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Pulp and Paper Processing

Edited by Salim Newaz Kazi

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Meet the editor

Salim Newaz Kazi, Ph.D., is an Associate Professor in the Department of Mechanical Engineering, Faculty of Engineering, University of Malaya. He has 18 years of engineering service experience in petrochemical industries and chemical plants where he worked as a senior engineer and as Head of engineering and construction. He worked as a part-time consultant for different international consulting companies, working in a consulting team for gas pipeline layout and installation, gas drilling environment management, air conditioning, chemical plant design and installation, vibration analysis for machinery protection, plant maintenance, etc.

Dr. Kazi has an academic background with a B.Sc. in Engineering (Mechanical), an M.Sc. in Engineering (Mechanical), and an M.Eng. (Mechanical) and Ph.D. (Chemical and Materials Engineering) in Heat Transfer and Fouling Mitigation. He received his Ph.D. degree from the University of Auckland in 2002. He started his service in the University of Malaya in 2009. He introduced sophisticated research approaches on heat transfer to two-phase flow and particle characterization, heat exchanger fouling and corrosion mitigation, separation flow, nanofluid synthesis and application as heat exchanging liquids. He has developed his laboratories to full-blown research laboratories. Later he acquired government grants for research and then became leader of a group of academics for research and innovation.

So far Dr. Kazi has completed supervision of 18 Ph.D. and 12 Master's theses. He has published 200 technical papers in national and international journals and conference proceedings, and has also published 9 technical book chapters and edited 3 engineering books. He has participated in 26 engineering international conferences, congresses and a facilitated workshop in the Malaysian Institute of Engineers. He has given a keynote speech and a speech as an invited speaker at Liverpool John Moores University in 2016 and Yildiz Technical University at Istanbul in 2017, respectively. Dr. Kazi has filed a number of patents and a number of others are in progress. He received a number of awards in recognition of his contribution to research and innovation. He is an active member of the editorial board of a few international journals and has evaluated many Ph.D. and Master's theses as an examiner. He has developed an active research network both at home and abroad, which contributed to upgrade the name and fame of the university where he works.

Contents

Preface

In the modern age, the use of paper as a commodity reflects the development of a nation. With the progress of the national economy the consumption of paper has increased at a faster rate. Raw materials, environmental issues, and cost of paper production have become a concern for paper producers. Due to the rise in paper demand and production, alternatives to wood as a source of paper raw materials have become prominent. Varieties of non-wood raw materials, including kenaf, rice straw, empty fruit bunches of palm trees, bamboo, bagasse, etc., are now being seriously considered. The process of fiber treatment also varies to meet environmental demands. Considering contemporary issues, a number of chapters in this book analyze the processing of wood fibers and non-wood fibers as raw materials. The effect of processing to improve paper quality and different by-products of paper production for multiple applications are also considered in this book.

In this text, Zhong Liu et al. (Pulping and Papermaking of Non-Wood Fibers) subdivide the main raw materials for pulp and paper making into three categories: wood, non-wood, and non-plant (mainly waste paper), of which non-wood fiber material is an important fiber source as an alternative to forest-sourced wood used for paper making. They reiterate that the use of non-wood fibers is an attractive alternative to the different sources of materials for pulp and paper manufacturing. Recognized non-wood fiber resources are grasses, cereal straws, corn stalks, bamboo, bagasse, etc., but there are other non-wood sources such as flax, hemp, jute, kenaf, cotton, sisal and abaca with properties as good as or much better than softwood materials.

Alejandro Rodríguez et al. (Different Solvents for Organosolv Pulping) studied organosolv pulping and reported that it is a two-stage process involving hydrolysis (decomposition of wood using a catalyst) and removal of lignin with an organic solvent (usually a mixture of alcohol and water). They note that common solvent alcohol has a low boiling point, which requires operating at a high pressure and hence uses special equipment that is expensive to purchase and operate. Later, the authors recommend alternative organic solvents that afford operation at pressure levels similar to those of classic pulping processes (e.g., the Kraft process). The chapter provides a comprehensive literature review on organosolv-based production of cellulose pulp by using alternative solvents such as glycols, phenols, esters, organic acids, acetone and amines.

Mayowa Akeem (Pulping of Non-Woody Biomass) notes that the use of trees for paper production is contributing to the problem of deforestation with radical negative impact on the environment by introducing imbalance to the ecosystem. Enhancement of demand and consumption of paper could only induce depletion of woods used for paper production, which eventually could limit the availability of raw materials. The author emphasizes that the non-wood biomass is easily accessible and can serve as raw materials in pulp and paper industries for producing the same or better qualities of pulp and paper than those obtained from wood.

Ahmed Koubaa et al. (Effect of Press-Drying Parameters on Paper Properties) explore the alternatives that can improve the internal bond strength (IBS) of paper by pulp refining and paper press-drying (PD). They study the improvement mechanisms of IBS and their impact on the strength development of high-yield pulps. In the experimental investigation, four pulp types were used (one spruce thermomechanical (TMP) and three chemithermomechanicals (CTMP) from spruce, birch and aspen). Refining of fiber changes its surface properties, thereby promoting mechanical adhesion. PD temperatures soften the fibers and change their surface chemistry, while PD pressures improve the contact area between fibers, which ultimately improve IBS to a large extent, and vary the paper properties. Compared to air-dried paper, PD paper showed much higher properties for most tested pulps at all refining levels. These results are due to the increase in bonded areas. The authors say that the impact on paper properties is less important in press-dried paper than in air-dried paper.

Elżbieta Mikołajczak et al. (The Value and Profitability of Converting Sawmill Wood By-Products to Paper Production and Energy Generation—The Case of Poland) investigate in depth the production of wood-based products and paper, and the derivatives, recovery and recycling of key raw materials and their value and profitability of production. They give emphasis to sawmill wood by-products for multipurpose applications. In Poland these by-products may be considered as briquettes, pellets, or be used for fuel. They say that a significantly higher increase in the value of further processed sawmill by-products could be achieved by entrepreneurs who process them at the place of their conversion without incurring any additional cost of transport.

Guangjun Gou et al. (Environmentally Friendly Method for the Separation of Cellulose from Steam Exploded Rice Straw and Its High Value Applications) formulate the separation of cellulose from agricultural straw. They describe at least three environmentally friendly ways for separating cellulose from agricultural straw pretreated with steam explosion, which includes delignification with recyclable water-polar aprotic organic solvent, selective bio-degradation of the lignin component, and extraction of cellulose with imidazolium-based ionic liquids from the steam-exploded rice straw. They report that the new non-derivative solvent for cellulose, tetrabutylammonium hydroxide (TBAH) aqueous solution with urea as additives, has been proved to be manipulable for dissolving cellulose. They recommend the isolated cellulose fiber from rice straw as the reinforcement material for the advanced mechanical property of composites where the cellulose/cement composites show a remarkable improvement in flexural strength and fracture toughness.

Finally, I highly appreciate the management at IntechOpen for their immense support while editing this book. I would like to dedicate this book to the living memory of my parents and want to thank my family members, my son Mehrab Newaz and my wife Nilufa Parveen for encouraging and supporting me all the way.

Thanking you.

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Section 1

Paper Processing and Improvement of Paper Quality

Pulping and Papermaking of Non-Wood Fibers

Zhong Liu, Huimei Wang and Lanfeng Hui

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].

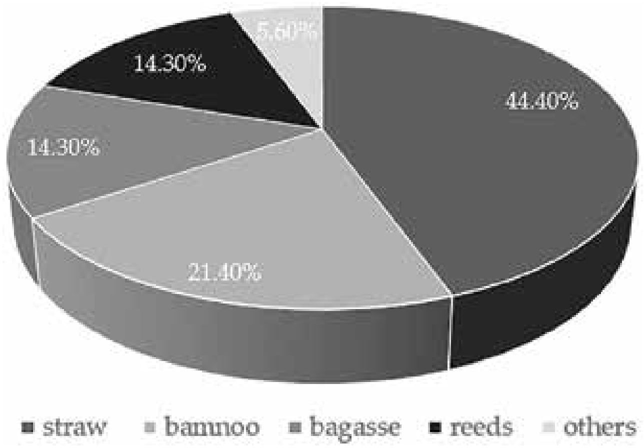

Figure 1. The ratio of non-wood pulp in paper production [5].

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.

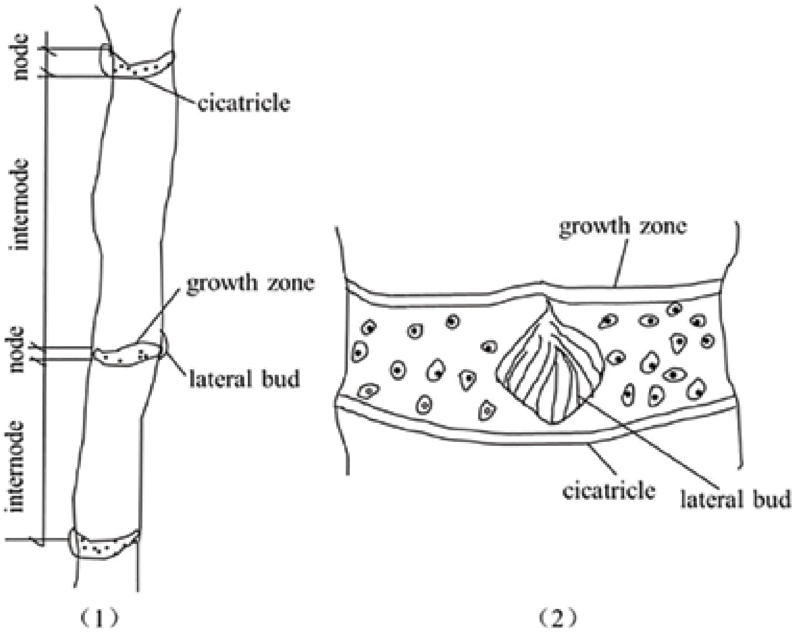

Figure 2. The structure of straw: (1) the composition of straw and (2) the structure of node.

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

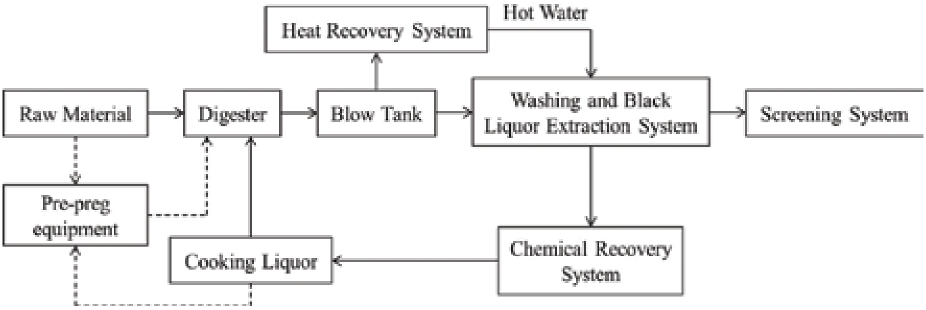

Figure 3. The flowchart of alkaline pulping.

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**.

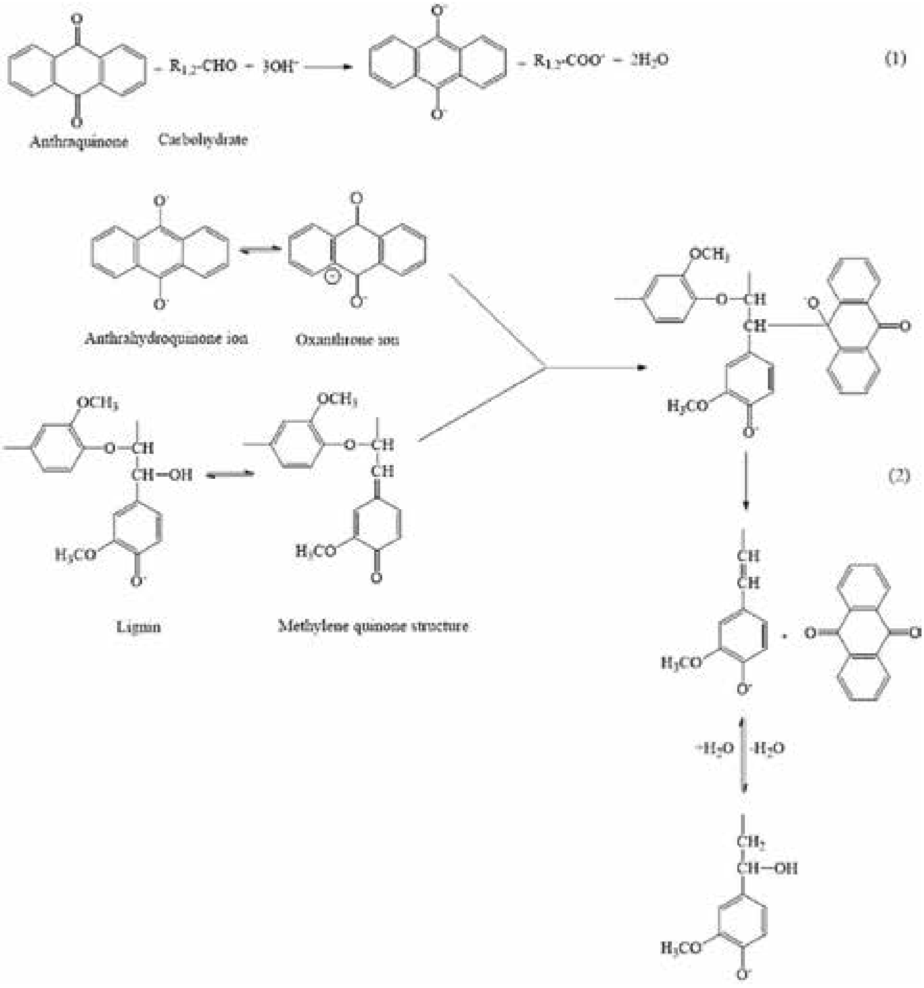

Figure 4. The reaction mechanism of anthraquinone with carbohydrates and lignin: (1) the reaction of anthraquinone with carbohydrates; (2) the reaction of anthraquinone with lignin.

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.

