adhesive force in the production process.

5. Summary

With the increase of paper demand, the existing wood resources may be inadequate to meet this growing demand for paper. It is, therefore, necessary to consider non-wood pulp to meet the possible shortfall of wood fiber for papermaking. Besides, this has also led to the developing of alternative pulping technologies that are environmentally benign.

As for raw materials of paper manufacturing, rice straw and wheat straw are easily available and relatively cheap to use. However, the environmental concerns over small mills that use straw offset this advantage. As the government enforces environmental regulations, the amount of rice straw and wheat straw used in pulping might be reduced considerably. Bamboo and other potential non-wood materials will become more popular in pulp and paper industry. Therefore, it is imperative to develop cleaner production technology, reduce pulping cost, improve product quality and realize industrial upgrading.

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Different Solvents for Organosolv Pulping

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Additional information is available at the end of the chapter

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Abstract

Organosolv pulping is a two-stage process involving hydrolysis (decomposition of wood by use of a catalyst) and removal of lignin with an organic solvent (usually a mixture of alcohol and water). The main disadvantage of using an alcohol is its low boiling point, which requires operating at a high pressure and hence using special equipment that is expensive to purchase and operate. One solution to this problem is using alternative organic solvents that afford operation at pressure levels similar to those of classic pulping processes (e.g., the Kraft process). This chapter provides a comprehensive literature review on the organosolv-based production of cellulose pulp by using alternative solvents such as glycols, phenols, esters, organic acids, acetone and amines.

Keywords: organosolv, glycols, phenols, ester, organic acids, acetone, amines, pulp, paper

1. Introduction

The increasing environmental awareness of developed societies has boosted the demand for more sustainable production processes for commodities such as paper and cardboard. Traditional chemical and semi-chemical pulping processes produce large amounts of waste called "black liquor" that is highly polluting (especially when sulfur compounds are used). In response to this problem, the industrial and scientific sectors are increasingly aiming at using new raw materials to replace traditional choices such as annual plants or agricultural and forestry residues, and also at developing new pulping processes based on less polluting, more easily recovered reagents such as organic solvents. Such processes are generically called "organosolv processes" and afford the production of high-quality pulp and paper with modest industrial investments and low production costs, as well as the efficient, integral use of raw materials to obtain pulp in high yields in addition to by-products and added value.

Since alcohols are the most widely used solvents for organosolv pulping, this chapter reviews the comparatively scant research conducted so far on the use of alternative solvents such as glycols, phenols, ester, organic acids, acetone, ammonia and amines for this purpose.

2. Background

The earliest scientific reference to delignification with organic solvents dates from 1893, when Kason used ethanol and hydrochloric acid for this purpose. This was followed by the work of Aronovsky and Grotner, and Kleinert and Tayenthal, in the 1930s; Brounstein in the 1950s and Kleinert in the 1970s [1, 2]. In those days, organosolv processes had not yet challenged the prevalence of traditional chemical pulping processes. During the 1970s, however, the scientific community began to devise solutions to the many drawbacks of the classical processes including unpleasant odors, low yields, high pollution, difficult brightening of pulp, large investments, and massive consumption of energy, water, raw materials and reagents. Initially, attempts focused on modifying the pulping process; then, new processes using no sulfur as reagent were developed. However, these attempts met new problems such as the difficulty of recovering reagents and the polluting nature of the waste [3].

In the 1980s, new processes using organic solvents started to emerge. Their greatest advantage was that they afforded full use of the raw materials. Some were used to obtain hydrolysable cellulose, phenolic polymers of lignin and sugars [4–6].

Although the Kraft process still prevailed in the 1990s, the environmental problems it caused, and the high investments involved led to the conclusion that alternative pulp production processes should be developed.

The most commonly pulping process used in industry is the Kraft or sulfate process [7]. The most common raw material for this process is wood, especially softwood for unbleached pulp, and hardwoods for bleached pulp, with a much higher consumption than alternative or non-wood vegetables, whose main disadvantage is that some of them have high ash content, which causes serious problems in the recovery circuits of black liquors.

In this process, the reagent replaced is sodium sulfate, although the real agent that acts during the delignification reaction is the sulfur that is generated. The process can be divided into two parts: the first is the production of the pulp and the second is the recovery of the chemicals used [8].

In Kraft pulping, some of the black liquor can be recirculated to be used as a pulping solution. In some cases, 40–60% of pulping solution may be black liquor without affecting the pulping yield or the characteristics of the pulps obtained. By this way, part of the reagents is reused without costly evaporation stage, the reagents' penetration into the chips is encouraged, and the heat energy of the black liquor is used.

Several authors propose modifications to the Kraft process. Wang et al. [9] propose the addition of anthraquinone to green liquor, achieving yield increases of 2% and substantial savings in reagents (23–26%) and energy. The use of polysulfides in the pre-treatment improves the pulp yield by 1.5–3.5% according to the data obtained by Luthe et al. [10]. Gustafsson et al. [11] propose a pre-treatment with polysulfide in an alkaline medium (0–2.5 molar sodium hydroxide), achieving significant improvements in the viscosity of the pulps with a low Kappa number. Brannvall et al. [12] describe hyperalkaline pulping with polysulfide, in which pre-treatment consists of two stages: the first one is an acid neutralization and the second one is a high concentration of alkali and polysulfide.

Research then focused on processes using organic solvents in order to extract not only cellulose fiber, but also other useful products from the raw materials. That is how the concept called "wood refinery" by analogy with the fractionation of crude oil was born [13].

In this way, much research into the delignification of traditional and alternative raw materials with organic solvents to obtain not only pulp, but also lignin, sugars and various other products was conducted [4, 5, 14–24].

The main advantages of organosolv process regarding Kraft process are as follows:

1. More economical than the kraft process for SME.
2. It achieves a good degree of brightness for the pulps, competitive with those obtained for conventional chemical pulps.
3. Less polluting than conventional processes, without bad smells and with less effluents and pollutants.
4. By-products are obtained in greater quantity and quality than in conventional processes.
5. Better use of the raw material due to its higher yields.
6. It requires less water than the Kraft process.

However, this process also has its drawbacks:

1. It cannot be applied to softwoods.
2. Higher production cost, due to the high cost of some solvents as ethanol.
3. Higher cost of recovery of by-products.
4. Requires more external energy than the Kraft process.

3. Organosolv solvents and catalysts

Organosolv processes use a broad range of organic solvents including methanol, ethanol, propanol, butanol, isobutyl alcohol, benzyl alcohol, glycerol, glycol, ethylene glycol, triethylene glycol, phenol, acetone, formic acid, acetic acid, propionic acid, diethyl ether, amines, ethers, esters, formaldehyde and chloroethanol, among others, either in pure form or in aqueous solutions to which a catalyst (an acid, base or salt) may be added. Solvents with a low boiling point (e.g., methanol, ethanol, acetone and ethyl acetate) can easily be recovered by distillation; on the other hand, those with a high boiling point (e.g., triethylene glycol and ethylene glycol) afford operation at low pressures but are difficult to recover [1, 2, 4, 5, 14–17, 25–64]. In any case, all allow softwood and hardwood to be efficiently delignified without damaging cellulose in the raw material [65].

Alcohols are the most widely used solvents in organosolv processes, and ethanol is one of the most effective for this purpose as it combines a high speed of delignification under favorable operating conditions with easy recovery [5, 66]. Primary alcohols provide more selective delignification than do secondary and tertiary alcohols. Also, methanol causes less marked losses of hemicelluloses than does butanol. Only poplar and aspen wood can be efficiently delignified in the absence of a catalyst [65]. However, the catalysts used for this purpose include mineral acids (sulfuric, hydrochloric and hydrobromic), organic acids (formic, acetic, propionic, oxalic, malic, salicylic, succinic, nicotinic, benzoic, citric and phthalic), salts (chlorides, chlorosulfonates, boric fluoride, chlorides, sulfates and nitrates of calcium and magnesium, sulfites and sulfides) and other compounds such as alkalis, ammonia or anthraquinone [14, 40, 42, 43, 55, 61, 65, 67, 68].

Organic acids are more efficient than minerals acids in delignifying softwood [87–89, 123, 124]. However, sulfuric acid at a concentration below 0.01 M, but particularly 0.01 or 0.02 M, allows the processing temperature of alcohol-based pulping of cottonwood to be lowered from 200 to 170°C [4, 69–73]. Lower sulfuric concentrations cause the acid to be neutralized by ash and other alkaline components, whereas higher concentrations can result in condensation with free lignin, hydrolysis of hemicelluloses, degradation of cellulose and formation of insoluble condensation products in the pulping liquor. Lignin condensing in fibers can only be removed after a large enough amount of hemicelluloses has been dissolved; therefore, the presence of pores facilitates the process but also degrades cellulose and detracts from pulp viscosity as a result. Condensed lignin is insoluble in alcohol-water mixtures and requires another solvent such as acetone, tetrahydrofuran, dimethyl sulfoxide or a 3–5% o.d.m. soda solution [5, 40, 65].

Sulfur dioxide dissolved in the pulping liquor acts as a weak acid; by reaction with lignin, however, it forms sulfonic acids that can be as strong as mineral acids [2, 40].

Adding an alkaline earth salt as a catalyst to the alcohol-water mixture is the only way of completely releasing fibers from some vegetable species and obtaining yields as high as 60% of high-viscosity pulp [65].

Base-catalyzed organosolv processes are highly effective with conifer wood and outperform some sulfite and Kraft processes in pulp yield and properties [40, 65].

4. Delignification mechanisms

Delignification with organic solvents is believed to be resulted from hydrolysis of α-aryl-ether and lignin-hemicellulose links with a pseudo-first order kinetics [65] and from dissolution of lignin by cleavage of α-aryl and aryl-glycerol-β-aryl-ether links [40, 74–77].

The rate of delignification in acid-catalyzed organosolv pulping processes is governed by the hydrolysis of α-ether links in lignin [98–102]. The process also involves other complex reactions such as condensation, partial hydrolysis of β-aryl links, release of formaldehyde and recombination of free radicals [40, 78–81].

In acid media, the delignification of lignin is preceded by cleavage of α-aryl-ether and β-aryl-ether bonds by H^+ ions. The concentration of hydrogen ions increases with increasing ethanol concentration and liquid/solid ratio but decreases with increasing processing time [82]. Although the cleavage of α-aryl-ether linkages is a primary factor, the cleavage of β-aryl-ether links is also influential (especially with hardwood). The hydrolysis of β-aryl-ether units in addition to α-aryl-ether links was found to have a direct impact on the initial rate of delignification of aspen wood with methanol; also, the extent of delignification was additionally affected by condensation reactions with lignin [83].

The reactions involved in the soda-methanol process are possibly similar to those of the soda process except that lignin is dissolved by the alcohol and formation of condensation products which is more limited [40]. In alkaline processes, the cleavage of β-aryl-ether bonds is more important than that of α-aryl-ether bonds [84].

Phenol as solvent reacts with lignin and facilitates its dissolution; subsequently, it causes some degradation of carbohydrates and lignin through mild acid hydrolysis [85]. With butanediol, lignin-carbohydrate complexes react with benzyl ethers, especially in the presence of acetic acid [86]. The kinetics of delignification of bagasse is first order with butanol but second order with soda [87].

