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Chapter 1

Pulping and Papermaking of Non-Wood Fibers

Zhong Liu, Huimei Wang and Lanfeng Hui

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].
Around the world, multitudinous non-wood fibers are used in the field of pulp and paper-making, 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.
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.

<table>
<thead>
<tr>
<th>Items</th>
<th>Softwood</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>The first stage of lignin removal</td>
<td>The initial stage of lignin removal</td>
<td>The main stage of lignin removal</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>&lt;140</td>
<td>&lt;100</td>
</tr>
<tr>
<td>The removal rate of lignin/%</td>
<td>20–25</td>
<td>60</td>
</tr>
<tr>
<td>The dissolution rate of hemicellulose/%</td>
<td>—</td>
<td>45</td>
</tr>
<tr>
<td>The second stage of lignin removal</td>
<td>The main stage of lignin removal</td>
<td>The supplementary stage of lignin removal</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>140–170°C and the earlier stage of heat preservation</td>
<td>100–160</td>
</tr>
<tr>
<td>The removal rate of lignin/%</td>
<td>60–70</td>
<td>25–28</td>
</tr>
<tr>
<td>The dissolution rate of hemicellulose/%</td>
<td>—</td>
<td>9</td>
</tr>
<tr>
<td>The third stage of lignin removal</td>
<td>The stage of residual lignin removal</td>
<td>The stage of residual lignin removal</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>The later stage of heat preservation (170°C)</td>
<td>Heat preservation at 160°C</td>
</tr>
<tr>
<td>The removal rate of lignin/%</td>
<td>10–15</td>
<td>5–10</td>
</tr>
<tr>
<td>The dissolution rate of hemicellulose/%</td>
<td>—</td>
<td>2–3</td>
</tr>
</tbody>
</table>

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.
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.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Fiber length (mm)</th>
<th>Fiber diameter (μm)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giant reed [12]</td>
<td>1.2</td>
<td>15</td>
<td>49.8</td>
<td>24–25</td>
<td>—</td>
</tr>
<tr>
<td>Rice straw [13]</td>
<td>0.5–1.4</td>
<td>8–10</td>
<td>28–36</td>
<td>23–28</td>
<td>12–16</td>
</tr>
</tbody>
</table>

Table 2. The fiber properties of grass fiber materials.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Fiber length (mm)</th>
<th>Fiber diameter (μm)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute [11]</td>
<td>2.0–2.5</td>
<td>20</td>
<td>57</td>
<td>15–26</td>
<td>16–26</td>
</tr>
</tbody>
</table>

Table 3. The fiber properties of bast fiber materials.
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 paper-making. Its relative properties are shown in Table 4.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Fiber length (mm)</th>
<th>Fiber diameter (μm)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>20–30</td>
<td>20</td>
<td>95–97</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cotton linter</td>
<td>0.6–3.0</td>
<td>20</td>
<td>90–91</td>
<td>—</td>
<td>3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Fiber length (mm)</th>
<th>Fiber diameter (μm)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
</table>

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

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 paper-making. 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 hemicelulose) 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, Na₂CO₃, 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 Na₂CO₃, 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$_2$S. 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$_2$S 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.](image-url)
4.1.3. Other alkaline pulping methods

4.1.3.1. NACO pulping

NACO method is developed from alkaline-oxygen pulping. At present, some pulp and paper-making mills have used NACO to produce straw pulp. The main principle of the NACO method is to remove the lignin in the Na$_2$CO$_3$ 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.