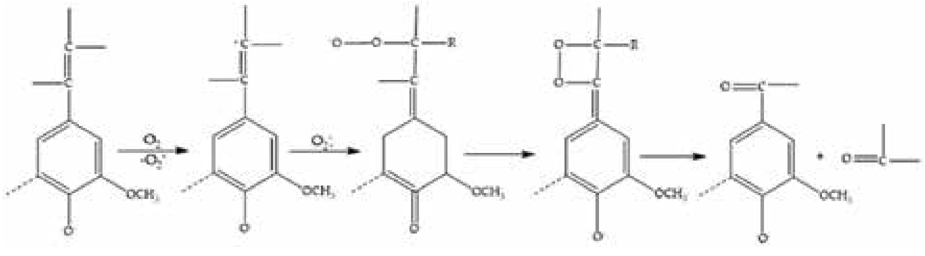

Figure 5. The reaction between oxygen and phenol-type lignin.

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

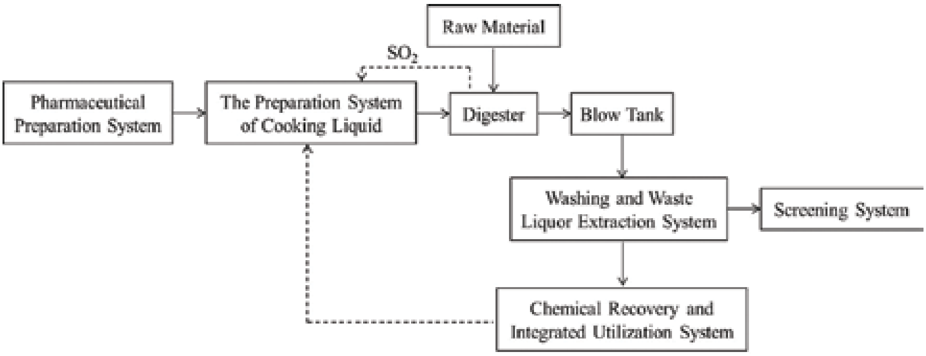

Figure 6. The flowchart of sulfite pulping.

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.

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

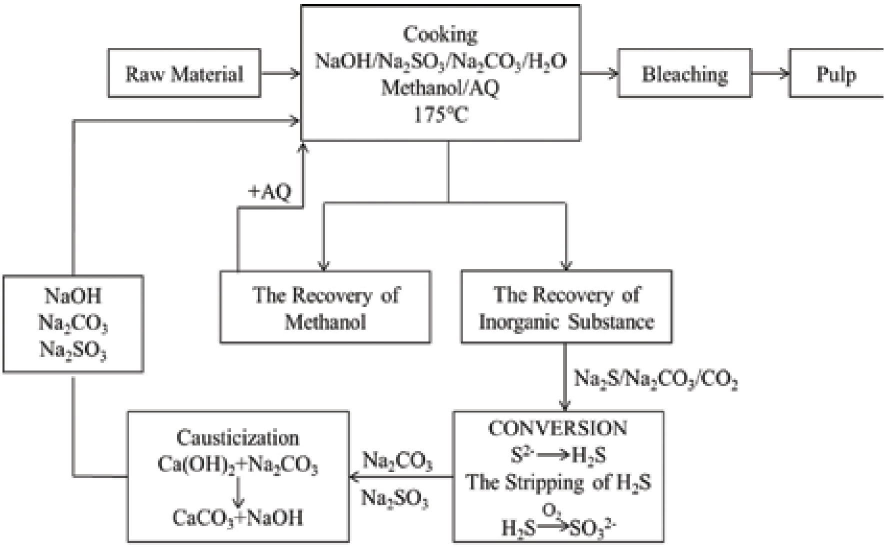

Figure 7. The flowchart of methanol pulping.

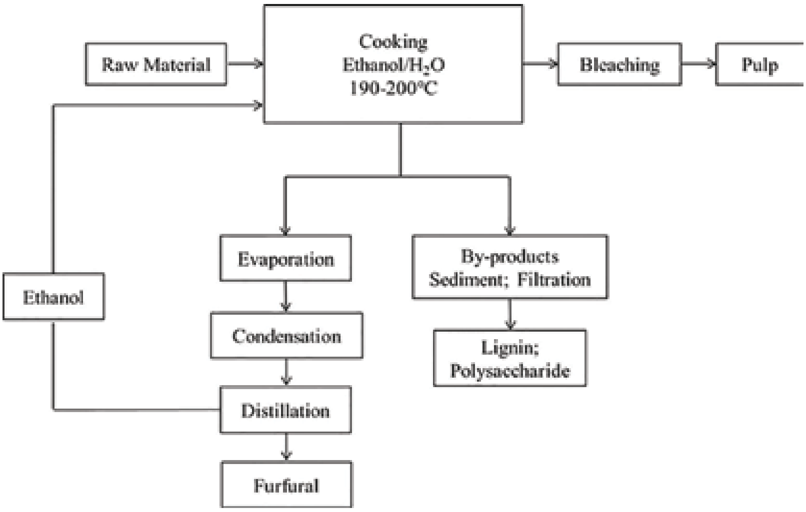

Figure 8. The flowchart of ALCELL pulping.

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.

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.

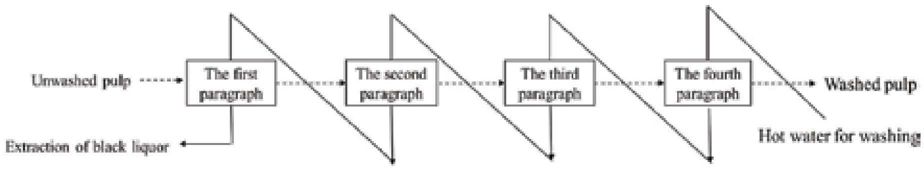

Figure 9. Four-stage washing process of multistage countercurrent washing method.

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,

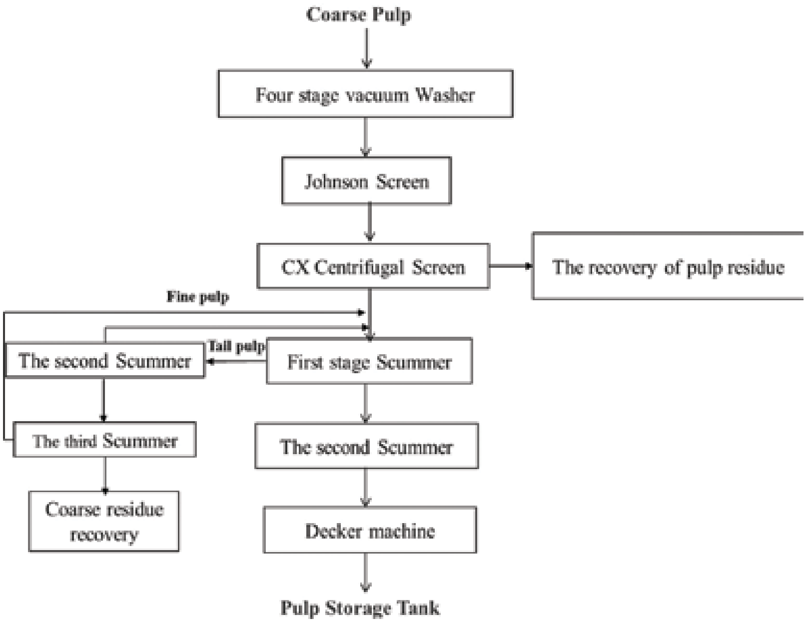

Figure 10. The flowchart of washing, screening and purification process of wheat straw pulp.

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,

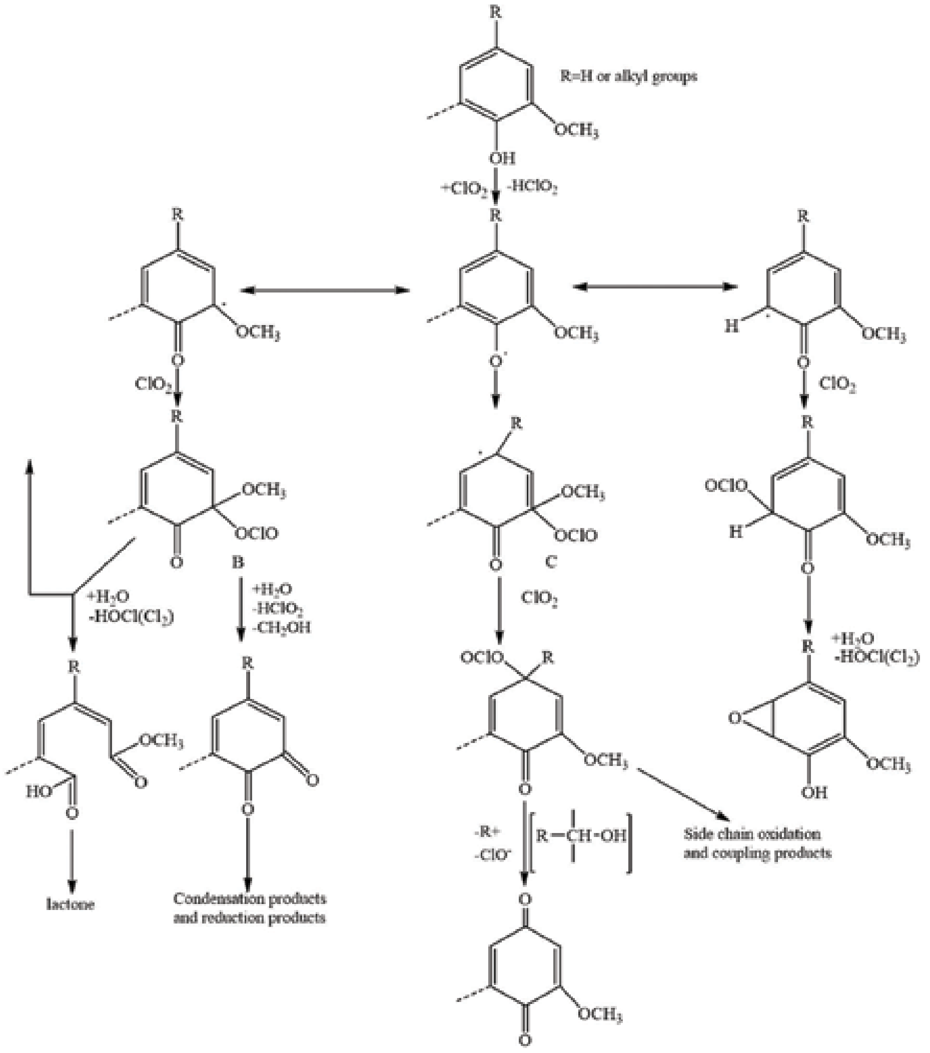

Figure 11. The reactions between phenol-type lignin and chlorine dioxide.

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 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.

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.

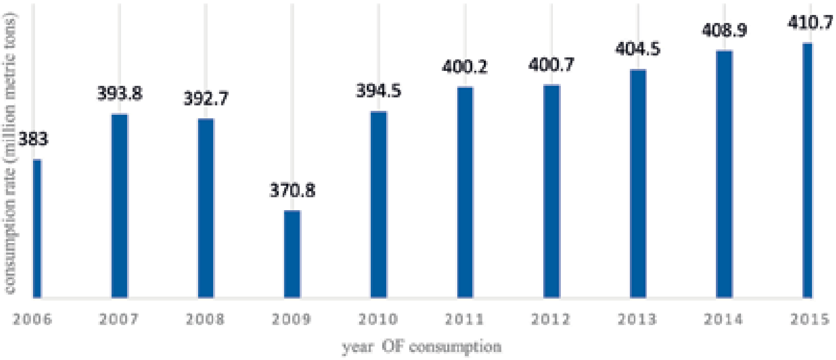

Figure 1. Global consumption of paper and cardboard from 2006 to 2015 (in million metric tons). Source: [5].

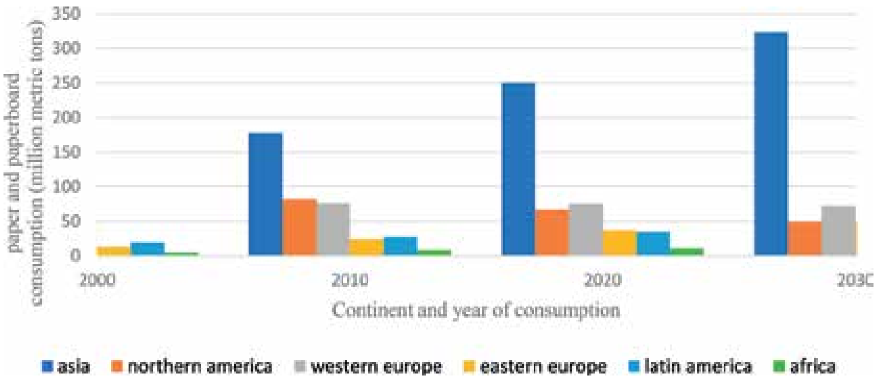

Figure 2. Paper and paperboard consumption in 2000 and 2010 and projections to 2020 and 2030 (in million metric tons). *Source:* [6].

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 (≤ 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.

				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 (%)
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												

				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									

				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 (%)
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			21						
			Dissolving pulp									
Cotton rags	Lime soda		Paper									
	Soda		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 papermaking, 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.

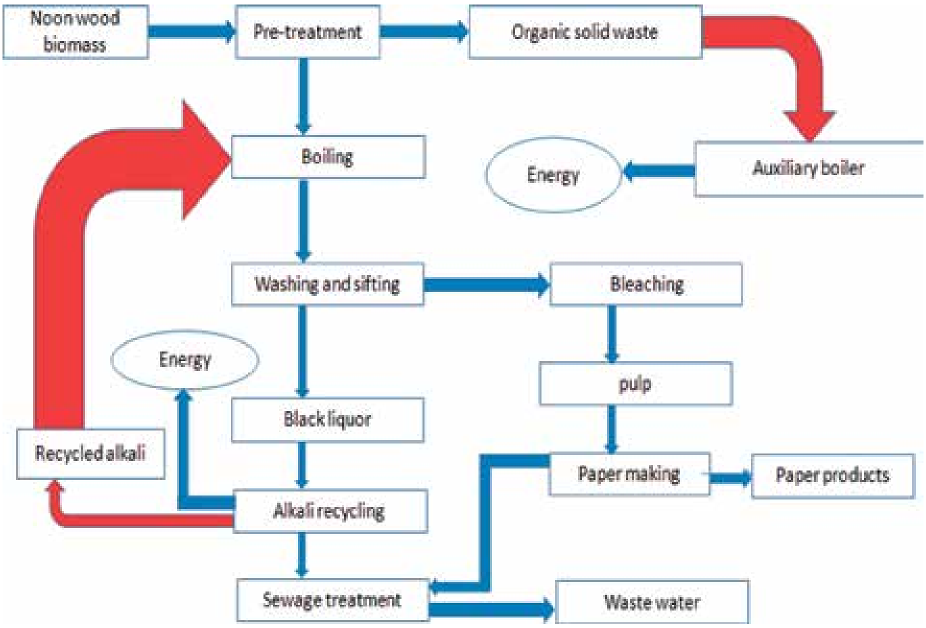

Figure 3. Process flow diagram for pulp and paper production [60].