Removal of lignin in the pulping of eucalyptus with acetic and hydrochloric acids results from the hydrolysis of α-aryl-ether links, which occurs in two parallel first-order reactions involving the hydrolysis of hemicellulose (the faster) and cellulose (the slower) [85]. The latter reaction does not occur at low temperatures and concentrations of hydrochloric acid [88–90]. The acetosolv pulping of pinewood also involves two parallel first-order hydrolysis reactions the first of which is faster than the second [91–93].

The pulping of spruce exhibits two distinct stages of delignification, both with first-order kinetics. In the first (the faster), 70% of the lignin is rapidly removed, the remainder being eliminated more slowly. Complete release of fibers is achieved when the yield drops to 57% and the kappa number is 72 (10% lignin). Delignification at these stages occurs largely in outer cell walls and the middle lamella, and is still relatively scarce in secondary walls. Although all lignin in the middle lamella is removed with a yield of 60%, some residual lignin remains in outer and secondary walls. As confirmed by various techniques, the ease of delignification of the middle lamella decreases in the following sequence: catalyzed organic solvents > acid chlorite > neutral sulfite > acid sulfite > Kraft. On the other hand, the sequence for the secondary wall is Kraft > acid sulfite > catalyzed organic solvents > neutral sulfite > acid chlorite. Delignification of the secondary wall is governed by diffusion (specifically, by physical and chemical differences between lignin in various morphological regions of plant tissues) [94].

Overall, hardwood is easier to delignify than softwood by virtue of its lower content in lignin, higher concentration of α-aryl-ether links—which make it easier to hydrolyze, lower tendency to lignin condensation and higher reactivity of β-aryl-ether links [82].

Brogdon and Dimmel have conducted interesting research into various types of reactions involved in quinone-based pulping processes [95–99].

5. Pulping with different organic solvents

5.1. Glycols

The earliest use of ethylene glycol to obtain cellulose pulp was reported in 1941 by Nakanun and Takanti, who applied it to spruce [15]. In the late 1970s, Unger [4] confirmed that propylene glycol, butylene glycol and other higher glycols were useful for pulping, especially if the raw materials were previously impregnated with sulfuric acid. In the 1980s, Gast et al. [100–102] found the efficiency of ethylene glycol to be improved by using aluminum sulfate or chloride as a catalyst; also they studied the kinetics of pulping of birch with the glycol. In the 1990s, Thring et al. conducted research into the by-products of lignin recovery in the pulping with ethylene glycol, and also the fractionation of poplar in a two-step process yielding cellulose in one and hemicellulose and lignin in the other [4].

Several authors have explored the pulping of aspen, birch, beech and pine wood, vine shoots, olive tree prunings, forest residues and bagasse with ethylene glycol [45, 46, 49, 64, 103–108]; rice straw with diethylene glycol-ethylene glycol and diethylene glycol-ethylene glycol-soda mixtures [109]; and cellulose linters, wood sawdust, *Miscanthus sinensis* and *Eucalyptus globulus* with glycols [110]. Using glycol-acid acetic-water systems with aspen and pinewood proved an effective modification of the glycol delignification method with substantial savings in energy (temperature and time) [106, 111]. A study investigated the origin of the losses of ethylene glycol during pulping [112].

Glycerols have also been used in pulp production [49, 113–115]. Thus, treating *Ailanthus altissima* and *Spruce orientalis* wood with glycerol provided optimal delignification results in the presence of an alkali, which, however, led to increased cellulose losses.

Butanediol and propylene glycol have also been used for pulping [56, 64, 115], and so have mixtures of ethanol and ethylene glycol [46, 116].

5.2. Phenols

The Battelle-Genoa process uses phenol as solvent. This is the best-known pulping process using a high-boiling point solvent in combination with HCl as a catalyst. The process is especially efficient with hardwood, spruce and herbaceous plants. With softwood, however, it usually takes a long time and yields pulp with inferior properties relative to the Kraft process. The advantages of the Battelle-Genoa process include a low cost of the industrial plant and the production of small volumes of black liquor; on the other hand, its disadvantages include problems arising from washing of the pulp, recovery of the reagents and detoxification of the effluents, which usually contain small amounts of phenols and cresols [2, 39].

The phenol-ethanol process is also well known [14] and has been successfully used to delignify wood [85, 117, 118], wheat straw [119] and *Ulex europaeus* [120]. Phenols have also been used for pulp production by Schweers et al. [53, 54].

Finally, cresols have been used as reagents for spruce pulping [121]; the raw material, at 70% consistency, was delignified at 180°C for 2 h in the presence of acetic acid.

5.3. Esters

The ester pulping process, patented by Young and Baierl, uses a mixture of water, acetic acid (catalyst) and ethyl acetate (solvent) to dissolve fragmented (hydrolyzed) lignin. This process is suitable for poplar, but not for other types of hardwood (e.g., red oak, eucalyptus) and softwood species (e.g., pine, white spruce); nor is suitable when the aim is to obtain pulp for subsequent bleaching. The properties of poplar pulp obtained with this process are in between those of sulfite pulp and Kraft pulp [39]. According to some authors, however, this process efficiently delignifies both hardwood and softwood and provides pulp with good mechanical properties [14].

5.4. Organic acids

The acetocell process uses acetic acid and, usually, hydrochloric or sulfuric acid as a catalyst. The process has been used with various raw materials including bagasse [120], birch and hardwood [121, 122], *Pinus pinaster* [123, 124], *Eucalyptus globulus* [61, 125–128] and *Eucalyptus grandis* [42]. Also, it has been applied to softwood and annuals, using a high temperature but no catalyst. With Norwegian spruce, the acetocell process provides pulp with high yield and a Kappa number of 16–20 that is easily bleached with ozone and hydrogen peroxide, and largely retains its mechanical properties [129].

A study examined the kinetics of delignification of wood and correlated kinetic parameters with the catalyst concentration [126, 130]. With acetic-hydrochloric acid mixtures, the selectivity of the process was independent of the concentration of HCl and temperature, and yields were as high as 50% [131]. Another study explored the delignification of red spruce with acetic acid-water, acetic acid-carbon dioxide and acetic acid-water-carbon dioxide mixtures under supercritical conditions; also, it examined the effects of the concentration of acetic acid, pressure, temperature and time on the extent of delignification. The best results were obtained with acetic acid-water mixtures [132]. Acetic acid has also been used in the pulping of birch with provision for the influence of pre-hydrolysis, hydrogen peroxide and some other variables [133], and also in the pulping of rice straw at atmospheric pressure [134]. More recently, a study examined the pulping of beech with acetic acid in the presence of hydrochloric acid as a catalyst [135].

The use of formic acid for delignification dates from 1917, when it was applied to wood and cereal straw. This process has some advantages over others using other organic solvents such as a low cost, and the ability to use low temperatures and pressures [136, 137]. In one study, it was applied to different types of hardwood such as that from *E. globulus* and *E. grandis* [138]. The best operating conditions for the latter species were 92% formic acid, 0.22% hydrochloric acid and 90°C for 90 min, the results being even better with refluxing. The presence of water was found to benefit fibers and yields as a result of its helping remove not only lignin, but also much hemicellulose and little α-cellulose [137].

The Milox process is a variant using peroxyformic acid spontaneously formed upon mixing of formic acid (80%) and hydrogen peroxide [2, 139–141]. This process is highly suitable for delignifying birch in three stages [142], namely: treatment with the acid at 80°C, application of formic acid at 100°C and bleaching with hydrogen peroxide to obtain pulp with 90% ISO brightness. The mechanical properties of the resulting pulp are on a par with those of Kraft pulp. The results with conifer wood are worse, however, as a consequence of solvent recovery by distillation leading to the formation of an azeotrope of inadequate concentration between formic acid and water (78%) [2]. The Milox process has also been used with spruce [139] and alternative raw materials [140, 141]. Several studies conducted in recent years were used to delignify different materials [57, 59, 143, 144] in addition to spruce [67, 145], eucalyptus [146–148], pine [149], bagasse [147], rice straw [150, 151], rods [152] and banana stems [153].

The formacell process, which uses acetic acid-water-formic acid mixtures, has enabled the production of pulp with small kappa numbers from beech, pine and aspen. With aspen and birch wood, a low temperature and a high concentration of acetic acid are recommended to prevent hemicellulose losses [154, 155]. With wheat straw, the process provides pulp with a small kappa number and a high viscosity [156].

Using acetic acid containing small amounts of sulfuric acid and phenols provided good results with birch [157], and so did the acetic acid-carbon dioxide-water system under supercritical conditions [158].

5.5. Acetone

Jiménez et al. used acetone alone [159–161] and in mixtures with ethanol [162, 163] for delignification. Other authors have used mixtures of formic acid and acetone [149, 164, 165] or acetone alone on previously steamed raw materials [166].

One process using oxygen in aqueous acetone was applied to cotton stalks, eucalyptus and poplar wood. The influence of temperature, time and oxygen partial pressure on the delignification rate was examined, and the transfer of oxygen found to be the parent stage of the delignification process [167, 168]. The process was also applied to spruce and other types of wood [111].

5.6. Ammonia and amines

The processes using ammonia or amino bases provide pulp with a high yield by effect of their preserving hemicelluloses. Thus, 1, 6-hexamethylenediamine (HMDA) gives pulp with a high yield from both hardwood and softwood, but the pulp is difficult to bleach. Ammonia in combination with acetone or methylethyl ketone provides spruce pulp with higher yields and better properties—tear index excepted—than the Kraft process. Using ammonium sulfide with ethanol allows one to operate at lower temperatures than with ammonia to obtain pulp with similarly good properties from hardwood, cereal straw and bagasse, and strong pulp with a high yield and low lignin content relative to softwood. However, the processes using ammonia and amino bases are subject to problems arising from the recovery of reagents, the high boiling point of HMDA, condensation of lignin and formation of polluting sulfur volatiles [2].

Pulping poplar chips with supercritical ammonia-water mixtures revealed that the extents of removal of cellulose, hemicellulose and lignin were a function of time, pressure and, especially, temperature and solvent concentration [169].

The earliest work on pulping with ethanolamines dates from the late 1970s, when Wallis [48] applied them to pine and eucalyptus wood, and monoethanolamine proved more effective than diethanolamine and triethanolamine; yields were 11–16% higher than with the Kraft process and the resulting pulp had similar strength-related properties. Wallis [170] also pulped *Pinus elliottii* with ethanolamine and obtained pulp similarly strong to Kraft pulp but in higher yields (5–10% higher).

Ethanolamines have also been used to pulp spruce [47] and rice straw [63]. Adding ethanolamine to the alkaline cooking liquor was found to increase the rate of lignin degradation [171]. Finally, some authors have also used amines to pulp various raw materials such as beech, spruce, olive tree prunings, jute and cotton [172–179].

5.7. Other solvents

Processing bagasse as raw material with formamide and dimethylformamide provided pulps with a high content in α-cellulose in addition to good physical and mechanical properties [180, 181]. Some authors have pulped eucalyptus with dioxane in the presence of hydrochloric acid (catalyst) [182] or its absence [55, 183–185], and hardwood with the sulfur dioxide-ethanol-water system [186].

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Pulping of Non-Woody Biomass

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Abstract

The use of trees for paper production has contributed to the problem of deforestation with radical negative impact on the environment thereby causing an imbalance in the ecosystem. An increase in the demand and consumption of paper has also induced depletion of woods resources for paper production, thus resulting in limited availability of the raw materials. This work examined the use of non-woody biomasses as alternative raw materials, which are accessible and convertible into pulp and paper of the same quality as those obtained from wood.