4.1.3.2. 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$_2$SO$_3$ prepared by dissolving SO$_2$ in Na$_2$CO$_3$ solution. With buffer function, the Na$_2$CO$_3$ 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$_2$SO$_3$ 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
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$_2$SO$_3$ 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.
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 \( \beta \)-ether bond is more important than that of \( \alpha \)-ether bond. In contrast, in the alkaline organic solvent cooking process, the cleavage of \( \alpha \)-ether bond in lignin is the most important reaction, but the cleavage of \( \beta \)-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 \( \text{NaOH}, \text{Na}_2\text{CO}_3 \) and \( \text{Na}_2\text{SO}_3 \). 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$_2$CO$_3$ 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.](image1)

![Figure 8. The flowchart of ALCELL pulping.](image2)
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$_2$SO$_3$ and NaOH. Therefore, the amount of Na$_2$SO$_3$ 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$_2$O$_2$ 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$_2$O$_2$, with the addition of DTPA, magnesium salts or silicates as inhibitors to reduce the decomposition of H$_2$O$_2$.

The typical APMP pulping consists of two segments: (1) steaming of raw materials after impregnation by chelating agent, residual alkali and H$_2$O$_2$; (2) impregnation by alkali, H$_2$O$_2$ and chelating agent to remove the metal impurities in raw materials.

<table>
<thead>
<tr>
<th>Pulping methods</th>
<th>Extrusion pulping</th>
<th>explosion pulping</th>
<th>APMP</th>
<th>APMP</th>
<th>APMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>Wheat straw</td>
<td>Bagasse</td>
<td>Wheat straw</td>
<td>Kenaf</td>
<td>Bagasse</td>
</tr>
<tr>
<td>Dosage of Na$_2$SO$_3$/%</td>
<td>-</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dosage of NaOH/%</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Dosage of H$_2$O$_2$/%</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>140</td>
<td>190–210</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>Reaction time/min</td>
<td>120</td>
<td>1–4</td>
<td>-</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Fine pulping yield/%</td>
<td>-</td>
<td>60</td>
<td>84</td>
<td>-</td>
<td>71</td>
</tr>
<tr>
<td>Beating degree/°SR</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>56</td>
<td>20</td>
</tr>
<tr>
<td>Tensile index /N·m·g$^{-1}$</td>
<td>-</td>
<td>56</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Burst index /kPa·m$^{-2}$·g$^{-1}$</td>
<td>2.41</td>
<td>3.00</td>
<td>-</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>Tear index /mN·m$^{-2}$·g$^{-1}$</td>
<td>3.2</td>
<td>5.7</td>
<td>-</td>
<td>4.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Brightness /%</td>
<td>-</td>
<td>-</td>
<td>50.0</td>
<td>53.2</td>
<td>72.1</td>
</tr>
</tbody>
</table>

Table 6. The conditions of chemical pretreatment and the properties of chemi-mechanical pulp.
4.1.3. 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$_2$SO$_3$, 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.](image-url)
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.

<table>
<thead>
<tr>
<th>Pulp species</th>
<th>Sieve diameter /mm</th>
<th>Feeding concentration /%</th>
<th>Fine pulp concentration /%</th>
<th>Pulp residue concentration /%</th>
<th>The rate of rejects /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reed pulp</td>
<td>1.0–2.0</td>
<td>0.8–2.0</td>
<td>0.6–1.5</td>
<td>1.0–2.0</td>
<td>2–4</td>
</tr>
<tr>
<td>Wheat straw pulp</td>
<td>1.0–1.8</td>
<td>0.6–1.6</td>
<td>0.5–1.0</td>
<td>1.0–1.8</td>
<td>4–6</td>
</tr>
<tr>
<td>Bagasse pulp</td>
<td>1.0–1.6</td>
<td>0.6–1.2</td>
<td>0.5–1.0</td>
<td>1.0–1.8</td>
<td>4–6</td>
</tr>
</tbody>
</table>

Table 7. The screen conditions of centrifugal screen.

**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.

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

Annotation: C- chlorination (Cl₂); E- alkali extraction (NaOH); H- hypochlorite bleaching; D- chlorine dioxide bleaching; P- hydrogen peroxide bleaching (H₂O₂ + NaOH); O- oxygen bleaching (O₂ + NaOH); Q- chelating treatment (EDTA,DTDPA,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,
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 a 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.

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

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

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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