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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Effect of Press-Drying Parameters on Paper Properties

Ahmed Koubaa and Zoltan Koran

Additional information is available at the end of the chapter

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Abstract

This study investigates alternatives that can improve the internal bond strength (IBS) of paper by pulp refining and paper press-drying (PD). The improvement mechanisms of IBS and their impact on the strength development of high-yield pulps are discussed. All experiments were conducted using a factorial design where the factors were four pulp types (one spruce thermomechanical (TMP) and three chemi-thermomechanical (CTMP) from spruce, birch, and aspen), three refining levels, three PD temperatures and three pressures. The effects of these treatments on the physical and mechanical properties of paper were studied using an analysis of variance. Refining changed the fibre surface, thereby promoting mechanical adhesion. PD temperature softened the fibres and changed their surface chemistry, while PD pressure improved the contact area between fibres. These changes led to an important improvement in IBS which explained, to a large extent, the variations in paper properties. Compared to air-dried paper, PD paper showed much higher properties for most tested pulps at all refining levels. These results were due to the increase in bonded areas. PD at 175°C substantially improved the wet tensile strength of paper due to the flow of lignin on the fibre surface, which protects the hydrogen bonds from moisture.

Keywords: press-drying, paper properties, internal bond strength, fibre properties, surface chemistry

1. Introduction

Fibre morphology, strength and adhesion are the main factors controlling paper strength [1–12]. Chemical composition is closely related to fibre strength and is an important factor in paper strength development [3, 5]. Among paper strength properties, tensile strength and tearing resistance are the most studied properties due to their importance during conversion and in end-use [1–12]. **Table 1** summarises the impact of the different fundamental fibre properties on paper tear, tensile and burst strength.

Properties	**Morphological [1, 7–14]**				**Chemical [5, 15–22]**			**Mechanical [1–7, 15, 23–32]**		
Strength Properties	**Length**	**Wall thickness**	**Coarseness**	**Microfibril angle**	**Cellulose**	**Lignin**	**Hemicelluloses**	**Strength**	**Flexibility**	**Adhesion**
Tear strength	+	−	−	−	+	−	+	+/−	−	+
Burst strength	+	−	−	−	+	−	+	+	+	+
Tensile strength	+	−	−	−	+	−	+	+	+	+

Table 1. Effect of increasing fundamental fibre properties on the development of the strength properties of paper.

The variation in tearing resistance is complex and researchers have carried out an impressive number of studies to understand this variation [2, 3, 5–8, 10]. Fibre length, strength and bonding are the main controlling factors. Although no clear relationship has been reported between tear index and fibre coarseness, in well-bonded sheets the tear index has been found to be higher in sheets with coarser fibres [6, 7].

Fibre length is an important factor in tearing resistance. Longer fibres improve tearing resistance, particularly for weakly bonded sheets [3, 6–8, 10–13]. However, fibre length is less important in well-bonded sheets having strong interfibre adhesion since sheet failure caused by tear is then controlled by the strength of the fibres [6, 7]. The tearing resistance is proportional to the square of fibre strength when fibre strength is modified without affecting other fibre properties or sheet structure [6, 7]. However, this does not necessarily imply that fibre failure is the prevailing mechanism of energy dissipation [8]. The elastic energy released when fibres or bonds fail depends on the load within the fibres and on the number of failures. All these entities are related to fibre strength.

The variation in the tensile strength of paper is controlled mainly by the internal bond strength. Indeed, several studies have reported clear positive linear relationships between the tensile strength and the internal bond strength [4, 25–27]. Fibre strength, morphology and coarseness are also important for the tensile strength development of paper. For example, the Page Equation [1] predicts the tensile strength from fibre properties including length, strength coarseness, fibre transverse perimeter, bond area and bond strength. This equation is widely recognised for predicting the tensile strength of paper. Clark [3] developed a statistical model to predict all paper properties from fibre properties. These models indicate the importance of the fibre properties for the development of paper strength.

The extent of fibre-to-fibre bonding is also important in determining paper strength. Improving this property is known to have beneficial effects on most sheet strength properties, except for tearing resistance. For the latter, the relationship is complex since it varies with the degree of interfibre bonding. **Figure 1** illustrates the general model that describes the variation of tear strength with the internal bond strength of paper. In poorly bonded sheets, increasing bonding strength improves the tearing resistance. However, in well-bonded sheets, higher bonding strength reduces the tearing resistance [3, 6–8]. This variation makes developing a model to predict the tear index from fibre properties difficult. Some attempts were made in the past to characterize this relationship using several approaches [7]. In general, fibre dimensions and physical properties are varied by either pulping different woods or fractioning a pulp. The paper properties from these pulps are generally modified by beating. The dependence of paper properties on fibre properties is then studied by statistical methods. This approach led to some good correlations, but there were no clear relationships because fibre properties are modified by beating and are generally interdependent.

The abovementioned studies have led to an excellent understanding of the tear mechanism and explained the role of each fibre property in the development of tearing resistance. For example, Page [6] elucidated the tear strength mechanism and determined the extent of its dependence on each fibre property by studying the effect on each property separately. Later, a model was developed [2] to describe the tearing energy of rupture of softwood pulps using

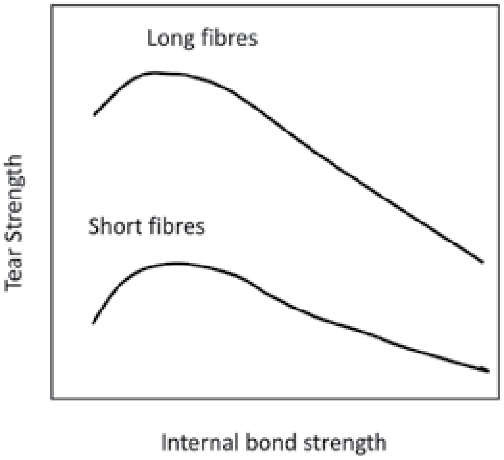


Figure 1. Typical model of variation of the tear index with fibre length and internal bond strength [6, 7].

the Page Equation [1]. However, most of these studies dealt with chemical pulps, particularly those made from softwoods. Only few studies dealt with the role of fundamental fibre properties of high-yield pulps [4, 12, 15, 28–30]. Moreover, few reports directly studied the effects of interfibre bonding [4, 15, 25–27, 30–32]. Generally, sheet density or light scattering coefficient or even tensile strength is used to depict changes in interfibre bonding.

There are few alternatives to improve the internal bond strength of paper. Chemical treatment and beating are the most used alternatives. Extensive literature exists on the impact of these alternatives on the strength development of paper. Press-drying is among the alternatives that can improve the paper properties especially internal bond strength due to improved compressibility by the combined action of pressure and temperature [30, 33–37]. In press-drying paper is dried under restraint through the application of pressure in the z-direction during the drying process while the paper is simultaneously in contact with a very hot drying surface, thereby leading to a web temperature in excess of 100°C [30, 33–37]. The important feature of this process is the fact that it takes advantage of the positive effects of high web temperature on both dewatering rate by reducing the viscous resistance of water and web consolidation by increasing the compressibility of fibrous material [34].

Several reviews are available on the physics of press-drying [33–38]. The main factors that control the mechanical properties of press-dried paper and the performance of this process are the mechanical pressure applied on the wet web, the moisture content in the web, the pressing time and the temperature [30, 33–37]. In addition to the improvement in drying rate, this process leads to substantial energy savings and improvement in paper properties [33–38]. This process has been commercialised as Condebelt drying [33, 38]. Despite the proven advantages to the Condebelt drying process, this technology is still not widely accepted in the pulp and paper industry [33, 38]. There are only two installations of this technology worldwide [33]. At an industrial level, Retulainen et al. [39] reported that the Condebelt drying process led to substantial improvement in the paper properties and in the process efficiency as compared to the Cylinder drying process.

Despite the abundant literature on press-drying process and physics, only few studies have investigated the impact of process parameters on paper properties. Thus, laboratory pulp beating and paper press-drying experiments were conducted during this study on softwood and hardwood high-yield pulps so as to investigate the impact of this process while using large variations in fibre length, strength and interfibre bonding.

The main objective of this study was to discuss the impact of interfibre bonding development, intrinsic fibre strength and fibre length on the strength properties of press-dried paper. The specific objectives were: (1) to study the impact of pulp beating and press-drying temperature and pressure on paper internal bond strength; (2) to investigate the effect of IBS, intrinsic fibre strength and fibre length on paper strength development; and (3) to contribute to the fundamental understanding of strength development in press-dried paper.

2. Experimental procedures

Four high-yield pulps were used: one spruce TMP sampled after the first stage of refining from the Kruger, Trois-Rivières Mill (Quebec, Canada); three commercial bleached CTMPs obtained from the Tembec, Témisccamingue Mill, (Quebec, Canada) from birch, aspen and spruce. Pulps were beaten to various degrees in a PFI mill to ensure variation in fibre bonding (**Table 2**). The PFI mill was used to modify the cell wall structure and to minimise fibre fragmentation. Canadian standard freeness (CSF) was measured for each pulp. CTMP white spruce (*Picea glauca* (Moench) Voss samples were classified in a Bauer-McNett fibre classifier to investigate the impact of fibre length and distribution on strength development of paper. A total of nine pulps were obtained through the classification (**Table 2**) to ensure large variations in fibre length. The average fibre length of each class was measured by image analysis. The average weighted fibre length of each pulp was calculated on a dry weight basis (**Table 2**).

Series of 60 g/m^2 handsheets from each pulp were wet pressed and air-dried according to standard Tappi procedures and used as control samples. Other series were press dried at three different pressures (0.375; 0.750; 1.50 MPa) and temperatures (105; 140 and 175°C) using a hydraulic press with two heated platens. The moisture content (MC) of a sheet before press-drying is critical to the development of its strength [33–37]. In this study, handsheets had moisture contents (MC) ranging from 100–120% before press-drying. After press-drying, MC ranged from 6–9%. Paper properties were measured according to Tappi standard procedures. The internal bond strength was measured according to the method described in a previous report [25]. All samples were conditioned and tested at 20°C and 50% relative humidity (RH).

An analysis of variance was performed using the general linear model (GLM) SAS procedure [40] to test treatment effects. Regression and correlation analyses were performed with the CORR and REG SAS procedures. Results were considered significant at 95% and 99% probability levels.

Canadian standard freeness (CSF) (ml)	**Fibre classification in a Bauer McNett (%)**				**Average fibre Length (mm)**
	14	**28**	**48**	**<48**	
Unbleached Spruce TMP pulps (pulp sampled after the first stage of refining)					
475	22.4	34.5	12.8	31.3	1.43
295	13.7	28.9	20.4	37.0	1.40
220	12.5	28.5	20.5	37.5	1.35
130	12.8	27.5	20.2	39.5	1.32
Bleached Birch CTMP pulps (commercial pulp obtained from Tembec)					
420	0	9.9	50.5	39.6	1.03
340	0	19.0	39.7	41.1	1.02
250	0	18.2	36.8	44.6	0.96
200	0	15.5	36.5	48.0	0.92
Bleached Aspen CTMP pulps (commercial pulp obtained from Tembec)					
405	0	4.6	38.5	56.8	0.83
375	0	4.7	40.4	54.9	0.82
235	0	5.1	40.1	54.7	0.82
125	0	5.2	39.9	55.4	0.80
Bleached Spruce CTMP pulps (commercial pulp obtained from Tembec)					
750	100	0	0	0	2.85
750	0	100	0	0	2.03
750	0	0	100	0	1.34
750	40	40	20	0	2.07
540	32	32	16	20	1.88
540	24	24	12	40	1.78
480	16	16	8	60	1.22
450	8	8	4	80	0.98
480	0	0	0	100	0.66
540	28	31.5	15.7	24.8	1.75
485	29.8	27.7	15.9	26.6	1.74
400	29.8	27.2	16.9	26.1	1.74
350	29.7	27.5	13.5	29.1	1.70

Table 2. General characteristics of the studied pulps.

3. Results and discussion

3.1. Impact of pulp type, beating and press-drying on paper properties

Table 3 shows the results of the analysis of variance on the effect of pulp type, beating intensity and press-drying temperature and pressure on selected paper properties. All studied factors showed significant effects on paper properties, except for specific bond strength, where only pulp type had a significant effect.

The differences in the initial intrinsic characteristics of the studied pulps, including morphology, length distribution, intrinsic strength, specific area and chemical composition explain the significant effect of pulp type on paper properties. These differences are due to variations in wood species and pulping processes (**Table 2**). The first pulp is a commercial TMP spruce while the three other pulps are commercial CTMP pulps from birch, aspen and spruce. The chemical treatment softens the chips and results in longer, and more flexible pulps compared to the TMP pulp. The birch and the aspen CTMPs have shorter fibres than the spruce TMP and CTMP pulps. Compared to aspen, birch has higher wood density and higher cell thickness and fibre coarseness than aspen wood. All these differences along with the different fibre specific areas resulted in different paper properties (**Figures 2** and **3**).

The impact of beating on high-yield pulp properties is well-documented in the literature. Pulp beating modifies the fibre surface by generating fibrils, delamination and activation; improves the fibre specific area; slightly reduces the fibre length and produces fines [41, 42]. Data from **Table 2** show the changes in pulp properties. Fibre length shortened, and the proportion of fines increased, as the CSF decreased with beating intensity. All these changes improve the

Source of variation	**DF**	**Paper properties**					
		Density	**ZSBK**	**IBS**	**SBS**	**BL**	**TI**
Model	29	97.7^{**}	11.1^{**}	39.6^{**}	n.s.	11.2^{**}	9.5^{**}
Pulp	3	897^{**}	345^{**}	358^{**}	4.9^{*}	322^{**}	58.9^{**}
Beating	2	33.2^{**}	n.s.	24.7^{**}	n.s.	29.3^{**}	6.2^{*}
Temperature	2	17.8^{**}	n.s.	11.9^{**}	n.s.	14.1^{**}	31.2^{**}
Pressure	2	14.7^{**}	8.5^{*}	6.0^{*}	n.s.	4.0^{*}	7.6^{*}
R^2		0.98	0.94	0.94	0.28	0.94	0.77
CV, %		4.4	4.6	7.6	11.5	9.0	7.8

*Significant at $\alpha = 0.05$.