Keywords: biomass, pulp, non-wood, cellulose, fibre length, fibre diameter, yield

1. Introduction

Before the industrial revolution, non-woody fibres were the primary raw materials for pulp and paper production [1]. Sources of fibre then included textile rags, cotton, cereal straw, reeds, grasses and sugar cane bagasse. Non-wood materials were in use for papermaking in China almost 2000 years ago until developed countries adopted the process of producing pulp and paper from wood sources. This process was invented in Germany by Friedrich Gottlob Keller in 1840 [2]. Nowadays, about 90–91% of the world's pulp and paper production is produced from wood [1]. It involves the extraction of cellulose from either hardwood or softwood fibres. The cellulose obtained is processed into pulp, used in papermaking. The world consumption of paper has grown to about 400% in the last 40 years and continues to grow about 2.1% yearly since 2009 with North America, Europe and Asia accounting for more than 90% of total paper and paperboard consumption [3]. The steady increase in the use of paper has resulted in the utilisation of about 35% of globally harvested trees in the production of pulp and paper [4]. Statistical data for global consumption and demand for paper and cardboard from 2006 to 2015 presented in **Figure 1** indicated a rise in the use of paper and cardboard until 2009 when there was a decline. There has been further increase from 394.5 million metric tons to 410.7 million metric tons in 2015 globally.

It has been estimated globally that the consumption of paper and paperboard has continued to grow averagely at approximately 2% per annum during the past decade [6]. A projection made indicated that this trend would elongate to the current decade with an increase in the global consumption by 83 million tons from 2010 to 2020. The forecast presumed rise in the use of paper and paperboard in the low-income countries and a reduction in the consumption of paper and cardboard in the high-income countries such as North America and Western Europe in the next decades as shown in **Figure 2** [6]. However, this development has attracted a lot of concerns due to the environmental threat it portends.

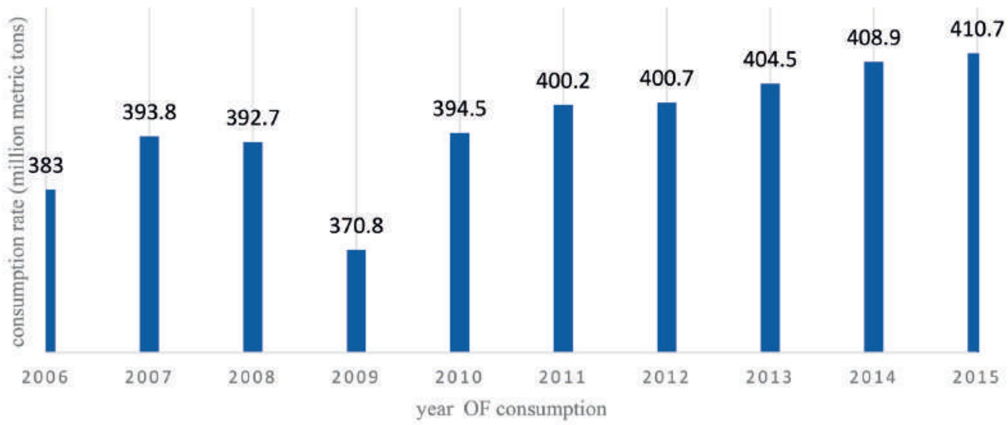

Figure 1. Global consumption of paper and cardboard from 2006 to 2015 (in million metric tons). Source: [5].

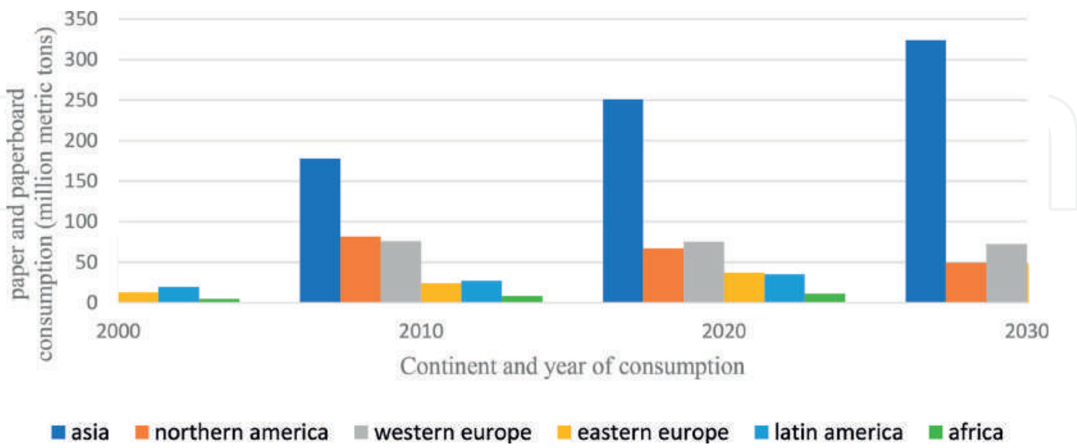

Figure 2. Paper and paperboard consumption in 2000 and 2010 and projections to 2020 and 2030 (in million metric tons). *Source:* [6].

Due to the depletion of wood resources, the use of low-cost raw materials has been introduced to serve as an alternative resource for pulp and paper production [7]. The alternative resources include non-wood fibres, such as agricultural residues and annual plants, considered as valid alternative sources of cellulose for pulp and paper production [8]. Properties that make them suitable include high yielding ability, high pulping quality, good adaptation to prevailing climatic conditions and low-cost [9].

This paper reviews the pulping and paper production from non-wood biomasses, which are mostly annual crops and agricultural residues. These materials are environmentally friendly, cheap and have an unlimited availability that can meet the demand and consumption of paper in an economy.

2. Components of plants

Chemical composition of most plant leaves and grasses have been investigated. They consist of cellulose, lignin, hemicellulose, some terpenes, resins, inorganic element and fatty acids [10]. Research carried out on these plant leaves, and grasses indicate their percentage composition of cellulose ranges from 32.6 to 88% [11]. Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked D-glucose units. Cellulose is the main component of the primary cell wall of green plants. It was first discovered in 1838 by a French chemist Anselme Payen who isolated it from plant matter and determined its chemical formula to be $(C_6H_{12}O_5)n$ [12]. The availability of lignin in plants serves the function of minimising the accessibility of cellulose and hemicellulose to microbial enzymes and also conferring mechanical strength by creating a cross-link with other cell wall components [11]. The application of non-wood raw materials in the pulping process has a lot of advantages such as pulping capability, fine fibres (speciality papers), high-quality bleached pulps [8]. It also allows the production of pulp without an extreme increase in pollution compared to when wood raw materials are used [13].

3. Non-wood fibres and classification

In recent years, the growing interest in alternative sources of raw materials for pulping and paper production other than wood has increased. According to Wisur (1993), in 1989, only 8% of the raw material for pulp and paper production was obtained from non-wood biomass. The use of non-wood raw materials accounts for less than 10% of the total pulp and paper production worldwide [14]. This comprises of 44% straw, 18% bagasse, 14% reeds, 13% bamboo, and 11% others [15]. In developing countries, 60% of cellulose fibres originate from non-wood raw materials, which include annual plants and agricultural residues. Non-wood fibres contain more cellulose and less lignin fraction and can, therefore, digest to produce pulp at low temperatures with lower chemical charges [8]. Non-wood fibres are used to produce pulps and papers with various qualities and strength. Non-wood fibres can be produced within a year compared to the long growth cycles of wood [16]. Fibres obtained from non-wood plants are similar to those of hardwoods. It has been found that their fibres are about 1 mm long, narrow and are usually composed of lignified walls [17].

Non-wood fibres are classified into three main categories according to their origin namely; agricultural by-products, industrial crops and naturally growing crops [18]. Agricultural by-products are the secondary products of principal crops such as cereals and grains and are usually characterised by the low raw material prices and moderate quality. They include rice straws and wheat straws. The industrial crops are high in cost. They include hemp, sugarcane and kenaf and they are used in producing high-quality pulps. The naturally growing plants are bamboo, and some grass fibres such as reeds, elephant grass, and Sabai grass [19]. Based on the position of the fibre in plants, non-wood plant fibres can be classified into four types namely; grass fibres (stalk/culm fibres), bast fibres, leaf fibres, and fruit fibres [20].

3.1. Grass fibres

Grass fibres are mainly obtained from the vascular bundles in monocotyledonous stems and leaves. They can also be obtained from separate fibre strands situated on the outer sides of the vascular bundles [21]. Grass fibres for pulping and paper production are largely obtained from cereal straws, sugarcane, reeds and bamboo. The vascular tissues can be distributed in two circles as in the cereal straw and in most temperate grasses, with a continuous cylinder of sclerenchyma close to the periphery. These tissues can also be scattered throughout the stem section as in corn (*Zea mays*), bamboo, and sugar cane [22, 23]. According to Hurter [24], the average length of grass fibres is 1-3 mm, and the ratio of fibre length to width varies from 75:1 and 230:1. Wheat straw fibres (*Triticum aestivum* L.) have an average length of 1.4 mm (0.4–3.2 mm) and a width of 0.015 mm (0.08–0.034 mm) [25]. It is the most commonly used monocotyledon in commercial pulping. Fibres obtained from cereal straws such as; rye *(Secale cereal* L.), barley (*Hordeum vulgare* L.) and oat (*Avena sativa* L.) are similar to those of wheat [23]. In countries of southern and eastern Asia, rice straw (*Oryza sativa* L.) is a major resource in paper production. The major challenges in the application of rice straw are the high cost of collection and storage. Also, rice straw contains a high amount of silica. However, these drawbacks notwithstanding, rice straw is a favoured fibre source in countries with a limited supply of wood due to its availability [20, 25].

Two other important agricultural residues in this category used for pulping are bamboo and bagasse. According to Atchison [26], Bagasse is used in the production of all grades of paper. While bagasse pulp is obtained from sugarcane waste, bamboo pulp, on the other hand, is commonly made from pruned stem [23]. Bamboo appears prominently in the natural vegetation of many parts of the world. Its growth is favoured mostly in warm tropical climates, and it grows from sea level to the snow line. It possesses two distinct growth forms in which it could be single stemmed or densely clumped. From research, bamboo has been proven to be the fasted growing plants available for pulp and attain their full height of 15–30 m in 2–4 months by diurnal growth rates of 20–100 cm. Its maturity stage is reached when the culm is about 3–4 years old [20]. It has an average fibre length of 2.7–4.0 mm with an average fibre diameter of 0.015 mm. It has got vast applications in the production of printing and writing paper, Bristol board, duplex and triplex paper, wrapping paper, bag paper, multiwall and newsprint substitute [25].

In the case of esparto grass (*Stipa tenecissima* L.), it is mostly found growing wild in the northern part of Africa and also the Mediterranean steppe areas of southern Spain. The location of fibre in this non-wood plant is the leaves. This is the region where the fibre is obtained. It occurs as long rolled up leaves with a length of about 1 m. It has a greyish green colour with a coarse and strong texture. The fibres obtained from this plant leaves are thin and round, approximately 0.01 mm in diameter and a little over 1 mm long. The lumen or canal is very tiny which makes it very springy. They are mostly used in the production of bulky, smooth and well-formed paper for fine printing and lithographic paper [25, 27].

3.2. Bast fibres

Bast fibres refer to fibres obtained from the phloem of the vascular tissues of dicotyledons [23]. Fibres obtained from hemp, kenaf, ramie (*Boehmeria nivea* L.) and jute (*Corchorus capsularis* L.) are derived from the secondary phloem located in the outer part of the cambium. In the case of flax, the fibres are mainly cortical fibres in the inner bark, on the outer periphery of the vascular cylinder of the stem [20, 22]. Flax is an annual plant cultivated in temperate climate for purposes of obtaining linseed oil and fibres. It has an average fibre length of 30 mm and an average diameter of 0.02 mm. Raw materials for flax pulp are derived from three sources namely:

- Textile wastes (old rags and new cuttings).
- Fibre waste remaining when bast fibres are removed from textile flax
- The entire plant after the removal of the seeds from seed flax.

The raw material obtained from the textile waste is of the purest form while that obtained from the entire plant after the seeds are being removed is of low quality and is known as seed flax tow [25]. Blended flaxes in various proportion serve important purposes in the production of speciality papers like book paper, lightweight printing and writing paper, condenser paper, currency and security paper, and cigarette paper.

Jute is characterised by high cellulose content with long fibres. It is primarily grown in Asian countries such as China, India, Thailand, Bangladesh and it attains a height of 2.5–3.5 m when fully grown. It possesses an outer bark comprising of about 40% of the stem by weight, and it is mainly used in the production of low value-added products such as ropes, cordage and gunny sacks [28]. Jute fibres have an average fibre length of 2–5 mm and an average fibre diameter of 0.02 mm. When blended into various proportions, it is used in printing and writing paper, tag, and wrapping and bag paper [20].

Hemp (*Cannabis sativa*) is an annual plant, which grows up to a height of 4.5 m. The fibre consists of 35% long bast fibres and 65% short core fibres [29]. The male plant of hemp produces more fibres compared to the female, which is known to produce more of seeds. This is due to the rapid lignification process which occurs in the female plants. Hemp plant attains maturity within 80–150 days and must be harvested at the proper time in other to be able to maximise its fibre quality. Early harvesting results in reduced yield and weak fibres, whereas delayed harvesting can produce stems that are difficult to separate during the process of retting. Fibres obtained from hemp have a length ranging from 15 to 55 mm and an average length of 20 mm.

The fibres are distinguished by having forked ends with a varying diameter between 0.016 and 0.22 mm [25]. It has found application in the manufacturing of speciality papers.

Kenaf (*Hibiscus cannabinus*) is a tropical crop native to Africa. It consists of an outer fibrous bark and an inner woody core. It is composed of approximately 65.7% cellulose, 21.6% lignin and pectin [30]. Pulp obtained from kenaf through Kraft, soda, or neutral sulphite is of more quality and superior to pulps obtained from commercial hardwood. Except for tear, it is comparable to softwood Kraft pulps and superior to softwood pulps [31]. The fibres obtained from bast (outer bark) are 3–4 mm long while those from the core are 0.6 mm long [32]. They are applicable in the production of newsprint, multi-sack, tissue paper, bleached paperboard, and other lightweight speciality papers.

3.3. Leaf fibres

Several plants have leaves containing fibres that are suitable for papermaking. Fibres obtained from leaves and leaf sheaths of several monocots, tropical and sub-tropical species are referred to as leaf fibres [33]. Some of these fibres produce papers with excellent qualities. The common plants in this category include abaca (Manila hemp) (*Musa textilis*) and sisal (*Agave sisalana*).

Strong Manila hemp or Abaca is plant grown mainly in the Philippines, and its fibre is obtained from leaf sheath of a banana-like-plant. The propagation of this plant is done through suckering or growing of shoots from roots. It attains maturity after 18–24 months after planting and can be harvested, and the fibres can be obtained and isolated to produce pulp.

The quality of abaca pulp is affected by the type of cleaning, which determines the grade of fibres [25]. Pulp isolated from the highly graded fibres are used in the production of high strength speciality tissues, such as tea bags and meat casings while fair to residual grades of fibres obtained are made into pulp for making speciality papers with high tear and tensile strengths such as vacuum bags and wrapping papers [34].

Sisal is a non-wood leaf native to Mexico. It has successfully thrived in semiarid regions of Brazil, Tanzania and Kenya. Sisal leaves have a width of about 10 cm, length of about 1–1.5 m and weight of 500–700 g. Sisal leaves are harvested manually and are transversely cut to 50 mm length before being hammer milled. The juice and pitch are removed through vertical screens and chaffed sisal fibres are transported by conveyors to the drying process. When the sisal fibre is thoroughly dried, it is then pressed into bales for pulping [25].

3.4. Fruit fibre

Fruit fibres are obtained from unicellular seed or fruit hairs. They are also referred to as the seed hair fibres. The most important is cotton fibre which is formed by the elongation of individual epidermal hair cells in seeds of various *Gossypium* species [33]. Cotton fibres come from the seedpod of cotton plants. Regular cotton fibres are too long and too expensive for conventional papermaking. The average fibre length of cotton fibres is 25 mm, and the average fibre diameter is 0.02 mm. It is used in the production of high-grade bond ledger book and writing paper [25].

Borassus (Palmyra palm) is another example of fruit fibre. It is native to tropical African and part of southern Asia. The mesocarp of Palmyra palm fruits is the fibrous material that can serve as a raw material for pulp and papermaking. Palmyra palm fruit fibres possess adequate properties that make it suitable as an alternative raw material of cellulosic pulps for papermaking [35].

3.5. Characteristics of non-wood fibre

Most non-wood fibre commonly used in pulp and paper production is obtained from annual plants, which attain pulp size (growth) within a short period. This makes their availability sufficient for papermaking in contrast to wood fibres, which takes years to grow to pulpable size [36]. Some exceptions in this category of non-wood fibres that do not grow within a short period include bamboo, sisal, hesperaloe etc. These fibres take a longer period to grow to size required for pulping. Various non-wood pulp can be grouped into two main categories:

- the common non-wood or hardwood substitutes and
- the speciality non-wood fibres or softwood substitutes

Major examples of the common non-wood fibres pulp include cereal straws, sugarcane bagasse (*Saccharum officinarum*) bamboo, reeds and grasses, kenaf, corn stalks (*Zea mays*), sorghum stalks etc. There are several types of cereal straws used in pulping and papermaking processes. They include straws from rye (*Secale cereale*), oat (*Avena sativa*) and barley (*Hordeum vulgare*). Of all these straws, rye is the most suitable for pulping. It is generally available and used to produce paper with high strength properties [9]. Speciality non-wood fibres include cotton stalk (*Gossypium*) and linters (flax, hemp) and kenaf bast fibres, abaca, bamboo, hesperaloe etc. [36]. The presence of lower lignin content and higher cellulose content in some of these non-wood plants, which include kenaf [31, 37], hemp [29, 38], jute [28], reed, bamboo [39] has been subject of many research works.

Non-wood plants like kenaf (*Hibiscus cannabinus* L.) and giant reed (*Arundo donax* L.) internodes give very good values in properties, which are comparable to some softwood and most hardwood species. Limitation in the use of some non-wood plants such as; cotton, miscanthus, switchgrass etc. is occasioned by their short fibres. Nevertheless, they possess other complementary qualities such as satisfactory slenderness ratio. Fibres obtained from reed internode (70.5 mm) are shorter compared to those obtained from kenaf bark (105.9 mm). These fibres have good slenderness ratio, close to those of some hardwoods (55–75 mm). They also have acceptable Runkle ratio. Owing to their low flexibilities, their properties such as tensile, bursting strengths as well as folding endurance are negatively affected. Node fibres show, less advantages in its use for pulp and paper production due to their shorter and thicker fibre production [40].

These non-wood plants have varying physical and chemical characteristics. Some monocots such as cereal straws, sugarcane bagasse and corn stalks have been compared to the hardwoods and are found to have similar fibre fractions as contained in the hardwoods [36]. The monocots have been investigated to contain a significant proportion of very thin-walled cells, barrel-shaped parenchyma cells, and vessel with fine epidermal cells in a wide range of dimensions [36]. On the other hand, dicots such as flax straw, kenaf and hemp contain two distinct fibre types. These include; an inner core of short fibres surrounded by a layer bast fibres in which the core fibres are mainly composed. Pulping process is so tedious in these samples due to high lignin content attributed to core fibres.

3.6. Morphological and chemical properties of non-wood fibres

Morphological and chemical characteristics of non-wood fibres have an essential role in the technical aspects involved in paper production. Rousu and Rousu [41] stated that the technical issues are related to the economic, environmental and ethical contexts. Morphological is based on the cell wall characteristic from which the fibre is derived. Anatomically, plant fibres are composed of narrow, elongated sclerenchyma cells in which most of the matured fibres have well developed usually lignified walls responsible for support of the plant [23]. The length and width of the fibre are important morphological characteristics, which can be used in estimating the pulp quality of fibres. Fibres suitable for pulp and paper production possess an estimated fibre length to width of about 100:1. This is different in other fibre such as the textile fibre with a fibre length to width ratio of about 1000–1 ratio. This ratio in coniferous trees (softwood) is 60–100:1 and in deciduous trees (hardwood) it is 2–60:1 [24, 36]. The average fibre length ranges from 1 to 30 mm being shortest in grasses and longest in cotton [23]. The average ratios of fibre length to diameter range from 50:1 to 1500:1 in non-wood species. In general, stalk fibres are short, having fibre lengths and length to diameter ratios of the same order as hardwoods. They also tend to be more heterogeneous and exhibit a wider distribution of lengths and length ratio to diameter ratio of hardwoods [24]. Mostly all non-woods are composed of a lower lignin content with a higher hemicellulose content. The varying chemical composition in these non-wood plants depends on the type of soil and the growing conditions, which could involve the climatic conditions [42]. Non-wood fibres have higher silicate, nutrient and hemicellulose contents than that present in wood [43]. **Table 1** contains summarised information on essential morphological properties of various non-wood fibres for pulping.

As reported by Rousu and Rousu [41], low bulk density, short fibre length and high content of fines are most important features of non-wood raw materials. The low bulk density affects the logistic of non-wood raw materials thereby restricting the size of the mills to be considerably smaller than that of the woody materials. It was emphasised that presence of large number of fines and short length of fibres affect especially the drainage properties of the pulp and dewatering process of the paper machine. Plants like miscanthus, switchgrass and cotton stalks show shorter fibres compared to the length of fibres from kenaf and reed. Pulped fibres of miscanthus and switchgrass results in satisfactory pulp tear indices and bursting strengths for producing papers with good printing and writing purposes [40]. These properties are also applicable to kenaf bark fibres. **Table 2** shows additional common properties of non-wood plant fibres while **Table 3** depicts properties of papers produced from some non-wood plant.

The most important physical properties of non-wood fibres are the presence of short fibres ($\leq$ 2 mm) and low bulk density with a high content of fines. These properties are responsible for the drainage properties of the pulp and also dewatering in the paper machine [8]. The strength and rigidity of papers produced are affected by the lumen size and cell wall thickness of the fibres. **Table 4** shows the mechanical properties of some selected non-wood plants such as the bast fibres and seed fibres.