**Significant at $\alpha = 0.01$.

DF: Degree of freedom; ZSBL: Zero-span Breaking length; IBS: Internal bond strength; SBS: specific bond strength, BL: Breaking length; TI: Tear index; CV coefficient of variation; n.s. non-significant at $\alpha = 0.05$.

Table 3. Analysis of variance for the effect of beating and press-drying (temperature and pressure) on selected paper properties.

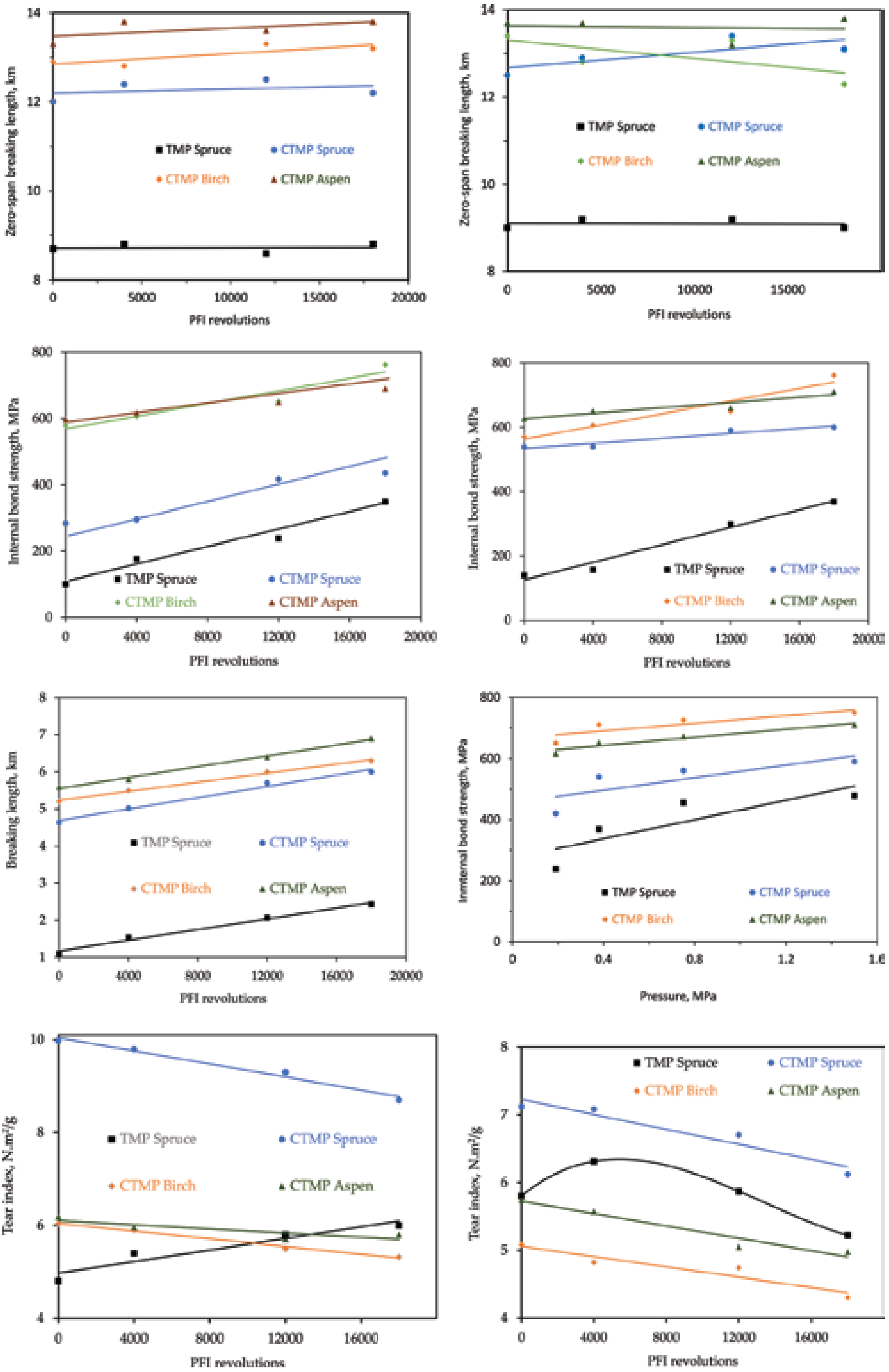


Figure 2. Effect of beating on selected properties of air-dried (left) and press-dried (right) paper made from high-yield pulps.

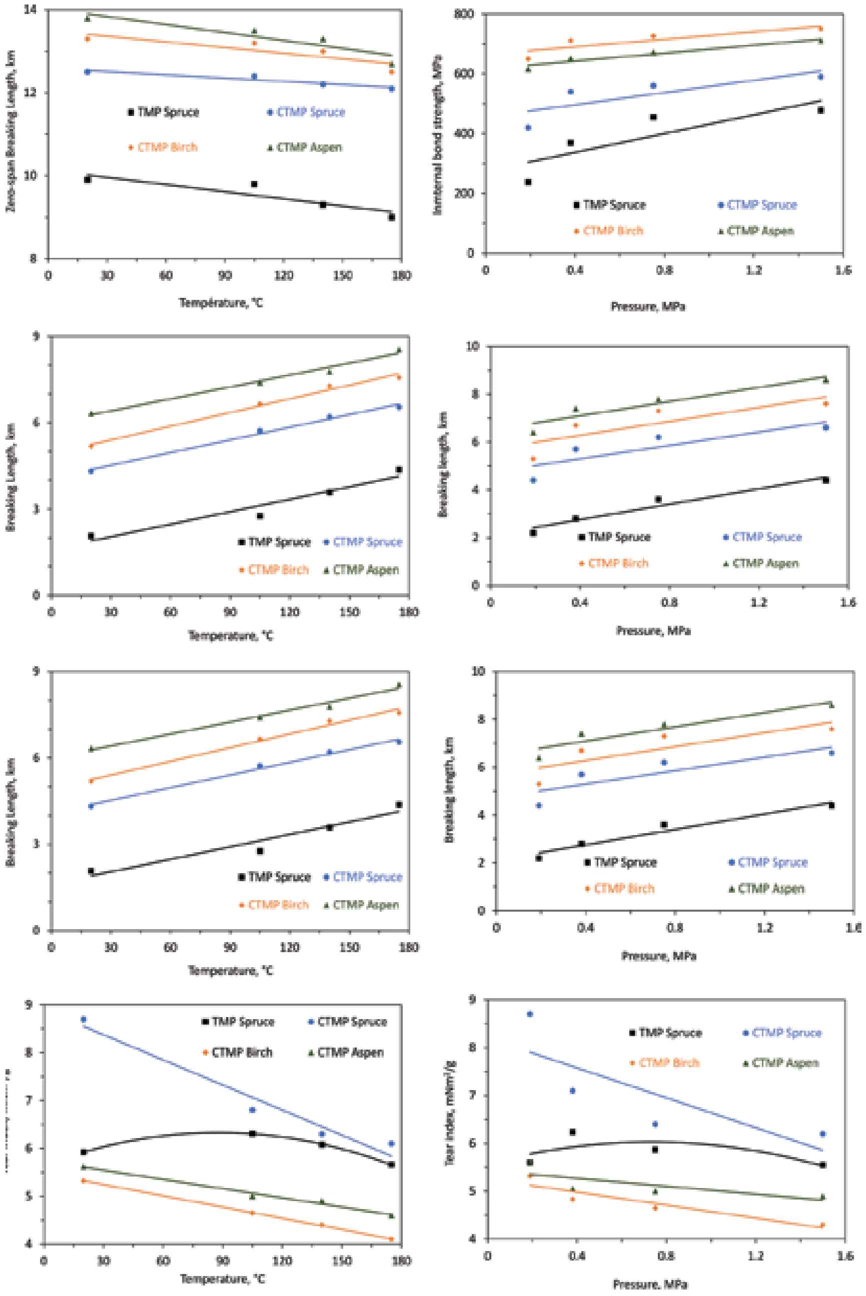


Figure 3. Effect of press-drying temperature (left) and pressure (right) on selected properties of papers made from high-yield pulps.

contact area between fibres, increase sheet density, lead to higher bonded areas and internal bond strength and consequently result in better tensile strength. **Figure 2** shows that beating improves the internal bond strength and the breaking length of both air-dried and press-dried paper from all high-yield pulps. However, beating decreases tear index, except for air-dried paper from the spruce TMP, where this property increased with beating (**Figure 2**). This increase results from an improvement in bonding. The press-dried TMP showed an initial increase after a slight beating and then decreased linearly outwards. This initial increase is also due to the improved bonding. The following decrease occurs because, at higher beating levels, the paper is well-bonded and the tear mechanism is then controlled by the fibre strength [6, 7].

Despite the observed tendency of a slight increase with beating, the effect of this treatment on the zero-span breaking length for the press-dried paper was not statistically significant. This result could be explained by the large variation in this property among the studied high-yield pulps. The variation in this property due to beating is marginal compared to that caused by pulp type (**Figure 2**). At all beating levels and pulp types, press-dried paper showed slightly higher zero-span breaking length than the air-dried paper. This result may be explained by the fact that the press-dried paper is denser than air-dried paper. In the testing zone, press-dried paper has a higher area occupied by the fibre wall and less void.

Press-drying temperature showed a significant effect on all paper properties except for specific bond strength and intrinsic fibre strength (**Table 3**). **Figure 3** shows the variation of selected properties with press-drying temperature and pressure. Higher temperatures soften the wood fibres and make them more compressible. Thus, paper density increases with increased PD temperature, which leads to a higher contact area, and therefore, to a higher bond strength. This result was expected, and is in good agreement with previous findings where close and positive relationships were reported between the bonded area, the internal bond strength and the tensile strength of paper [4, 6, 7, 25–27, 30, 31].

The effect of beating and press-drying temperature and pressure on the specific bond of paper was not statistically significant (**Table 2**). At the tested beating and press-drying parameters, little variation of the specific bond strength is observed for spruce TMP (1600–1800 MPa), spruce CTMP (1400–1700 MPa), birch CTMP (1700–1900) and aspen CTMP (1500–1800). This result suggests that the improvement in the internal bond strength is attributed to the increase in the bonded area and not to a change in the nature of the fibre-to-fibre bonds. These are thought to be mainly hydrogen bonds that break easily under the action of water [15, 30, 43]. Zerhouni et al. [32] also concluded that press-drying temperature did not change the nature of fibre-to-fibre bond in papers made from CTMP, TMP and kraft pulps and sludge. The specific bond strength did not vary with neither the press-drying temperature nor the paper composition.

The variation in press-drying temperature also affects the fibre chemical structure as demonstrated in a previous report [15]. In this study, the surface chemistry of air-dried and press-dried spruce and birch CTMP papers were analysed by electron surface chemical analysis (ESCA) and the oxygen to carbon ratios (O/C) were reported. A decrease in the O/C ratio indicates an increase in the lignin content at the fibre surface. Results from this investigation showed that, at 105°C, only water and volatile matter were evaporated and no chemical change occurred on the fibre surface as the O/C ratio remained constant at 0.53 (**Table 4**). At 140°C, hemicelluloses start to degrade, but lignin and cellulose are not affected. However, the ESCA results did not show any notable change in the fibre surface at this press-drying temperature since the O/C ratio also remained constant at 0.53. A PD temperature of 175°C

	Birch CTMP				**Spruce CTMP**			
	25°C	**105°C**	**140°C**	**175°C**	**25°C**	**105°C**	**140 °C**	**175°C**
Carbon concentration, %	64.5	65.0	65.2	67.0	65.1	64.8	64.7	64.8
Oxygen concentration, %	34.6	34.4	33.8	32.2	34.5	34.1	34.5	32.4
O/C ratio	0.54	0.53	0.52	0.48	0.53	0.53	0.53	0.48
Wet breaking length, m	65	77	82	110	64	100	120	192

Table 4. Effect of drying temperature on the concentrations of carbon and oxygen, O/C ratio and wet breaking length of press-dried birch and spruce CTMP [15].

showed significant chemical changes at the fibre surface as indicated by the O/C ratio which decreased from 0.53 to 0.48. At this temperature, lignin flows at the fibre surface and protects the formed hydrogen bonds from moisture [15].

The variation in the wet breaking length of press-dried papers with temperature supports this finding (**Table 4**). For example, for the press-dried spruce TMP at 175°C, the wet breaking length improved by 364, 151 and 73% compared to those dried at 25, 105 and 140 °C, respectively. This improvement in the wet breaking length for press-dried CTMPs at 175°C was less important than that for the TMP. For the aspen, birch and spruce CTMPs, the improvement from 25–175°C was 136, 131 and 63%, respectively. The fact that the CTMPs were bleached led to less lignin present on the fibre surface, and these fibres were more hydrophile than the TMP fibres.

The PD pressure had a significant effect on all paper properties except for specific bond strength. Increasing pressure increases the bonded area, which improves the probability of hydrogen bond formation and also improves the density of the paper. This led to improved bond strength and consequently to improved tensile properties. The increase in the internal bond strength caused by pressure also led to a decrease in the tear resistance, as previously explained. Surprisingly, the press-drying pressure showed a significant effect on the zero-span breaking length (**Table 3**). Increasing the pressure decreased this property (**Figure 3**). The compression effect on the fibre increases the area occupied by the fibre wall in the testing zone, which is expected to improve the zero-span. However, a slight decrease in this property is observed with increasing press-drying pressure (**Figure 3**). This decrease could be attributed to the mechanical damage of the fibre due to increased pressure [5].

3.2. Impact of fibre strength on the development of paper properties

Intrinsic fibre strength plays an important role in the development of different paper properties. Indeed, rupture during testing could occur in the fibre or in the bond between fibres. Several studies [5, 26, 41, 44–51] demonstrated that during rupture in tensile testing of paper, some fibres pull out and others break. Beating weakens the fibres and the proportion of broken fibres during paper testing increases with the beating level.