	Pulping Process	Pulp yield (%)	Uses	Kappa number	Length (mm)	Fibre diameter (μm)	Lignin (%)	Ash (%)	Silica (%)	Alpha cellulose (%)	Pentosans (%)	Cross & Bevan cellulose (%)
				Morphological properties			**Chemical properties**					
Stalk fibres												
Cereals												
Rice[a]	Soda[d]	40–43 39[d]	Paper		1.48	13	12–16				23–26	43–49
Rice[b]		38.8		13.6	1.48	13						
Wheat	Soda[d]	39–62 67[d*]			1.48	13	16–21	4–9	3–7	29–35	26–32	49–54
Wheat[b]	Soda[d]	46.7 50[d]		16	1.4[b]	13						
Rye					1.48	13	16–19	2–5	0.5–4	33–35	27–30	50–54
Oats					1.48	13	16–19	6–8	4–7	31–37	27–38	44–53
Barley					1.48	13	14–15	5–7	3–6	31–34	24–29	47–48
Mixed cereal straw	Lime	55–65	Coarse paper			12.9[d]						
	Lime	70–82	Strawboard									
	Soda or Kraft	44–46	Paper									
	Soda or Kraft	65–68	corrugation									
Corn[b]		50.5		23.4		18						
Cotton[b]		44.5		33		20-30						
Grain sorghum												
Hesperaloe												
Grasses												

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				Morphological properties			Chemical properties					
	Pulping Process	Pulp yield (%)	Uses	Kappa number	Length (mm)	Fibre diameter (μm)	Lignin (%)	Ash (%)	Silica (%)	Alpha cellulose (%)	Pentosans (%)	Cross & Bevan cellulose (%)
Esparto	Soda Soda[d]	45–50 52[d]	Paper		1.10		17–19	6–8	2–3	33–38	27–32	50–54
Sabai	Soda	45–50	Paper		2.08		17–22				18–24	54–57
Lemon												
Switchgrass					1.37 0.76[c]		34–36	1.5–2		43	22–24	
Miscanthus												
Reeds												
Papyrus	Soda	38–35			1.50							
Phragmites	NSSC	50–53	Paper				22				20	57
Communis reeds	Soda or Kraft	46–51 53[d***] 62[d]	Paper		1.50		22	3	2	45		
Arundo donax					1.18		21	4–6	1.1–1.3	29–33	28–32	
Elephant grass[c]					0.75[c]							
Canes												
Sugar cane (bagasse)	Soda or Kraft	60 70 63 50–52	Industrial paper Corrugating Linerboard Bleached paper		1.51[c]-1.7	20	19–24				27–32	49–62

				Morphological properties			Chemical properties					
	Pulping Process	Pulp yield (%)	Uses	Kappa number	Length (mm)	Fibre diameter (μm)	Lignin (%)	Ash (%)	Silica (%)	Alpha cellulose (%)	Pentosans (%)	Cross & Bevan cellulose (%)
Bagasse[b]		50.5		13.3	1.7	20[d]		1.5–5	0.7–3	32–44		
Bamboo	Soda	44–45	Paper		1.36–4.03	8–30	21–31	1.7–5	1.5–3	26–43	15–26	57–66
	Kraft	46–47	Paper									
		45[d]										
Bamboo[b]		45.9		24.6	2.7	14.4[d]						
Bast fibres												
Textile flax tow	Soda	60–67	Paper		28	21	10–15	2–5	<1	50–68	6–17	76–79
Seed flax tow	Soda	42–45	Cigarette paper		27	22	23	2–5		34	25	47
Kenaf	Soda or Kraft	46–51	Paper		2.74	20	15–18	2–5	<1	31–39		
Jute 1	Lime	62	Industrial paper		1.06	26	21–26	0.5–1		39–42	18–21	57–58
	soda	55	paper									
Jute 2					2	20						
Whole jute[b] plant		55.6		30.3		20						
Common hemp			Cigarette paper, Strength additives to waste paper, Light weight papers		20	22						
Leaf fibres												
Abaca	Monosulphite	60–63	Thin paper			20	9	1	<1	61	17	78
	Soda or Kraft	45–54	paper									

	Pulping Process	Pulp yield (%)	Uses	Morphological properties			Chemical properties					
				Kappa number	**Length (mm)**	**Fibre diameter (µm)**	**Lignin (%)**	**Ash (%)**	**Silica (%)**	**Alpha cellulose (%)**	**Pentosans (%)**	**Cross & Bevan cellulose (%)**
Sisal	Soda	69	Paper			17	8–9	0.6–1	<1	43–56	21–24	55–73
Seed hull fibres												
Cotton staple	Soda or Kraft		Paper			20						
Cotton linters	Soda or Kraft		Paper Dissolving pulp			21						
Cotton rags	Lime soda Soda		Paper paper									
Golpata fronds[b]		37.2		27.2	1.73	10						
Kash[b]		57.9		20	1.52	16						
Dhanicha[b]		43.3		29								
Banana stem[c]					1.55[c]							
Date palm rachis[c]					0.89[c]							
Core fibres												
Kenaf					0.6	30	17.5				19.3	
Woods												
Coniferous					3.0	30	26–34	1	<1	40–45	7–14	53–62
Deciduous					1.25	25	23–30	1	<1	38–49	19–26	54–61

[a][36], [b][2], [c][7], [d][8, 25, 29]. *uncleaned fibre, ***clean reeds, [10, 24, 44].

Table 1. Morphological properties and chemical properties of non-wood fibres [36].

Non-wood plants	Cold water solubility	Hot water solubility	1%NaOH	Lumen Diameter	Cell wall thickness	Alcohol/benzene extractives %	Bulk density (kg/m^3)
Prosopis alba		4.7	20.8				
Chamaecytisus		3	16.1				
Phragmites		5.4	34.7				
Retama monosperma		3.8	16.9				
Arundo donax		6.7					
Banana pseudo-stems		5.4					
Paulownia fortuna		9.6	31.5				
Wheat straw	5.8–11	14	41–42.8			0.5	
Rice dishes	10.6	13	49.1				
Barley fodder	16	16	47				
Rye straw	8.4	9.4	37.4				
Oat straw	13.2	15	41.8				
Sorghum stalks		21.7	41.6				
Amaranth	23.5	28	46.8				
Orache	4.6	6.5	27.5				
Jerusalem artichoke	26.6	31	48.5				
Cynara cardunculus L.		10					
Miscanthus sinensis		9.1		3.7–8.9	3.3–4.9		
Kenaf							1220–1400
Kenaf core				9.6–16.8	3.6–5.0		
Kenaf (whole)				12.7	4.3		
Date palm rachis	5.0	8.1	20.8				
Posidonia oceanica	7.3	12.2	16.5				
date palm leaves		10.8	29.9				
Switch grass				1.9–9.7	5–6	1.1	
Cotton				9.9–15.7	2.7–4.4		1550
Reed (nodes)				6.3–10.9	2.7–4.1	1.1	
Bagasse							550–1250
Hemp							1400–1500

Source: [40, 45–47].

Table 2. Additional common fibre properties of some non-wood plants.

	Density (kg/m^3)	Brightness	Tensile (kNm/kg)	Burst (Kpa)	Tear index (Nm^2/kg)	Folding endurance
Poplar	669–683.4	77.1–77.9	47.9–52.1	189–211.4	5.5–6.1	25.4–30.6
Willow	698–709.4	74.8–76.2	58–61.8	248–264.8	4.2–5	50.1–63.9
Switchgrass	824–854.8	78.1–79.1	86.4–96.4	389–415.6	5–5.6	1093–1169
Alfalfa	719.9–742.2	79.2–79.8	97.2–106.8	510–548.6	5.6–6.6	491.2–544.8

Source: [48, 49].

Table 3. Paper properties of some bleached non-wood plants.

Properties	Tensile strength (Mpa)	Specific tensile strength (Mpa)	Young's modulus (Gpa)	Specific Young's modulus (Gpa)	Failure strain (%)
Abaca	12		41		3.4
Banana	529–914	392–677	27–32	20–24	1–3
Pineapple	413–1627	287–1130	60–82	42–57	0–1.6
Sisal	80–840	55–580	9–22	6–15	2–14
Bamboo	575	383	27	18	
Flax	500–900	345–620	50–70	34–48	1.3–3.3
Hemp	310–750	210–510	30–60	20–41	2–4
Jute	200–450	140–320	20–55	14–39	2–3
Kenaf	295–1191		22–60		
Ramie	915	590	23	15	3.7
Coir	106–175	92–152	6	5.2	15–40
Cotton	300–700	194–452	6–10	4–6.5	6–8
Kapok	93.3	300	4	12.9	1.2

Source: [48].

Table 4. Mechanical properties of some non-wood fibres.

Fibres with large lumen and thin walls tend to flatten to ribbons during pulping and paper-making, thereby causing a good contact between the fibres and consequently having good strength characteristics [50]. The low bulk density of the non-wood raw materials makes it easy to access the amount of cellulose contained compared to wood raw materials. The chemical composition of the non-wood fibrous raw materials also varies over a broader range than wood (**Table 1**) [24]. Analysis obtained in the past has not produced a consistent data about the actual chemical composition of these non-wood plant materials. According to Hurter [24], plant stalks like cereals, grasses, reeds and bamboos have high pentosan contents higher than the pentosan content of hardwoods. The lignin content in some cases could be the same or lower than the content present in wood materials. In corn stalk fibres, it is reasonable to assume that lignin is the principal binding material. Delignification of this fibre result to an increment in the fineness and a corresponding decrease in the strength of the fibres. The complete removal of lignin results in the single cells that are too small to be suitable for high-quality fibrous applications [51]. Ash and silica content is high, and this is exceptionally feasible in rice straw. The high amount of hemicellulose content contributes to little stiffness and strength of fibres during paper production [52].

The chemical composition of most non-wood raw materials explains the feasibility of these materials in pulp and paper production. The fibres, which are the most valuable constituents in pulp production, are embedded within the cell walls of the plants. The amount of fibres obtained is dependent on the cell walls [44, 53]. Cellulose is the principal component of cell wall and fibre. Other parts include lignin, pectin, hemicellulose, proteins and certain minerals which are contained in the epidermal cells [53, 54]. Variations in cell walls of plant species and plant parts result in differences in pulping properties of the plant materials [33, 44]. Some of the non-wood fibre plants have properties compared to hardwoods as they contain more pentosans (over 20%), holocellulose (over 70%) and less lignin (about 15%) [55] with higher hot water solubility gotten from the easy accessibility of cooking liquors. Grasses and annual non-wood plants have lower lignin content which enables lowers the requirement of chemicals for cooking and bleaching [44, 55].

The chemical composition of some non-woody fibres used for pulp and paper production was examined in other to determine their qualities, and to improve the industrial processes in which these fibres are used as raw materials. The chemical composition of plant materials for pulp and paper production which are most commonly determined includes holocellulose (total cellulose), ethanol-benzene extractives (this contains terpenes, resins, and fatty acids), 1% NaOH extractives (low molecular weight carbohydrates), lignin, and ash content. These compositions are analysed majorly using some conventional methods which have been identified in most literature [11];

- Holocellulose: The holocellulose content of plant fibre is determined using the Norman and Jenkin's standard method. During this analysis, the dry ground raw material of 40–60mesh is prepared and extracted using alcohol-benzene combination. The known weights of the fibrous material are treated with a sequence of the mixture of hypochlorite and sulphite to remove other binding materials. High content of holocellulose contained in a plant fibre results in a high yield of pulp when extracted with suitable pulping technique.

- Ethanol-benzene extractives: The method of determination of these extractives involves the use of Soxhlet extraction of the air-dried plant materials with a combination of ethanol and benzene at 1:2 v/v for about 8 hours. This method is a standard method of analysis known as the standard Tappi method T204 om-88. Plant fibres with a high content of ethanol-benzene extractives tend to leave stains on the paper sheet during papermaking process. The presence of dyes is as a result of precipitation of these extractives upon pulping [46].

- 1%NaOH Extractives: In determining this, the standard method T212 om-88 is used. This is the most common method of analysis which has been employed. It involves the extraction of the air-dried raw materials with 1% of NaOH solution to remove and determine the low molecular weight carbohydrates. An appropriate mass of the material is then treated with hot NaOH solution (1%) for 1 hour. The extract obtained is then evaporated to dryness, and the residues are determined gravimetrically. Fibres with a higher amount of these extractives tend to produce medium to low pulp yield [46].

- Lignin: This is determined by cold treatment of dry residues from the alcohol-benzene Soxhlet extraction with concentrated sulphuric acid. Lignin is then precipitated by refluxing in diluted acid, and its content is determined gravimetrically. This method of analysis is known as the Norman and Jenkins' method.
- Ash content: This is determined gravimetrically by drying the plant material and combusting it at 525°C in a muffle furnace. This method of analysis is the TAPPI standard method T211 om-93. When the ash content determined in a plant fibre is high, there may be difficulty in refining and recovery of the cooking liquor [46].

The chemical composition varies depending on the non- wood species and the local conditions such as soil and climate, but non-wood materials have higher silicon, nutrient and hemicellulose contents than wood [43]. Owing to these reasons, non -wood materials are pretreated. Part of the leaves and non-fibrous materials may be removed, and this has a positive influence on the ash content and properties of the pulp and paper. Judt [43], explained that the chemical composition of these non-wood materials remains different from that of wood.

The qualities of the pulp to be used in paper production, depends on the morphological characteristics of the fibre obtained from the non-woody plants used as raw materials. These characteristics include the fibre length, width and some other relevant parameters, necessary for estimating pulp properties and qualities. The higher the fibre length, the higher the tearing resistance of paper. Reports made by most researchers show that flax has almost the highest fibre length [10, 24]. The fibre length contributes to the tearing strength of the paper [10]. The strength of paper also depends on the lignin and cellulose content of the raw plant materials. The pulp mechanical and tensile strength is a function of the content of cellulose present in the plant material. The physical characteristics of the fibres are influenced by the functions individual fibres have to perform in the plant itself. These functions include conduction of sap, strengthening of the stalk, and water-proofing the surface of the plants [43]. Presence of a large number of fines and short fibre length affect mostly the drainage properties of the pulp and also the process of dewatering in the paper machine. The primary components of ash content present in most non-wood fibres are the inorganic contents of the plant. This includes different metal salts such as carbonates, silicates, oxalates, silicon, magnesium, calcium, iron, manganese and potassium phosphate. Presence of ash content in vast quantities contributes to the low yield of pulp after the pulping process is carried out [52].

Fines in pulp from bamboo consist of thin-walled cells which collapse easily. The presence of these fines in the pulp tends to strengthen the fibre to fibre bonds in the unbeaten and lightly unbeaten state. These fines in bamboo pulp also give the unbeaten pulp lower freeness value than fines-free pulp. This is a different case in bagasse pulp. Fines in bagasse pulp are mostly pith elements. The wetness and the drainage time of bagasse pulp increase considerably when the number of fines from pith elements is increased. Pulps containing such fines have longer drainage time and this reduces the capacity in the filtering and washing steps of the pulp production and also lowers the paper machine capacity. Fines in pulps of both wood and non-wood fibres may be used to give the final sheet of paper a smooth surface and a high light scattering which are desired properties of paper used for printing. The yield of fibres from leguminous plants is reported [17] too low for being a source of fibre for pulp and paper production.

Report from Marques and Rencoret [10] showed that flax and hemp have extraordinary lengths of fibres as high as 2.8 mm. They have been used traditionally as primary furnish for cigarette paper (burning tube), where strength, opacity and control of air permeability are required. They are used to enhance the strength characteristics of banknote paper. Jute pulp is used for high porosity papers. Its fibre length and diameter make it suitable for finishing paper purposes. Sisal and abaca pulps have an unusually high tearing resistance and high porosity and are well suited for the production of papers with high strength and high porosity. Ibarra and Köpcke [56], reportedly characterised hemicelluloses as undesirable impurities obtained when dissolving pulps and this affects the cellulose processing ability.

4. Sources, handling, forms and preparation of non-wood materials

The handling, storage and preparation of non-wood raw materials for pulping differ in most cases from the well-established systems used for wood pulping processes. In mills using non-wood raw materials, the major drawback is the storage, handling and the process of preparing of these materials. This is because most of these plants (reeds, bamboo, and some grasses) are harvested explicitly for the aim of producing pulp and paper. The non-wood raw material preparation includes chipping (sawmill residue), digesting, washing, screening, cleaning and other processes such as depithing (when bagasse is used as raw material) before processing in the paper machine or pulp drier.

Small bamboos and reeds are handled and stored in bundles while the large bamboos are handled and stored in ranked piles as the woods are stored [24]. The harvested grasses are usually baled for transportation unlike cereals, which are baled before being transported to the mill, and are stored in bale form in large piles. Sugarcane bagasse is obtained from the sugar mills after which sugar cane is being processed, and the residue (bagasse) is collected and baled for storage. Here enlisted various forms of fibres from leaf and bast fibrous raw materials are presented. These include;

- Rags, sacking, ropes, twine and threads made from leaf and bast fibres
- Waste (tow) from the preparation of leaf and bast fibres for textile and rope production
- Waste from the actual manufacture of textiles and ropes
- The retted bast ribbons or stripped leaf fibres that are the raw materials for textile and rope manufacturing
- The whole plant

Cases whereby the whole plant is processed at the pulp mill for the production of bast fibres pulp, there is a high necessity for the removal of the bast fibrous material from the woody stem and also the removal of the leaf fibrous material from the fleshy materials of the leaves. In other cases, the separation or removal has been made, and it would not be necessary. The pulp obtained after the entire stem of kenaf plant is chipped and pulped, is composed of a mixture of both long blast fibres and short fibre pulp from the woody core [24, 25].

Large bamboos are sometimes crushed and chipped, or simply chipped in disk chippers similar to those used for wood or in large drum chippers. In other to attain more excellent results, the chippers for bamboo should be coupled with a force feed. After the chips are obtained, they are then screened stored before pulping in bins. The dust generated during the chipping process is usually collected as used as fuel in the mill boilers [24]. In most cases, reeds and small bamboos are cut in cutters similar to those used for cereal straws, but these cutters are of heavier designs. Air separation stage is required for the removal of leaves from the reeds since there are a lot of leaf materials which are attached to the stalks. This is an important process included in the reed screening system. The chips obtained from bamboo and reeds are usually stored in live bottom bins or bins with travelling screws at the bottom.

Special cutters are employed in the cutting of cereal straws, after which the cut hay is cleaned and screened by pneumatic and mechanical screening systems designed for this purposes [24]. The straws are then hammer milled using hammer mills of special designs which are used to break the bales and cut the straw to the desired length. In most cases, the straw cutting and preparation may be operated only during digester filling. Rice straw contains a lot of impurities such as dirt and leaf materials. For this reason, it is subjected to a wet cleaning stage in addition to the standard dry cleaning process [24]. The difference in the genetics of the biomass can result in variation and the quality of the pulp when the entire plants are used in the pulping process [20].

Before cooking is done in the pulp mill, separation of dust leaves and dirt is done using air fractionation. The bleaching quality of the pulp is improved by the use of mechanical pretreatment in which favours the decrease or removal of the silica and other unwanted particles from the raw material [44]. In Sweden, a dry fractionation system was developed which is composed of a shredding, chopping, milling compartment in a disc mill and also used for the screening of reed canary grass.

Bio-pulping is the treatment of lignocellulosic materials with oxidative lignin-degradation fungal enzymes before the pulping process. This is carried out to increase the strength of the paper and reduce the consumption of energy and also prevent environmental threats. It involves the use of some enzymes such as lignin and manganese peroxidase for oxidative biodegradation processes. Besides the mechanical fractionation fines (small particles other than fibres) are decreased by treating the biomass with white rot fungi (*Phobia radiate* Fr., *P. tremellosa, Pleurotus oestreatus Jacq., Ceriporiopsis subvermispora*) in oxygenated bioreactors before chemical pulping is carried out [57]. This involves the decomposition of lignin and attack of the cellulose contained in the material by fungi by the breakdown of the parenchyma cells thereby decreasing the number of fines [44].

5. Pulping processes

Alila and Besbes [58], reported that non-wood plants generally have lower lignin contents, shorter growing cycles with moderate irrigation requirements, annual renewability and a high annual yield of cellulose compared to wood. Pulping of non-wood plants is of more advantage compared to wood fibre in such that non-wood materials can be pulped with simple chemical systems (caustic soda). The alkali charge required for these materials is normally lower than what is required for wood-based raw material in which the same degree of delignification is achieved thereby reducing the energy required during this process. The pulping strategies which are commonly used for pulp extraction are categorised as mechanical, thermal, semi-chemical or wholly chemical methods. Statistical report has shown that 74.1% of the world pulp was produced using the chemical pulping techniques while 21.4% of pulp is attained by mechanical pulping process and 4.5% of the pulp is produced by using other techniques [59]. Chemical methods are mostly utilised when pulping non-wood fibres and they include Kraft, sulphite, soda, and organosolv pulping processes. The major aim to be achieved when using chemical pulping is the degradation of lignin and hemicelluloses into small water-soluble molecules which can be washed away from the cellulose fibres without depolymerising the cellulose fibres. Specific end-products are produced from a given non-wood fibrous raw material based on the choice of process such as; technique used, size of mill, the chemicals available, and their relative cost [24]. The pulping process applied in pulping of non-wood fibres (**Figure 3**) determines the quality and properties of the total yield of pulp to be obtained. This is a significant factor in considering the type of paper to be produced. Some of these pulping techniques have been in use since the ancient times and are ultimately due for improvement in other to overcome their drawbacks.

In addition to pulping techniques, special processes have been developed, and this includes the; pomilio process, the two-stage Cusi process and the NACO and the nitric acid process. In some certain cases, the lime and lime-soda techniques are often required during pulping. They are very old pulping process used in ancient times [24].

The lime or lime-soda pulping methods are usually used for the production of lower grade unbleached pulps. This process is applicable in pulping of rags and jute bast fibre in other to obtain high-grade pulps. Report from Hurter [24] showed that the use of acid sulphite process gave a poor result when used to pulp rags and jute. Most of the pulping techniques are used in pulping non-wood plant stalks and this result in the production of bleachable and high-grade unbleached pulps. The Kraft, soda and the sulphite processes are used majorly in the pulping of leaf and bast fibrous raw materials. Leaf and bast fibres have excellent pulp strength properties which are greater than softwood pulps. Of all the bast fibres, when jute pulped using the soda or Kraft method, the jute fibre strands is reduced to the ultimate fibres, and jute pulps with weaker properties compared to softwood are produced. Jute is an exceptional case of the bast fibres. The use of mild lime or sodium carbonate during pulping process, results in the production of pulp with durable, strong and hard properties. When jute is pulped using this process, long fibres are obtained with increased strength similar or greater than those of softwood pulps.