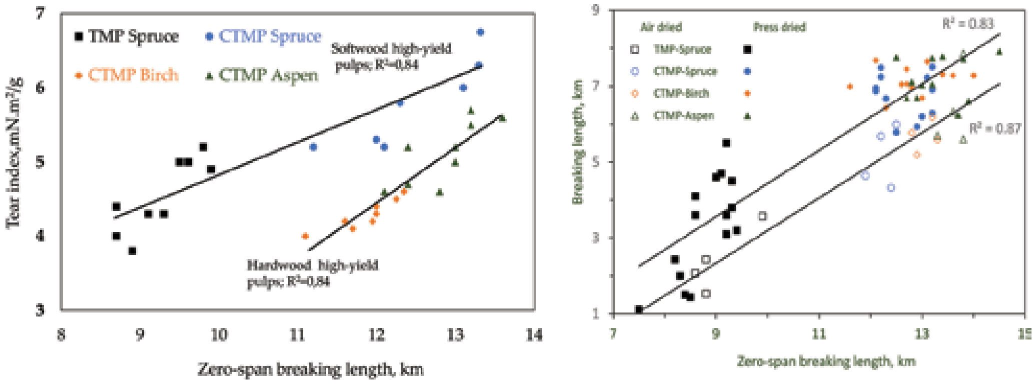
There was no clear relationship between the tear index and the zero-span breaking length of the pulps at any of the beating levels tested. This is not because fibre strength did not influence tear index, but because the effects of bonding and fibre length on tear index were more important and also because of the low range in fibre strength variation compared to those of internal bond strength and fibre length. Thus, the impact of fibre strength on the tear index could be hidden.

The relationship between zero-span breaking length and the tear index for beating levels where there was enough data with similar bond strength values was studied. Two distinct relationships were found at the same level of bonding, one for softwoods and one for hardwoods. These relationships were highly significant and explained more than 81% of the total variation in tear index (**Figure 4a**). This close relationship between the zero-span breaking length and tear index is in good agreement with previous findings [5–8, 51]. The difference between hardwood and softwood pulps is due to the impact of fibre length on the development of tear index.

For tensile strength, a linear relationship between breaking length and zero-breaking length was found for air-dried and press-dried paper (**Figure 4b**). This pattern of variation was expected, considering the variation in fibre strength among the TMP and CTMPs. Indeed, the TMP fibres showed lower fibre strength than the CTMP pulps at all beating levels and press-drying conditions. The press-dried paper tended to have slightly higher fibre strength and tensile properties compared to the air-dried paper. Better bonding can explain the higher tensile strength, while better fibre compressibility explains the better fibre strength of press-dried paper. The better fibre compressibility results in a higher area occupied by the fibre wall and lower void area in the test zone, which explains the higher zero-span breaking length of press-dried paper compared to air-dried paper.

Despite the high coefficients of determination ($R^2 > 0.85$), one can still observe a high scattering of the experimental data around the relationships for air-dried and press-dried papers. The variation in fibre morphology and bond strength, along with the experimental errors, explains this high scattering.

The close relationships between fibre strength and paper tensile and tear strengths are well documented in the literature [1–11, 26, 41, 44–51]. However, previous studies used chemical



(a) (b)

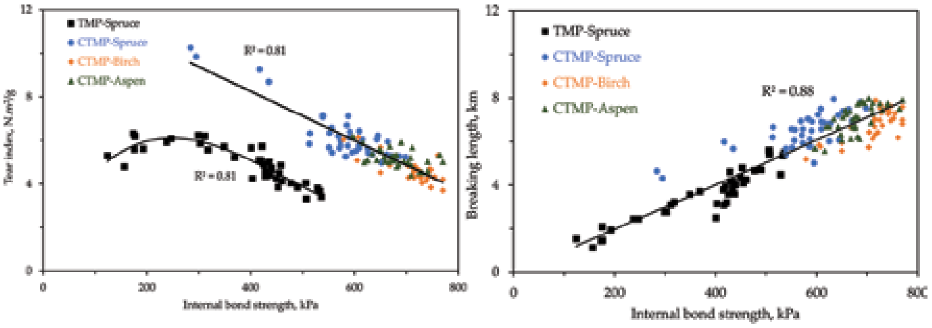
Figure 4. Effect of fibre strength on (a) the tear index and (b) the tensile breaking length of air-dried and press-dried papers made from high-yield pulps.

treatments or modification to vary the fibre strength to investigate this relationship [18–20, 49]. In addition, only a few studies investigated the impact of fibre strength on paper mechanical properties of high-yield pulps [12, 15, 28–30]. This study confirmed the importance of fibre strength in the development of tensile and tear strengths of high-yield pulps. Variations in pulp type, wood species and drying parameters along with refining led to an important variation in the fibre strength.

3.3. Impact of internal bond strength on paper properties

The observed variations in paper properties, namely the tear index (**Figure 5a**) and the breaking length (**Figure 5b**), are due to the effects of both beating and press-drying on internal bond strength. Data from the TMP and CTMP pulps followed two distinct relationships (**Figure 5a**). This result is due to several differences in the properties of TMP and CTMP pulps including fibre flexibility, compressibility and strength. Data from the present study show that the zero-span breaking length of the TMP ranged from 7.5 to 9.9 km while that of the CTMPs ranged from 11.7 to 14.7 (**Figures 2** and **3**). CTMP fibres are reported to be more flexible and more compressible than TMP fibres [29, 30]. The tensile modulus of elasticity of paper is closely related to fibre flexibility [9, 10, 30]. The tensile modulus of elasticity for the TMP papers ranged from 0.75 to 1.85 GPa while that of CTMP papers was much higher and ranged from 1.4 to 4.8 GPa [30]. Thus, CTMP fibres were more flexible than TMP fibres, thereby explaining the distinct relationships of TMP and CTMP paper (**Figure 5a**). As stated earlier, flexible fibres are more compressible and result in denser paper and in a higher area occupied by the fibre wall and a lower void area in the test zone.

For the TMP, the pattern of variation is typical of the tear index variation with interfibre bonding (**Figure 1**). The tear index initially increased with increasing bond strength to reach a maximum around 6 N·m^2/g, beyond which it started to decrease consistently with increasing bond strength (**Figure 5a**). The initial increase is due to the fact that below the maximum tear index the paper is weakly bonded. Thus, more fibres pull out than break in the tear zone and the tear index is controlled to a greater extent by the number of bonds that break than by the fibre breakage. Beyond the maximum tear index, where the level of bonding is high, more fibres break than pull out along the tear zone [3, 6–8].



(a) (b)

Figure 5. Effect of the internal bond strength on (a) the tear index and (b) tensile breaking length of press-dried and air-dried paper made from high-yield pulps.

In the case of CTMPs, the tear index of the pulps decreased consistently with increasing internal bond strength (**Figure 5a**). The three pulps tended to follow the same relationship. For each CTMP pulp, air-dried handsheets showed a higher tear index than press-dried ones (**Figures 2** and **3**). The experimental data of the internal bond strength and the tear index are scattered around both relationships (**Figure 5a**). This scattering is due to several factors including variations in fibre strength caused by beating and press-drying, to changes in fibre length due to species variation and to experimental error.

Fibre strength variation could also explain the differences between the tear index of various pulps. Despite its shorter fibre length, the aspen CTMP showed higher tear index values compared to the birch CTMP (**Figures 2** and **3**). The lower fibre coarseness and higher fibre strength of the aspen fibres compared to those of birch explain this result. The spruce CTMP showed the highest tear index because of its higher fibre length.

A close linear relationship was found between internal bond strength and tensile breaking length (**Figure 5b**). It is interesting to note that all the experimental data generated in the present study follow this relationship with a high coefficient of determination ($R^2 = 0.88$). This suggests that internal bond strength is the main controlling factor in the development of tensile strength of paper. This result is in good agreement with previous findings [4, 25, 41]. **Figure 5b** shows that the experimental data is scattered around the regression despite the high coefficient of determination. This scattering can be explained by the experimental error and the role of intrinsic fibre properties in the development of paper strength, namely fibre strength and fibre length.

3.4. Impact of fibre length and distribution on paper properties

Fibre length also plays an important role in the development of paper tearing resistance and tensile strength. The effect of fibre length is clearly seen in **Figure 4a** where the softwood pulps presented higher tear index values than the hardwood pulps at all constant fibre strengths. Similarly, the spruce CTMP showed a higher tear index than the birch and the aspen CTMPs (**Figure 4a**).

The tear index of both air-dried and press-dried paper was proportional to the fibre length of all classified spruce CTMP (**Figure 6a**). However, the tear index of press-dried handsheets was lower than that of air-dried ones. This result also shows that increasing bonding through press-drying decreases the tear index. The slope of the tear index variation with fibre length was also lower for the press-dried paper compared to air-dried paper. Thus, the dependence of tear index on fibre length was less important for press-dried paper. These results agree with Seth and Page [7] and can be explained by the tear mechanism as discussed in the previous sections. In the air-dried handsheets, the fibres were weakly bonded (internal bond strength varied from 80 to 290 kPa). Thus, tear index is controlled to a greater extent by the number of bonds that break along the length of the fibres. However, in press-dried handsheets, interfibre bonding was high (internal bond strength varied from 480 to 610 kPa), and consequently, the tear index is controlled to a greater extent by fibre breakage than by bond breakage.

Fibre length distribution also showed an important impact on the tear index (**Figure 6b**). An increasing proportion of fines led to a linear decrease in the tear index. In fact, higher proportions

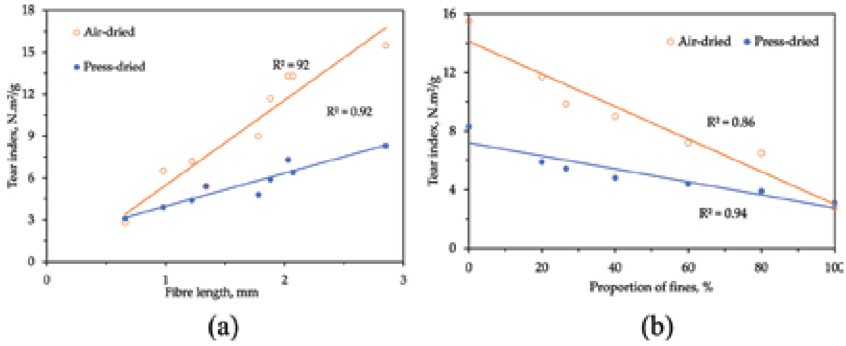


Figure 6. Effect of (a) fibre length and (b) distribution on the tear index of air-dried and press-dried paper at 175°C and 0.75 MPa made from white spruce classified CTMP pulps.

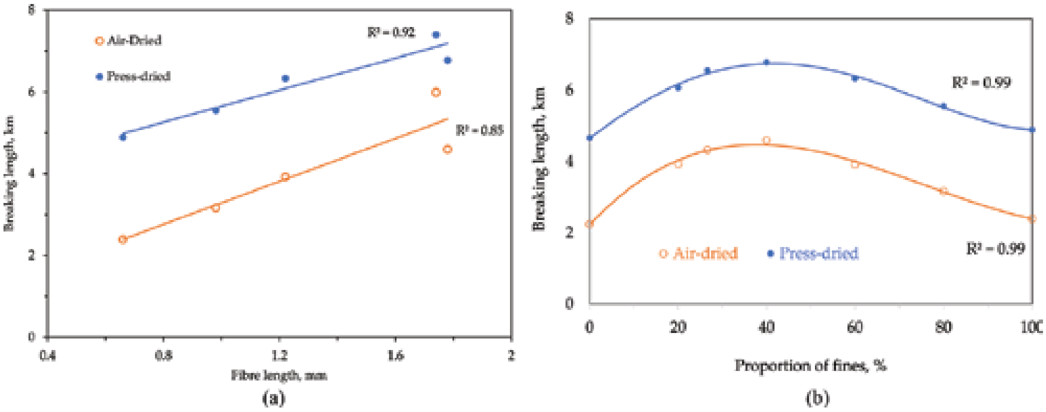


Figure 7. Effect of (a) fibre length (comparable CFS at 450 ± 30 ml) and (b) fibre distribution on the tensile breaking length of air-dried and press-dried paper at 175°C and 0.75 MPa made from white spruce classified CTMP.

of fines improved bonding and reduced the average fibre length in the paper. Both changes are known to decrease the tear index.

Figure 7a and **b** shows the impact of fibre length and distribution, respectively, on paper tensile strength. At comparable CSFs (450 ± 30 ml), an increasing fibre length led to a linear increase in the tensile breaking length. The latter is also controlled by the fibre distribution. The optimum breaking length occurred at around 40% of fines. The initial improvement in the tensile strength from 0% to about 40% is due to the improvement in fibre contact area. Beyond a 60% proportion of fines, the tensile strength showed a linear decrease due to the reduction in the proportion of long fibres. Long fibres lead to better stress distribution along the fibre network while fines lead to stress concentration in the fibre network [52], which explains the decrease in tensile strength when fines content is above 60%. The decrease in the tensile strength with high fines content is in a good agreement with previous findings [3, 11, 12, 41, 53].

4. Conclusion

The properties of high-yield pulps can be improved by beating and paper press-drying. Pulp refining changes the fibre surface morphology, promoting mechanical adhesion between fibres. Compared to air-dried paper, PD paper showed much higher internal bond strength, breaking length and wet breaking length for all tested pulps and at all refining levels. These results are due to the increase in the bonded areas. PD temperature softens the fibres and changes their surface chemistry, while PD pressure improves the contact area between fibres. These changes led to an important improvement in internal bond strength, which explained to a large extent the variations in the tensile strength properties of paper. Two opposite tendencies were observed for the tear index. In the well-bonded paper, press-drying leads to a lower tear index compared to air-drying, while in the weakly bonded paper, press-drying leads to a higher tear index compared to air-drying.

Fibre length and intrinsic strength also played important roles in the strength development of paper. However, their impact was less important for the press-dried paper as compared to the air-dried paper.