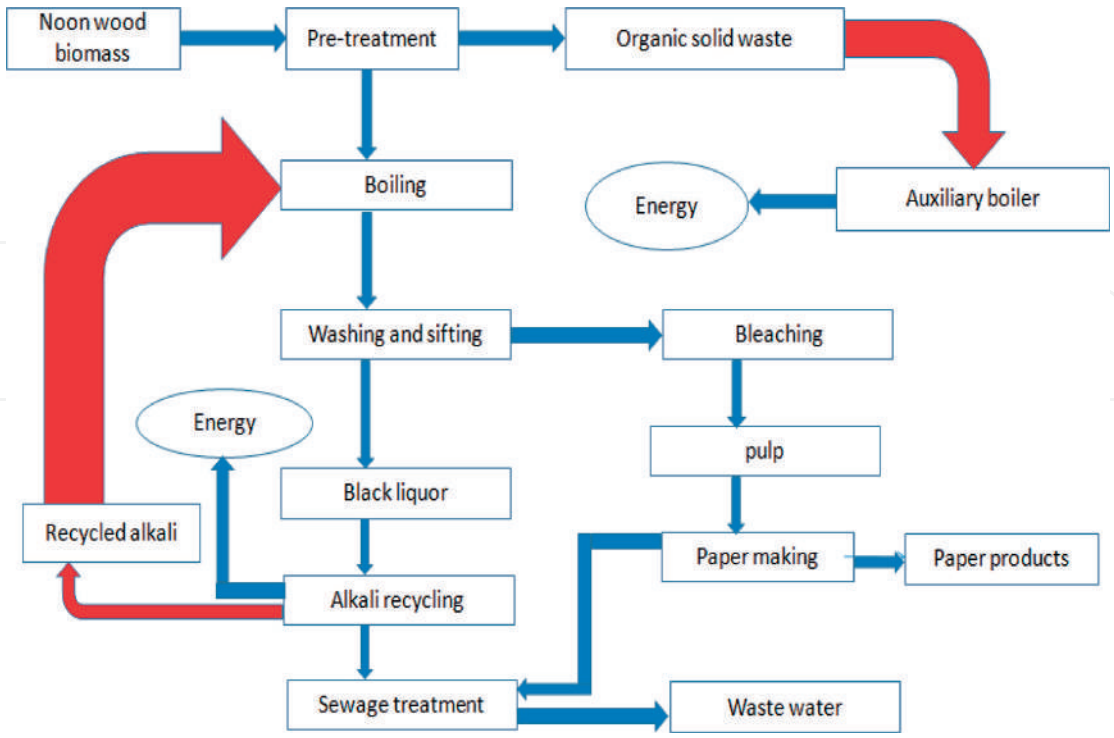

Figure 3. Process flow diagram for pulp and paper production [60].

The favourable method which could be applied in the pulping of bagasse and rice straw is the nitric acid process of pulping. This results in the production of mechanical pulps. The pomilio process has virtually been out of use due to the economic reasons. It consumes a lot of chemicals and has no feasible recovery process for these chemicals. The Kraft pulping technique has a versatile application in dealing with different raw materials coupled with superior pulp quality and more efficient recovery of cooking chemicals. Most of the world's chemical pulp is obtained using this process, and the pulp obtained by the utilisation of this technique is of low and robust brightness properties [11]. This technique is associated with easy recovery and recycling of chemicals, and this has been effective for years with the use of dissolved organics as fuel during this process. Kraft pulping method requires very efficient bleaching sequence to yield the desired level of brightness. This pulping method has been improved by the addition of anthraquinone and extended cooking in other to provide solutions to its shortcomings. Of the numerous advantages associated from the utilisation of this method of pulping, it was reported that release of malodorous and hazardous materials is associated with this pulping technique due to the bleaching process thereby resulting into water pollution [61].

The pulping of cotton is done using the soda pulping technique. Cases where coloured rags are involved, lime-soda may be used. 45–50% yield of chemical pulps was obtained during the pulping of oil palm fronds using soda pulping process [62]. The soda pulping method is also reported to be the most exciting process of pulping empty fruits bunches (EFB) when its efficacy and environmental friendliness is taken into consideration.

Production of bleachable and high-grade unbleachable pulps is highly favoured by the use of conventional Kraft or soda processes. Sulphite or biosulphite pulping process requires stainless steel pulping equipment. The recovery of chemicals using this pulping process is tedious and more complicated. Sulphite pulping is a costly method of pulping. When used in pulping of bast and leaf fibres, pulps obtained are of higher yields and good qualities.

Even though the utilisation of non-wood fibres in pulp and paper production has significant benefits, the production of non-wood pulp is problematic. The alkaline process of pulping non-wood materials results in serious environmental problems during the delignification process [41]. More sophisticated versions of the alkaline process have been developed as far as possible in other to provide a solution to the problems of chemical recovery and environmental challenges. In bigger paper mills, the recovery of alkali has not been successful because the dissolution of silicon into cooking liquor has resulted in scaling problems in liquor evaporation. In general, pulps obtained by the alkaline method of extraction are of short fibres.

Organosolv pulping method is one of the most promising alternative methods which is solvent based processed using organic solvents such as acids or alcohols; aqueous ethanol [61] as cooking materials. The major advantage of using organic solvent for lignin removal lies in the fact that such a process offers the possibilities for more efficient utilisation of the lignocellulosic feedstock. The dissolved lignin together with other dissolved components such as extractives can be recovered by simple distilling off the solvent after the digestion process [61]. In some cases, the organic solvents are mixed with alkali; for instance, methanol-NaOH in which involves two stages. The first stage is the dissolution of 20% lignin in a mixture of methanol and water at a temperature of 195°C while the second stage involves the addition of caustic soda to the mixture of methanol and water in other to get rid of the remaining lignin present in the non-wood plant material. This is carried out at a temperature of 170°C. The disadvantage of this method is that it requires additional chemical recovery process for the alkali present. Baptist [11], reported that the properties of pulp obtained by organosolv process are still being investigated and evaluated. The methanol organosolv process has been used in the alkaline sulphite-anthraquinone-methanol process (ASAM) and the soda pulping method with methanol (organocell). The ASAM process is basically alkaline sulphite pulping with the addition of anthraquinone (AQ) and methanol (CH_3OH) to achieve a higher delignification level.

The active cooking chemicals of the ASAM process are sodium hydroxide, sodium carbonate and sodium sulphite. The addition of methanol to the alkaline sulphite cooking liquor considerably improves delignification, and the process produces pulp with better strength properties, higher yields and better bleaching ability compared to the Kraft process. According to literature, four other improved pulping processes have been tested and found most promising. These four methods as reported by Rousu [41] includes; auto catalysed ethanol pulping (ALCELL), acetic pulping combined with minor amounts of formic acid (FORMACELL) [8], peroxyformic acid pulping (MILOX), formic acid pulping (CHEMOLIS). Of all these techniques listed, the Chempolis process is the only one to have survived up to the recent time. Research based on the other techniques has been discontinued. Delignification carried out using the Alcell process is carried out in ethanol-water solution at a high temperature of about 200°C. This process results in the several degraded products which include acetic acid, formic acid and furfural. Acids are applied to act as catalysts during delignification process in this pulping method. Products obtained using this process must be separated from water and ethanol, and this is done by distillation. This separation process is difficult and costly.

Acetic acid serves a dual purpose during delignification. It could serve as a solvent and as a catalyst.

The Formacell process involves the addition of formic acid to the acetic acid delignification process. The addition of these acids lowers the delignification temperature and pressure. The stronger the acids used, the higher the tendency of reducing the delignification temperature and pressure.

The primary objective of Chempolis process is to produce high-grade pulps while operating economically within the size restrictions imposed by the logistic of the raw material acquisition. Rousu [41], gave a vivid report on the improvement made on the attainment of the main goal in which this pulping process was discovered. In other words, to satisfy the process is its main purpose and serve as an alternative method of pulping of non-wood materials with reduced economic and environmental problems as recorded for the previously used pulping techniques, the design of well-defined recovery to recycling cooking chemicals and washing filtrates with no harm from silicon was required. Chlorine and sulphur-free chemicals were prioritised using this process in other to achieve an effluent free mill.

Bio pulping process is another pulping technique which has potential to overcome problems associated with mechanical manufactured pulp and decrease chemical consumption in chemical pulping operations. This technique is environmentally friendly in such that it reduces the use of electrical energy and reduces the amount of chemicals consumed thereby avoiding pollution. It was reported that bio-pulping has an economic and environmental advantage compared to the other methods of pulping. Fungus appears to be the best candidates for bio-pulping process. They are selected for rapid delignification and can demonstrate selective delignification (leaving fibres untouched).

6. Bleaching of pulps

Pulps of non-wood plants with increased content of calcium, potassium, manganese, copper, iron (which makes up the ash content) when bleached without the use of chlorine chemicals, the transition elements form radicals that react unselectively with the pulp resulting to a loss of yield and strength properties. These pulps can be bleached with oxalic acid. Calcium reacts with oxalic acid to form calcium oxalate which deposits easily. This bleaching process impedes the effluent-free operation of the bleaching plant [41]. A solution to the recovery problems encountered during pulping as reported by Rousu [41] is by omitting the recovery of cooking chemicals.

In other to avoid environmental challenges, bleaching should be carried out without the use of chlorine chemicals. This is not feasible in alkaline pulping process due to the presence of inorganic compounds. Rousu [41], suggested a temporary solution to this problem, by the separation of silicon from the liquor.

Presence of lignin and other discolouration in raw pulp makes bleaching or brightening process necessary. Bleaching process through chlorination and oxidation stages further delignify the fibres by solubilising additional lignin from the cellulose. Bleaching agents such as chlorine gas, chlorine dioxide, sodium hypochlorite, hydrogen peroxide and oxygen may be used and applied in a stepwise fashion within the bleaching sequence. Strong alkali (NaOH) is usually added between bleaching sequence to extract the dissolved lignin from the surface of the fibres. The bleaching agents used during bleaching process depends on some factors such as; relative cost of bleaching chemicals, type and condition of the pulp, desired brightness of the paper to be produced, and environmental guidelines and regulations. Chlorine is used as a bleaching agent for pulps obtained from bagasse. Bagasse requires less bleaching chemicals to achieve a bright white sheet paper [63]. In other to reduce the bleaching chemicals and the discharge of harmful chlorinated organic pollutants, oxygen delignification method of non-wood fibres is being adopted. The use of this method results in a decrease in the kappa number after cooking is done at the range of 40–50%.