List of abbreviations

AD	air drying
BL	breaking length
CSF	Canadian standard freeness
CTMP	chemi-thermomechanical pulp
CV	coefficient of variation
DF	degree of freedom
ESCA	electron surface chemical analysis
IBS	internal bond strength
MC	moisture content
O/C	oxygen to carbon ratio
PD	press drying
RH	relative humidity
SBS	specific bond strength
TI	tear index
TMP	thermomechanical pulp
ZSBL	zero-span breaking length

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Section 2

Application of By-Product Raw Materials for Paper Production

The Value and Profitability of Converting Sawmill Wood By-Products to Paper Production and Energy Generation: The Case of Poland

Leszek Wanat, Elżbieta Mikołajczak and
Jan Chudobiecki

Additional information is available at the end of the chapter

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Abstract

Analyzing the relationship between production of wood-based products and the production of paper and its derivatives ever more often attention is paid to complementarity of the processes of production, recovery and recycling of key raw materials and finally to their value and profitability of production. In this context, two main trends in converting wood by-products are noticed: paper production and energy generation. Development of market of sawmill by-products constitutes a challenge for wood industry, which requires determination of the most efficient means of utilizing those by-products. One of the crucial criteria of making business decisions is the value of wood by-products. A method of valuation of those sawmill by-products when converted into briquettes, pellet, or energy was presented. This method allows for multilateral analysis of profitability of various means of utilizing wooden by-products, on the example of Poland. Based on comparative analysis, recommendations for wood-based industry were formulated.

Keywords: paper production, sawmill by-products, wooden pellet, wooden briquettes, energy, wood market, economic efficiency, Poland

1. Introduction

The competitive position of the Polish wood industry is relatively strong. It is an effect of the domestic forest resources, the quantity and quality of round timber acquired from the national resource base, as well as continually growing significance of wood-based products in global production and trade. The total forest area in Poland amounts to 9.2 thousands hectares, which means the afforestation rate is 29.5% (0.24 ha of forest per capita). Public forests hold a domineering position (80.8%), mainly those managed by National Forest Holding "The State Forests" (77%), which is a natural monopolist on the wood market. Polish gross wood resources amount to approximately 2.5 billion m^3 of large timber (out of which almost 2.0 billion m^3 belongs to The State Forests). The position of forest and wood-based sector in Polish economy is determined by key factors: forests cover about 30% of Poland's territory, its share in GDP equals 2%, it creates workplaces and stimulates regional development. The contribution of forestry and wood-based sector to gross domestic product (GDP) in Poland amounts to: in case of forestry—0.3, and in case of wood industry—1.7%, which comes to an average share of forest and wood-based sector at the level of 2% (which is almost twice the world average) [1, 2]. Despite the imbalance in Polish wood- and wooden products market and the deficit of wood (a permanent phenomenon being an effect of the application of the principles of sustainable forest management), there is no threat for the development of wood-based industries in Poland [3, 4]. The following factors have a decisive impact on that: dynamic increase of demand for wood, wood being trendy and popular as an environmentally and human friendly raw material [5, 6]. A study of inter-sectoral cooperation seems justified with reference to the wood-based sector, especially owing to its territorial dispersion [7].

Polish wood industry plays an important role in the development of the national economy. The most important sectors based on wood include: sawmill industry, furniture industry, cellulose and paper industry, and market of wood-based panels. Coincidentally, it may be noticed that Polish market of wood by-products has developed dynamically. This industry is highly fragmented and focuses on small and medium-size businesses (with only a few large enterprises). A significant number of microenterprises (covering more than 30% of the entire sector) are not included in any official statistics. The share of wood-based industry in the production of the entire Polish processing industry is estimated at approximately 9%. Wood industry processes on average more than 38 million cubic meters of round timber per year, purchased mainly from National Forest Holding State Forests and worth more than 1.6 billion euro [8]. The potential of the wood sector is additionally confirmed by the level of employment—more than 260 thousand employees (including 125 thousand in furniture- and 50 thousand in paper industry). Value of production in wood-based sectors exceeds more than 20 billion euro (including 8 billion euro in paper industry and more than 7 billion euro in the furniture industry); here, the upward trend is maintained. The value of total export of wood industry products in Poland reaches more than 15 billion euro and there is a growing trend. Poland is the fourth largest exporter of furniture in the world (following China, Germany, and Italy), while other EU countries are the main recipients of Polish furniture [8]. Based on the case study of Poland, an attempt was made to evaluate the value and profitability of converting sawmill-wood by-products to paper production and energy generation. The aim of this study was to show a relatively easy method of verifying research hypothesis, which has assumed that the refining conversion of sawmill by-products, based on the example of selected new products processed in Poland enhances their value.

2. Paper and paper industry in Poland and its economic significance

Despite domination of electronic economy and sometimes forecast marginalization of paper, it remains present in a modern society as one of the basic products of everyday use. Paper and paper industry still plays a significant role in creating economy of products based on wood. Contemporary knowledge allows us to state that paper which has been used for over 2000 years still successfully competes with electronic media, as well as the most modern multi-component packaging materials made of plastic, etc.

The areas of main functional utilization of paper and cardboard along with an attempt to identify the most important tendencies in its development were shown in **Table 1** [9]. In case of an increment, the enhancement was estimated. Based on own research the level of changes was measured (using a 5-grade scale: very high, high, medium, low, and neutral enhancement). Analyzing the main fields in the functional usage of paper and cardboard, the following key developmental trends were identified: Packaging and Specialty—a great variety (average

Paper functional use	Types of paper	Ready made products made of paper	Developmental trends
Information: - collection - distribution - storage	Newsprint; Coated and uncoated magazines (SC and LWC); Coated and uncoated woodfree printing and writing	Newspapers; Journals-Books; Computer printouts; Xerographic copies; Inserts; Illustrations	Increased use of multicolor printing and copying; Electronic media taking over banking/trading docs; Increased recycling as raw material and use of additives (high enhancement)
Packaging: - transportation - distribution - protection	Liner; Sack; Corrugating medium Folding box board; Liquid packaging board; Wrapping	Bags Boxes Wrappings Containers	Increased: use for distribution of food and composites; General increase in recycling of packaging materials; (average medium enhancement)
Hygienic: - personal care - cleanliness - disease prevention	Tissue - dry crepe - wet crepe	Toilet tissue; Kitchen towels; Facial tissue Napkins; Hand towels; Hospital clothing; Wipers	Use increases with general living standard; End of chain for recycling of fibers; Use of virgin fiber for top-end products (high enhancement)
Specialty—a great variety	Official papers; Filter paper; Fire resistant papers	Notes; Stamps; Air filters; Coffee filters; Baking paper	An ever-increasing number of new applications (average medium enhancement)
Multi-functionality	All papers	Packaging labels (source of information and form of advertising); Printouts on sanitary papers. Multi-functional packaging	Trend towards multi-functionality takes multiple usage of paper products: new model of product life cycle and the cycle of usage of goods made of paper (very high enhancement)

Source: Own elaboration based on [9].

Table 1. Main fields of functional use of paper and cardboard.

medium enhancement); Hygienic and Information (high enhancement), and above all Multi-functionality (which appears to be dominant). Leading identified developmental trend is the emphasis on multi-functionality of paper products (very high enhancement). This trend accounts for not only versatile, but also multiple usages of paper products. It therefore results in creating a new model of product life cycle and at the same time a new model of cycle of usage of commodities made of paper, which aims at an attempt to develop a closed cycle of production and utilization of paper.

3. Poland as a consumer of paper and cardboard

One of the determinants of level and quality of life and simultaneously competitiveness of regions is the volume of paper consumption per capita [10–19]. Annual average paper consumption in Poland amounts to 130 kg per person per year (**Figure 1**).

An upward trend is observed with a declining rate of increase (**Figure 2**). Between 1995 and 2015, the ratio of annual paper consumption increased more than three times. It is the biggest growth among all European countries included in the survey. Further increase in paper consumption in Poland may be expected, as an average for countries of Western Europe, to be

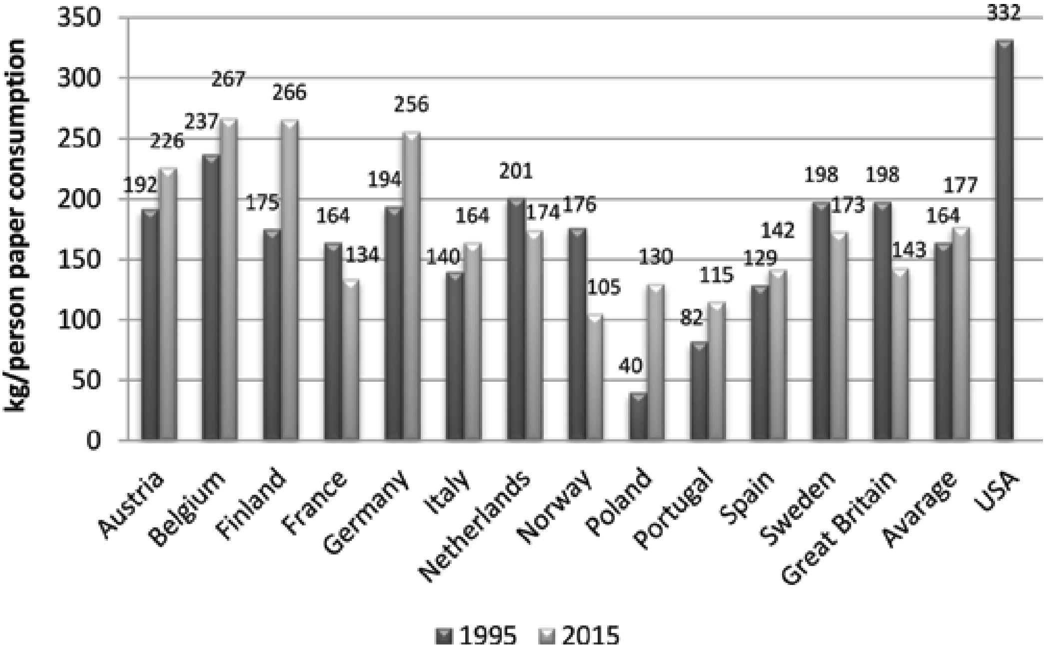

Figure 1. Comparison of paper and cardboard consumption in Poland and selected European countries in 1995 and 2015 [kg/person]. Legend: [X-axis label]: years 1995 and 2015; [Y-axis label]: kg/person paper consumption. Source: own elaboration based on [10, 11].

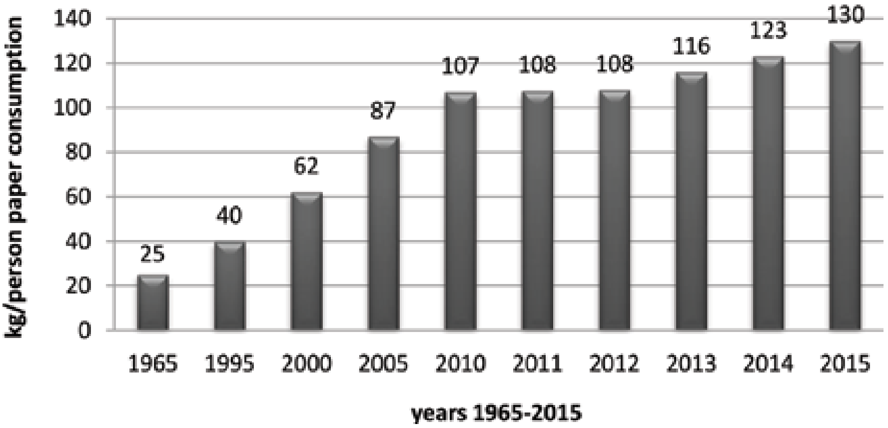

Figure 2. Paper consumption per capita in Poland [kg/person] in years 1965–2015. Legend: [X-axis label]: years 1965–2015; [Y-axis label]: kg/person paper consumption. Source: own elaboration based on [11–19].

177 kg per person. In some countries, the level of paper consumption is even two times higher than in Poland (Austria, Belgium, Spain, and Germany).

Even though a demand for newsprint decreases this trend is balanced by a growing demand for sanitary paper, packaging paper, and cardboard [20, 21].

4. Poland as a producer of paper and cardboard

Poland ranks eighth among CEPI member states as far as the production of paper and cardboard is concerned (the share of Poland is estimated at 5%) (**Figure 3**). Among the biggest paper industries or companies in Poland, there are [23]: Arctic Paper Kostrzyn SA GK with registered office in Poznan, Mondi Świecie SA GK in Świecie, International Paper-Kwidzyn sp. z o. o. in Kwidzyn, DS Smith Packing GK in Kielce, Polska Wytwórnia Papierów Wartościowych SA in Warsaw, and TFP sp. z o. o. in Kórnik.

In 2016, over 4.6 million tons of paper and cardboard was produced in Poland (**Table 2**), 5.6% more than in 2015. Transformation of Polish economy and direct foreign investments in paper industry led to 2.5 times increase in the volume of production, as compared to year 2000. Moreover, analyzing the dynamics of paper and cardboard production in Poland, one may indicate a steady upward trend in the period between 2006 and 2016 with a maximum reached in 2010 (13%) and high production ratios in 2009 and 2013 (over 7%).

According to product criteria, the most dynamically developing segment of production is the segment of paper hand towels made from paper pulp, paper, cellulose wadding, or webs of cellulose fibers. In the decade under analysis, there has been a steady increase in the production with a maximum in 2012 (30%) and short-term slump in 2013 (decrease by 5.8%).

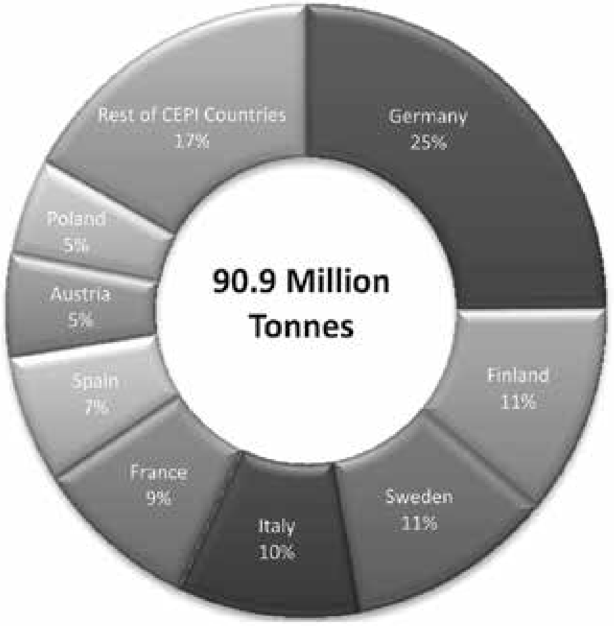

Figure 3. Major producers of paper and cardboard in Europe (2016). Source: own elaboration based on [22].