Some non-wood material and extraction methods used for pulp extraction

i. **Switchgrass:** Different methods have been used for the extraction of pulp from the fibres obtained from the switchgrass. These methods include the combination of soda and sulphite pulping process and also the Kraft process. The fibres after being isolated from the plant are short fibres with low extractives and ash content. It was digested at a temperature of 170°C for 30–45 min with cooking agents in liquor to sold ratio of 6:1 of sodium hydroxide and sodium sulphite [64]. Due to the high crop yield and presence of a high level of high content of cellulose, 49% of the pulp was yielded with a kappa number of 13. Soda pulp of excellent properties was obtained which shows useful application in the production of newsprint.

ii. **Alfalfa stems:** the use of soda and soda anthraquinone (AQ) pulping and also Kraft and Kraft (AQ) methods of extraction at a temperature of 170°C resulted to the production of pulps with economic advantage over traditional pulpwood [49]. The digestion process of alfalfa stems with an average fibre length of 0.78 mm was carried out using 18% alkali level and 25% sulphidity with a biomass ratio of 10:1 for 40 min.

iii. ***Hesperaloe funifera*:** This is composed of a little lignin and large content of α-cellulose. It has fibres with good morphological characteristic. Soda anthraquinone pulping was the major pulping process used to isolate pulp from the fibres. This was performed at a temperature range between 155 and 180°C with the use of soda having concentrations varying between 5 and 15%. The pulp obtained has a vast application, and it is a potential raw material for paper making [65].

iv. **Rice straw:** Rice straw has been pulped using various pulping techniques. Of all these techniques, the highest yield of pulp (42.82 wt%) was obtained with the use of potassium hydroxide. Fibres such as straw are currently not optimal to be used on a 100% basis for papermaking. This is due to the poor drain ability and low tearing strength. Shortcoming from the utilisation of straws includes the high content of silica, low bulk density and the higher water retention capacity of the straws.

v. **Kenaf:** There are two kinds of Kenaf fibres with distinct characteristics. They are the long bark fibres and the short core fibres. Pulp obtained from the kenaf bark fibres are utilised in the production of paper with an increased mechanical strength which is suitable for writing, printing, wrapping and packaging purposes. On the other hand, pulps obtained from the short core fibres are shorter and thicker thereby producing poor slenderness ratio, which induces reduced tearing resistance of paper but having a high tensile and burst strength [59]. This is probably due to the weak surface contact and also a weak fibre to fibre bonding which is a major characteristic of short and thick fibres [40]. The whole stem of kenaf could be isolated to produce pulp of good quality and strength with practical and economic advantages. Pulp obtained from the whole kenaf stalk is mostly efficient in the production of newsprint paper of excellent quality. Utilisation of conventional soda and Kraft pulping of the whole kenaf plant yields pulps with high strength properties. A recent report from Sabharwal, Akhtar [59], demonstrated that blends of 82–95% kenaf chemo-thermomechanical pulp with 5–18% Kraft pulp could produce commercial grade newsprint. Kenaf possesses several advantages over wood pulp. It requires less energy to pulp and produces naturally bright pulp due to the absence of lignin. Newsprint produce from kenaf pulp do not become yellow with age and exposure to light

vi. **Palm fronds:** The utilisation of sulphite pulping in isolation of pulps from oil palm fronds using a high dose of sodium sulphite under slightly alkaline conditions failed to yield pulps with acceptable yield and papermaking properties. According to Wanrosli et al. [62], the reasons for this inefficient sulphite treatment were not clear. It was assumed that the chemical nature of the raw material might have caused liquor impregnation problems. However, pulping of oil palm fronds using soda pulping method resulted in an increase in yield of pulps. The pulp obtained using the soda pulping is of high yield (44%) with excellent strength properties compared to those of hardwoods.

vii. **Bagasse:** the most suitable method of pulping bagasse is the soda pulping technique using sodium hydroxide only. This enables the extraction of sulphur-free pulps. Addition of pulping additives such as anthraquinone in bagasse soda pulping improves pulp yield and delignification rates [66]. In other to avoid wastage of chemicals and minimise ash or silica content in pulps obtained from bagasse, effective depithing is required. Silica can be removed by precipitation from black liquor by partial acidification with carbon dioxide from flue gasses or by addition of calcium oxide.

viii. **Jute:** fibres obtained from the bark of the jute plants produces pulps of good quality with a yield above 60%. It has paper making properties similar to that of softwood materials [2]. Pulp from jute fibres could be used in production of increased quality. The addition of anthraquinone of amine in soda liquor results in the production of excellent quality pulps. Utilisation of the whole jute plant for pulping results in pulp yield of about 45–55% with a good kappa number (gives a measurement for the lignin content relevant for the bleaching ability of pulp) of about 20–35. Jute stick contains high lignin and has short fibre length, hence pulp produced from whole jute plant shows higher tensile but moderate tear strength compared to jute fibre pulp.

ix. **Bagasse:** Pith in pulping of bagasse result in difficulties during pulp washing and clogging of machine. This was reported by Jahan and Gunter [2]. It was emphasised that adequate removal of pith during bagasse pulping result in the production of satisfactory pulp, and this also prevents the wastage of chemicals. The removal of pith is possible with either dry or wet bagasse. Bagasse pulps are usually soft and smooth and have been applied in the production of paper grades suitable for writing, printing, tissue grade, corrugating medium and newsprint.

x. **Corn stalks:** Corn stalks have been analysed according to Jahan and Gunter [2], and it has been made feasible that the papermaking properties of pulps obtained from this non-wood plant materials are very useful and efficient with a high water retention ability (due to the high content of fine contained). However, pulp obtained from the corn stalk fibres has lesser tear strength properties. Pulping process of corn stalk fibres produces 50% pulp yield. The application of the alkaline sulphite anthraquinone methanol process improves the bleaching ability of the pulps obtained from the corn stalk. Research on the soda-anthraquinone method of pulping corn stalk has shown higher yield in the pulp yield production and also the kappa number of the pulp [67, 68].

xi. **Kash:** The pulp yield obtained from kash is very high with a low kappa number. Pulp yield from kash is very high and its papermaking properties are comparable to that of tropical hardwood [69]. It has an initial brightness which is suitable for newsprint. The pulp yield obtained is between 56 and 58% [68, 70].

xii. **Dhaincha:** the pulp yield obtained from the fibre of dhaincha is between 42 and 44%. The papermaking properties are prospect of the chemical and morphological properties of this non-wood material. It has a higher slender ratio which facilitates the production of pulp with better tear strength than other similar fibre length material. It has similar papermaking properties to hardwood. The unbleached pulp of dhaincha is highly suitable for packing paper. In other to increase the tear index of the dhaincha pulp, pulp obtained from jute fibre is added [2, 70].

xiii. **Cotton stalks:** anatomically, cotton stalks are similar to hardwood. The pulp yield is about 40–45%, and the kappa number obtained using the soda-anthraquinone process is within the range of 30–35. Pulp from cotton stalk has good papermaking properties with high tensile strength and low tear index [71]. Blended cotton stalk pulps with jute pulp as well as bagasse pulp produce an improved tear index and other properties [2, 72].

xiv. **Golpata fronds:** The chemical and morphological properties of golpata fronds are compared with some non-wood and hardwood raw materials [73]. The anatomical properties showed that the vascular bundles in golpata fronds are very low. Pulp yield from this non-wood material is very low (37%) compared to other non-wood materials such as bamboo, rice straw, whole jute plants.

7. Problems associated with the utilisation of non-wood plant fibres

The use of non-wood biomass is a feasible alternative to wood in pulping regarding environmental conditions, income produced, variety products obtained availability and cost efficiency. This view is although popular but has certain inherent drawbacks [25]. Majority of these problems are technological that require improvement. In some cases, the drawback is as a result of the composition of the non-wood fibres. For instance, plants with higher mineral contents require further processing before pulping can occur. They make pulping process tedious and produce pulp of lesser quality. Few amongst these problems are discussed as follows:

i. **Availability:** Due to the bulkiness of agricultural residue, the handling of these materials is challenging. There is need to develop efficient bailers in other to increase the density of the materials for efficient handling, transport and storage [25]. Aside the bulkiness, there is a low yield of the raw materials per hectare of land and this result in insufficient supplies. The yield of most of these raw materials per hectare is low, and this affects the production. As a result of this, they need to be collected over a large area to meet the needs of paper mill [25].

ii. **Storage and handling:** Most of the non-wood raw materials are annual plants, and they have short harvesting periods. Most of these materials are stored for the rest of the operating year in which it deteriorates, thus limiting the yield required for paper production. As reported by Chandra IV [25], it is evident that efficient storage methods need to be developed to prevent or reduce deterioration of non-wood raw materials. Deterioration of these non-wood raw materials tends to reduce pulp yield and also limit the production of paper. The problem of deterioration is most peculiar with sugar cane bagasse. This occurs as a result of the action of undesirable microorganisms which aid the biodegradation process of bagasse. Presence of residual sugar, heterogeneity of tissues, and environmental conditions facilitate the growth of microorganisms in bagasse piles. The biodegradation process results in the chemical degradation (this is the consequence of biochemical reactions) and discolouration of bagasse thereby reducing pulp yield. The efficient depithing method has been a major boost in bagasse pulping process. Straw is also prone to microbial degradation and decay when stored with high moisture content contained in it.

iii. **Pulping:** Most of the non-wood plants have high silica content, and this has resulted in several problems during washing and yield of pulps. The difficulty in washing is as a result of poor drainage of pulp and high viscosity of black liquor. For this reason, pulps obtained from non-wood materials are washed using washers twice the normal size. The lime-alkali-oxygen pulping process has been developed further to favour the washing process of these pulps. When lime is added to the cooking liquor, silica reacts to form calcium silicate, which is insoluble in water and high content in the black liquor results in various problems in the chemical recovery loop. These problems include; formation of glassy materials, the formation of colloidal gels, hard scales in the evaporator. The anthraquinone pulping method has been developed to improve pulp yield by 5% and kappa number by up to 5 [25]. Due to the low density of crops, in other to favour the pulping of non-wood fibres, they need more pulping liquid and more volumes in process equipment. Pollution from non-wood fibre mills can be up to 20 times that from wood pulp mills.

iv. **Bleaching:** Owing to the rapid discolouration during storage of these materials, most of them have low initial brightness. Bleaching of bagasse and other non-woody fibrous raw materials have proved much difficulty.

v. **Paper production:** paper machines are run at low speeds to prevent the destruction of the machine. This is because most non-wood materials take a long time during drainage. Fibres with low wet strength are not easy to be picked up on the couch during papermaking [25]. Some of these fibres are being blended with some certain amount of wood pulp in the furnish in other to improve the run ability in the paper machines. Technically, in other to obtain the necessary quality profile and run ability of bagasse-based newsprint, 15–20% of chemical pulp must be added to the furnish. Paper machines running on bagasse must also operate at lower speeds than those of wood fibre machines.

vi. **Chemical recovery:** Most of the non-wood paper mills almost never had a chemical recovery system. Large mills, where chemical recovery is practice, have their problems. Black liquors from non-wood fibre pulping typically have viscosities 10 times higher than Kraft liquor from pine, for example, so they are hard to handle at high solid contents. This high solid content, also causing trouble in evaporators, recovery boilers, causticizing equipment, and lime kilns. Scale formation in the evaporator tubes, deposits on the furnace walls of the recovery boilers, slow setting rates of recausticizing white liquor and lime sludge unsuitable for reburning (calcination) are also problems that need to be addressed [25].

8. Conclusion

In order to reduce the effects of environmental hazard, induced by imbalance in the ecosystem due to deforestation, the use of non-wood biomass is an option that can be adopted by paper mills. Non-wood biomasses such as agricultural residues and annual crops have amenable properties appropriate in the production of pulp and papers of high quality. They have similar characteristics to those obtained from paper woods. Non-wood biomasses are readily available and are cost-effective compared to wood materials. Development of efficient pulping and bleaching processes is required for easy production. Majority of the non-wood fibres have almost similar chemical and morphological properties of wood fibres. This makes them efficient and useful in the production of pulp with required qualities and for speciality papers. Fibres with higher lignin content are not readily pulped and therefore produce pulps with low yield.

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