Production of corrugated cardboard increases from 3.3% in 2009 to 15.4% in 2011, subsequently reaching average values of 6% annually (2013–2016). Stable increase in the production is also observed in packaging segment including cartons, boxes, and cases made of paper and corrugated cardboard. An increase in the production of those commodities was noted from 4.5% in 2016 to 10.2% in 2012. The only decrease by 1.2%, took place in 2008.

Dynamic development of paper hand towels production as well as a steady increase in the production of cardboard and paper packaging compensates falls in the segment of newsprint in rolls or sheets.

Paper and paper-based products	**2000**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
	Units in thousands tons												
Soda or sulfate chemical woodpulp	751	802	825	814	820	826	881	894	848	881	881	873	877
Mechanical wood pulp*	244	249	345	353	331	319	299	307	304	306	301	286	303
Paper and paperboard/of which	1934	2732	2857	3005	3055	3275	3670	3756	3822	4106	4278	4399	4644
Newsprint	211	221	191	204	170	166	149	149	149	142	125	110	112
Graphic paper** and paperboard/of which	317	596	624	649	715	782	710	696	716	720	730	714	731
Graphic paper paperboard***	296	595	623	648	673	704	707	691	712	719	729	712	729
Uncoated, unbleached kraftliner	—	597	762	802	622	675	662	681	733	751	769	781	769
Semi-chemical fluting	—	136	189	180	185	280	178	188	178	180	178	154	170

Paper and paper-based products	**2000**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
	Units in thousands tons												
Uncoated Kraft paper and paperboard****	172	153	147	139	128	115	136	126	93	96	102	107	109
Corrugated paperboard	457	958	1054	1158	1210	1249	132	1528	1588	1703	1811	1933	2040
Sacks, bags of paper	83	90	104	117	102	126	124	126	115	113	121	124	131
Cartons, boxes of paper and corrugated paperboard	583	1155	1193	1417	1400	1523	1666	1747	1864	2010	2186	2408	2516
Toilet paper	116	215	208	219	237	259	255	268	297	298	304	330	367
Hand towels of paper pulp, paper, cellulose wadding, or webs	13	88	108	122	140	142	143	166	215	202	214	229	239

Source: own elaboration based on [24].
*Mechanical wood pulp; semi-chemical wood pulp; pulps of fibrous cellulosic material other than wood;
**Paper and paperboard of a kind used for writing, printing or other graphic purposes;
***Graphic paper and paperboard containing 10% and less by weight of the total fibers (by a mechanical process);
****Uncoated kraft paper and paperboard; sack kraft paper, creped or crinkled.

Table 2. Production of pulp and paper commodities in Poland (2000–2016).

This tendency is driven by competition from electronic media; however, one cannot explicitly state that this trend is sustainable. Within the period under the study, there has been production decline in this segment by more than 10%; however, in recent years, an increase was recorded (including that of 4.1% in 2016). The changes in the dynamics of production of

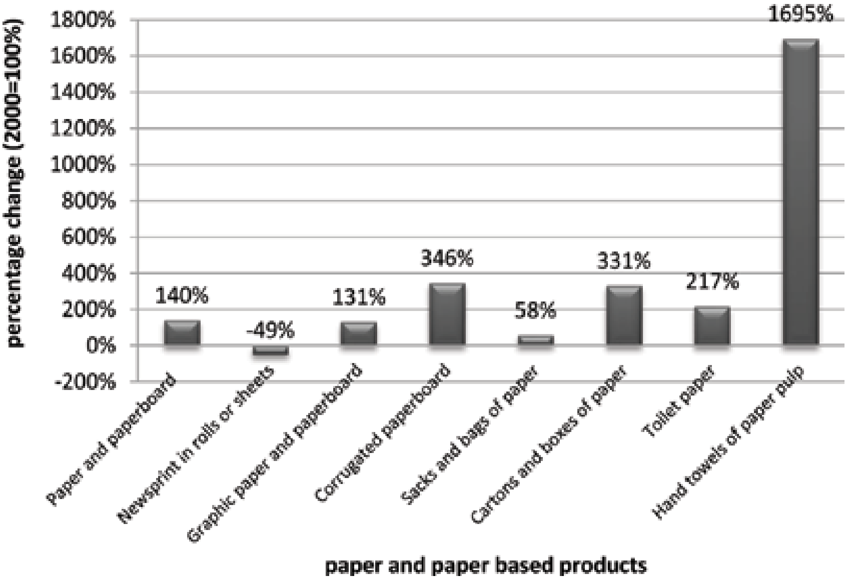

Figure 4. Dynamics of production of paper and cardboard and its different assortments in Poland in the period 2000–2016 (2000 = 100%). Legend: [X-axis label]: paper and paper-based products; [Y-axis label]: percentage change (2000 = 100%). Source: own elaboration based on [24].

individual paper, commodities were identified as a special example, which was also based on the carried out case study. It allows identifying the more important market trends with regards to products orientation. Analyzing changes in the total size of paper and cardboard production, as well as production broken down into the most important assortment groups in the period between 2000 and 2016 (**Figure 4**), the biggest growth (almost 18-times) was observed in the group of paper hand towels made of paper pulp, paper, cellulose wadding, or webs of cellulose fibers.

Also production of corrugated cardboard increased over four times, as well as the production of paper and corrugated cardboard packaging, such as cartons, boxes and cases. The smallest increase by "only" 60% was observed in the group of paper sacks and bags. While the production of newsprint in rolls or sheets dropped by almost 50%.

In a comprehensive approach as of year 2000 (that is within a period of 16 years, till year 2016), Poland recorded a total increase of 140% in the production of paper and cardboard.

5. The potential of Polish paper industry: international comparison

Presented results and conclusions were based on the data of Polish Main Statistical Office. Inclusion of international comparisons requires, at least within classification (assortment) used in Europe, adaptation of classification used by CEPI (**Table 3**). Structure by type of paper and cardboard production in CEPI member states (**Figure 5**) is dominated by graphic paper (39% share) as well as paper and corrugated cardboard (30% share).

In Poland, half of the production constitutes paper for corrugated cardboard production and the share of newsprint amounts to 20%, the next assortment group is sanitary papers with the share of 13% in the overall volume of paper industry production (**Figure 6**). The structure of Polish production is similar to the trends observed on paper and cardboard markets world-wide.

Analysis of CEPI statistics allows for a positive evaluation of the condition of European paper market, which in an analogical study period achieved better results than the USA or Canada [22]. In 2016, the total of 90.9 million tons of paper and cardboard was produced in Europe, which is a good result despite the 0.1% drop in overall production, as compared to year 2015. European market follows general trends of reducing weight of produced packaging materials, and most importantly focuses on efficient usage of resources [26]. In 2016, graphic papers production was limited (by 3.8%), and simultaneously there was an increase in the production of sanitary papers (by 1.1%) and packaging papers (by 2.4%). In the group of packaging papers, there has been an increase in the production of papers assigned for the production of corrugated cardboard (by 2.2%), used for manufacturing boxes (cartons) and other packaging used for transport purposes. Already, previously, indicated convergence of global trends with those observed on Polish paper and cardboard market, one may conclude that identification of economic tendencies for Polish case study concerning a selected Central and Eastern European country may be used as a source of forecast for the development of paper industry in other countries and the world regions.

CEPI paper assortment group	CEPI Countries Production (P) and consumption (C)				Poland Production (P) and consumption (C)			
	2014		2015		2014		2015	
	P	C	P	C	P	C	P	C
	Unit in thousands of tons							
Newsprint	7594	7061	7042	6606	126	9.6	110	—
Uncoated mechanical	5634	4684	5503	4623	0	275	0	247
Coated mechanical	7050	5142	6789	4926	0	266	0	239
Uncoated woodfree	9017	7149	8934	7036	730	239	714	287
Coated woodfree	7364	4938	7020	4754	0	248	0	285
Total graphic papers	36,659	28,918	35,265	27,946	856	1039	824	1052
Sanitary and household	7001	6700	7153	6925	562	418	568	414
Case materials	26,205	24,870	27,059	25,894	2044	1981	2166	2205
Carton board	8551	5744	8710	5891	239	474	265	517
Wrappings	4106	2994	4071	2866	89	269	95	276
Other paper & board for packaging	4591	4159	4733	4300	90	166	96	177
Total packaging papers	43,452	37,767	44,572	38,951	2462	2890	2622	3174
Other paper & board	3910	3642	3881	3594	399	355	385	346
Total paper & board	91,019	77,028	90,872	77,416	4278	4701	4399	4986

Source: own elaboration based on [11, 25].

Table 3. Paper and Board Production and Consumption in 2014 and 2015 (CEPI).

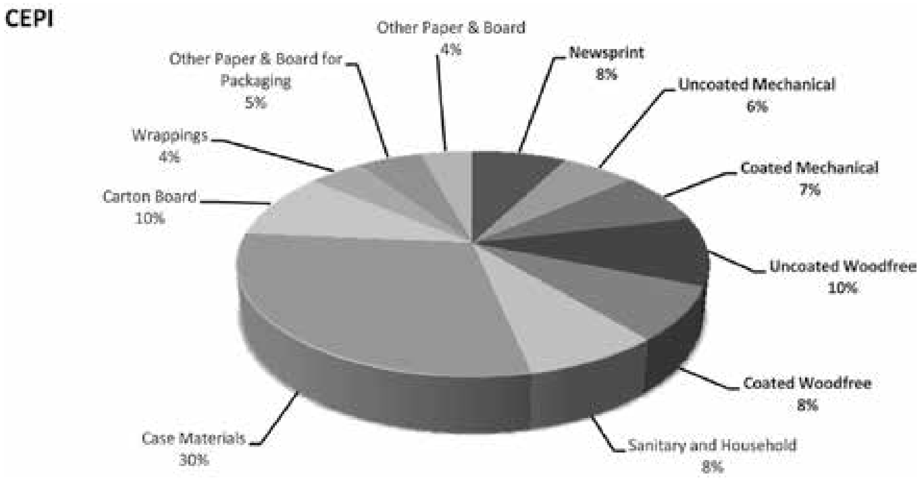

Figure 5. Structure of paper and paperboard production in CEPI countries in 2015. Source: own elaboration based on [11, 25].

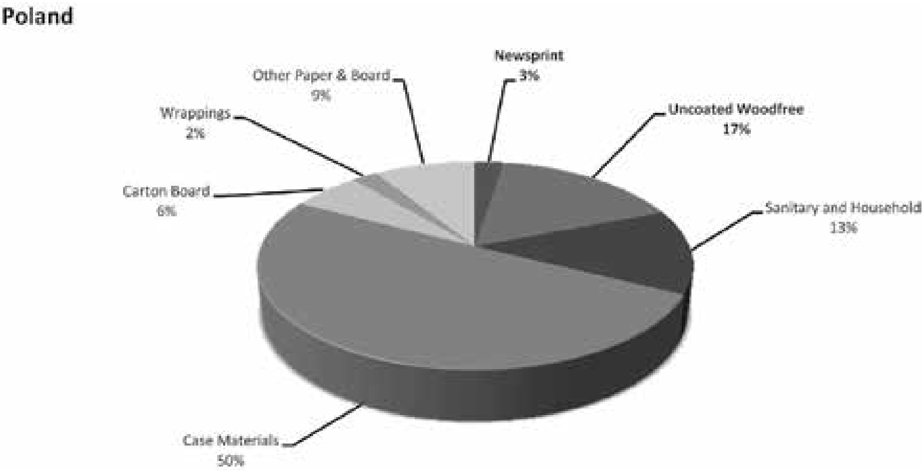

Figure 6. Structure of paper and paperboard production in Poland, in 2015 (CEPI). Source: own elaboration based on [11, 25].

6. Development prospects of paper and cardboard market

An attempt for identification of global development trends on the market of paper commodities based on a case study of local market (Poland), although seems to be a risky assumption, as reflected in the observations of consumers behaviors in Europe and world-wide. Those trends mainly concern two segments: paper and cardboard packaging (I) and sanitary papers (II). In the first case, development is determined by knowledge and belief of consumers regarding the endurance of packaging and the possibility of its recycling based on paper resources, while a growing demand for sanitary papers is determined by socio-economic factors related to the improvement in standard of living and demographic situation. China is a good example allowing us to draw conclusions that there is a link between growing GDP and an increase in the consumption of sanitary papers (**Figure 7**).

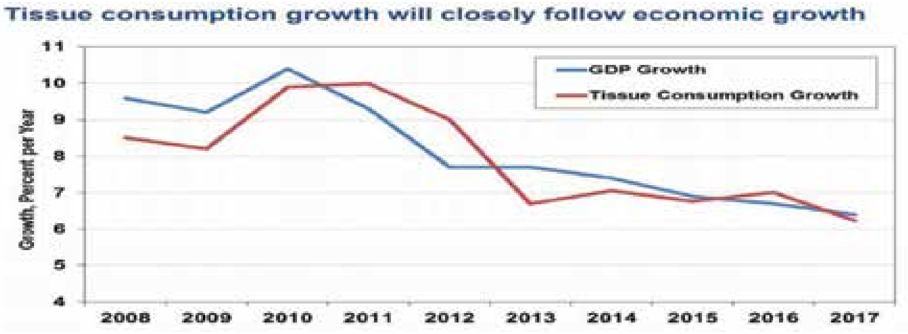

Figure 7. Comparison of GDP and tissue consumption changes in China (2008–2017). [X-axis label]: Years 2008–2017. Source: [27].

This trend is stimulated by other complementary factors: urbanization, growth of net income, as well as consumer spending and primarily standard of living, natural element of which is access to high quality paper sanitary products. Moreover, even in the group of graphic papers, which is threatened by a decreasing demand due to a partial substitution by electronic media, a domineering position of new technologies over paper is not yet sealed.

Using descriptive approach, the following most important development trends of individual groups of paper products simultaneously reflect the formulated key trends in the development of the whole sector. Firstly, trends on the market of graphic papers were verified. Despite adverse opinions, the electronic media will not totally substitute paper as the medium of press, journalistic and scientific information as well as books and documents. Naturally, they will become a partial substitute facilitating and supplementing exchange of information on paper and communication. This investigation is supported by the following studies:

- The results of survey among office employees of 2400 small and medium-size enterprises from EMEA countries conducted on behalf of Epson Europe (2016–2017), which do not leave any doubts: pro-paper option dominates. 76% of respondents have an opinion that printing is a "very important" factor facilitating work and 75% states that "running paper-free office is unreal" (e.g., Poles print on average 29 pages a day) [28].
- 70% of Americans (including 69% aged 18–24) stated, in the survey conducted in September 2012 by Two Sides, that they prefer to read information printed on paper rather than displayed on a screen [29].
- Similar results were brought by research undertaken by Pew Research Center, which noticed that 6% of the respondents read books in digital format and 38% only in printed version. Hence, an imminent death of traditional books cannot be forecasted [30].
- Exchange-listed Association of German Book Sellers announced that in 2014, the existing buyers of electronic books ever more often read in printed formats (a drop in the number of e-book readers from 46% in 2013 to 33% in 2014) [31].
- A group of leading American companies removed advertisement promoting electronic invoices as more ecological. It has been justified by the statement that printing on paper has many unique features of environment protection (renewable resources), argument on rescuing forests is misconceived (more trees are planted than harvested), an actual cost of launching electronic documents is not known, while the majority still collects paper printouts of their e-documents for archive purposes [32].
- On the request of association of Consumers for Paper Options (CPO) in 2013, in the USA (and previously American post), it has been assessed that 80% of respondents are in the opinion that forcing clients to receive invoices (including those for energy consumption) only in electronic form is unacceptable [33].
- Scientists from McMaster University in Canada developed a method of printing on paper biosensors, which will be warning consumers against contaminated foods [34].

- At Bologna University, it has been proved that fruit sold on trays made of corrugated cardboard stay fresh for longer and are better protected than those sold on reusable plastic trays [35].
- Report “Paper and Productive Learning” [36] confirms domination of paper in academic education. 82% of students always or very often use paper when revising for exams, 74% uses paper for taking notes. Simultaneously, 64% of teachers are convinced that students better understand texts which are put on paper.
- Also, the study of artists’ opinions revealed their conviction about greater efficiency of art expressed via paper than in digital format [37].
- Finally, association of German paper mills (*Verband Deutscher Papierfabriken* (VDP)) using research method of interview and observation of usability of paper in everyday life of Germans identified a significant role of paper in context of hygiene (80% respondents), transport (69%), and information (66%). Paper environmental safety was recognized and 79% of respondents were for invoices and documents delivered in paper format [38].

Meanwhile, economies worldwide record decreases in the production of graphic papers; however, stating its imminent decline or total elimination from usage would be unjustifiable. A totally reverse trend is observed on the market of paper packaging including corrugated cardboard packaging. Demand for this product grows in BRIC countries (Brazil, Russia, India, and China). Already, over 65% of packaging in Germany is manufactured from corrugated cardboard. This market in Europe is considered to be a growth pole (the pace of growth is estimated at 4.8% annually). Over half of British consumers (57%) prefer to pack their fresh food products in paper bags [39], and similar preferences are declared by 68% of European consumers [40]. Development of corrugated cardboard is also stimulated by new products manufactured based on cardboard, including: ULD pallet with honeycomb structure [41], corrugated cardboard bicycle helmets for self-service bike rentals [42], and KarTent, manufactured entirely from cardboard designed by a Dutch start-up [43]. In reaction to those trends, some factories producing graphic paper change their profile and launch production of corrugated cardboard: (a) Pro-Gest is reconstructing newsprint mill in Mantua, Italy, planning the production of corrugated cardboard in 2018 [44], (b) a similar investment takes place in Heinzel factory in Laakirchen in Austria [45], (c) a change of profile for corrugated cardboard will be launched in Madrid by International Paper, following their acquisition of newsprint paper from Holmen [46], (d) new investments are also carried out by LEIPA in Schwedt [47], Mondi (Slovakia)—production of “Kraft top white” [48], in Poland Stora Enso in Ostrołęka [49], Prinzhorn group (Eurobox Polska) [50], and Schumacher Packaging Group in Myszków [51].

European tissue paper market is growing at a quite stable pace, on average by 2–3% per year. A decline was recorded only in 2009. Western European markets record lower increase rate (up to 2%), while developing markets of Eastern Europe including Russia and Poland constituting 60% of the market record higher which increases (up to 4–5%) [52]. Tissue paper market is steadily developing (13% of Polish market of commodities made of paper in 2015) [53], and consumers are looking for goods in both economy and, ever more frequently, premium

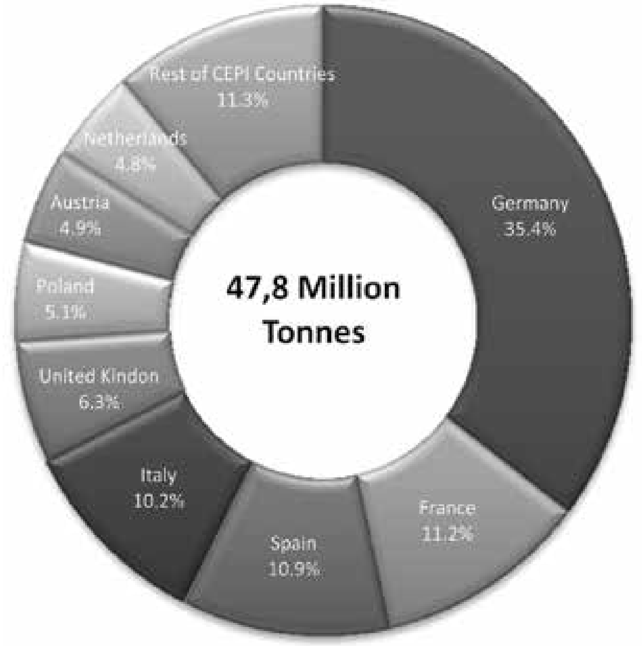

Figure 8. Use of recycled paper in CEPI countries in 2016. Source: own elaboration based on [25].

segment [54]. Along with the development of paper commodities market, one may also predict an increase in the usage of recycled paper. Currently this level is relatively stable with a slight growth in 2016 and amounts to 47.8 million tons (**Figure 8**). Collection of paper for recycling grew by 1% reaching the level of 56.4 million tons. Simultaneously, export of recycled paper increased by 5.6%, most of which was sent to Asian markets (91.7%). Level of recycling in EU countries, Switzerland, and Norway reached to 72.5% (increase by 0.7%).

Despite the fact that paper sector has to fight myths, such as “paper production destroys forests and environment,” market of paper commodities is well perceived by consumers and will be developing. This development will include mainly those segments which are based on wood, and maximize the added value by trying to implement the principle of “zero waste.” It is therefore about the type of industry which facilitates multiple recycling and converts into energy only, the materials which cannot be reused.

7. The value of sawmill wood by-products

In Poland, the use of sawmill by-products, which share in the total supply of all industrial wooden by-products (including veneer sector) amounts to 60%, becomes even more significant [55]. The aim of this analysis was to show a method of verifying research hypothesis, which has assumed that the refining conversion of sawmill by-products, based on the example of selected new products processed in Poland enhances their value. The research used the data related to the prices of sawmill by-products, which was obtained via questionnaire and in-depth interview carried out at sawmills in Poland in 2015. Sawmills were selected using nonrandom sampling technique, in accordance with the minimum size of the sampling and the verification of statistical correctness of selection [56]. Evaluation of the profitability of processing the sawmill by-products into bio-fuels and energy was proposed based on:

1. Determining the value of sawmill by-products in the given areas of application

   a. Processing into bio-fuels [55]:

$$W_{pi} = \frac{1}{a_{pi}}\left[c_{jp}\left(1-\frac{m_j}{1-P}\right)-k_{pi}-k_{ti}\right] \qquad [\mathrm{EUR/m^3}] \tag{1}$$

   b. Processing into energy [55]:

$$W_{ei} = c_{je}g\frac{19{,}5-2{,}5w_o}{1+w_o}\left(1-\frac{m_j}{1-P}\right)-k_{pi}-k_{ti} \qquad [\mathrm{EUR/m^3}] \tag{2}$$

   where W_{pi} is the value of wooden residue being processed into any wooden fuel [EUR/m^3], I is the number of the type of by-product being converted, i ϵ <1, n>, P is the type of generated wooden fuel, p ϵ <1, n>, a_{pi} is the ratio of material intensity when processing the given by-product "i" into wooden fuel "p" [m^3/t, mp/t], c_{jp} is the unit sales price of the fuel "p" generated while processing by-products [EUR/t], m_j is the assumed net profit margin level m_j: {0.01; 0.05; … 0.15}, P is the Corporate Income Tax (CIT), in 2015 = 0.19, k_{pi} is the cost per unit of processing wooden residue [EUR/t], k_{ti} is the cost of transporting a unit of wooden residue [EUR/t], W_{ei} is the value of a given type of by-product of "i" number converted into energy [EUR/m^3], c_{je} is the unit price of selling energy generated from burning by-products [EUR/GJ], G is the bulk density of the type of by-product being burnt [t/m^3], and w_o is the absolute moisture of the by-product being burnt.

2. Comparing the determined value with the sales price of unprocessed sawmill by-products [55, 57]. Determined value of various types of sawmill by-products being processed into pellet, wooden briquettes, and energy was estimated and presented in **Table 4**, along with the sales prices of the post-production by-products from which they were processed.

The presented data indicate that a significantly higher increase in the value of sawmill by-products is reached by the entrepreneurs who process them at the place of their creation; hence, they do not bear any transport costs. The highest here is the value of post-production by-products processed into wooden briquettes, and slightly lower, in case of those being processed into pellet. The least profitable is processing "by-products" into energy, yet not for all types of by-products. The formula rationalizing the utilization of the stream of sawmill by-products via determining the value of their individual types which facilitates the selection

Types of by-products		**Sawmill by-product average price [EUR/m^3]**	**Value of by-products in conversion divided into**								
			Pellet with margin			**Briquettes with margin**			**Energy with margin**		
			0.05	**0.10**	**0.15**	**0.05**	**0.10**	**0.15**	**0.05**	**0.10**	**0.15**
			Without transport cost [EUR/ m^3]								
			Including transport cost [EUR/ m^3]								
Sawdust	MSTR = 10%	28.10	46.48	39.89	35.68	49.52	45.54	41.56	29.21	**27.14**	**25.07**
			36.92	32.72	30.75*	42.35	38.37	34.40	**26.49**	**24.42**	**22.35**
	MSTR = 50%	24.12	39.67	33.52	29.59	42.65	38.94	35.23	33.85	31.46	29.06
			30.36	26.43	24.60*	35.57	31.86	28.14	31.51	29.11	26.72
De-fibered chips	MSTR =25%	28.10	44.93	39.96	34.99	52.62	47.87	43.13	33.60	31.22	28.84
			39.33	34.36	31.00**	47.02	42.27	37.52	31.75	29.37	**26.99**
	MSTR =50%	28.10	37.13	32.94	28.76	43.59	39.59	35.59	40.62	37.74	34.87
			31.51	29.59*	**23.14**	37.97	33.97	29.97	39.10	36.22	33.35
Pulp chips	MSTR =25%	35.36	50.25	44.93	39.61	57.05	52.01	46.97	**33.60**	**31.22**	**28.84**
			44.65	39.33	36.85*	51.44	46.40	41.36	**31.75**	**29.37**	**26.99**
	MSTR =50%	35.36	41.63	37.15	**32.67**	47.31	43.07	38.82	40.62	37.74	**34.87**
			36.01	**31.53**	**27.05**	41.69	37.45	**33.20**	39.10	36.22	**33.35**
Waste wood MSTR = 25%		24.59	52.68	46.75	40.82	61.88	56.22	50.55	33.60	31.22	28.84
			47.11	41.18	35.25	56.31	50.64	44.98	31.75	29.37	26.99

Source: own elaboration based on [55].

MSTR, moisture content; *, bb—sales only in big bag; **, bulk—only bulk sales. In **bold**, values of those converted by-products which came out as lower than the average sales price of sawmill wood by-products.

Table 4. Value of wood-sawmill by-products converted into pellet, briquettes and energy including and excluding cost of transport in Poland (2015).

of the most profitable one, from the sawmill perspective, and the way of utilizing its post-production by-products.

8. Criteria for evaluating profitability of processing sawmill wood by-products

Research attempts are taken to evaluate profitability criteria of converting the wooden by-products into wooden briquettes and pellets. Selected factors have been studied: namely threshold margin, maximum price (at which the raw material can be purchased for further

Type of wood by-product		Sawmill wood by-product average price [EUR/m^3]	Profitability of processing wood by-products generated as by-products and basic products						
			Break-even margin, m_{gr}		Maximum unit costs of conversion including transport	Maximum cost of transport per unit	Maximum distance from which raw materials can be transported*	Maximum purchase price of raw materials for conversion	Minimum selling price of finished product
			By-production	Basic production	$k_{pmax} + k_{tmax}$ [EUR/t],[EUR/m^3]*	k_{tmax} [EUR/t]	l [km]	c_{pub} [EUR/m^3]	c_{min} [EUR/t]
			Pellet						
			Briquettes						
Sawdust	MSTR 10%	28.10	23.76	15.23	88.33	44.37	232.89	40.80	122.83
			31.64	22.63	80.29	55.94	293.65	45.96	103.21
	MSTR 50%	24.12	22.12	13.09	94.11	41.31	204.97	34.44	126.82
			26.98	16.86	77.79	44.96	223.04	35.97	106.86
De-fibered Chips	MSTR 25%	28.10	21.86	16.22	91.82	38.13	254.76	44.18	112.98
			30.73	**24.82**	85.50	51.20	342.02	51.60	93.60
	MSTR 50%	28.10	15.52	9.88	82.27	27.06	151.54	36.30	124.05
			26.63	20.99	82.27	46.45	260.07	45.54	104.66
Pulp Chips	MSTR 25%	35.36	18.93	12.66	89.04	35.35	236.16	48.79	127.63
			26.41	19.79	81.00	46.69	311.95	55.24	108.24
	MSTR 50%	35.36	11.68	5.41	77.02	21.81	122.13	40.17	141.17
			18.75	12.13	68.98	33.16	185.65	45.57	121.78
Waste Wood MSTR = 25%		24.59	28.69	23.99	105.14	50.05	400.30	33.60	53.06
			37.34	**32.42**	98.81	61.70	493.48	31.75	60.98

Source: own elaboration.

MSTR, moisture content; *, transport 25 m^3, rate 1.06 EUR/km (**In bold** the highest values of: break-even margin level for various forms of utilizing sawmill-wood by-products); data presented excluding cost of transport.

Table 5. Profitability of processing wood by-products into pellets and briquettes and basic products in Poland (2015).

processing), maximum unit cost of processing (including and excluding cost of transport), and the minimum acceptable by the producer sales price of the wooden biofuel (**Table 5**).[1]

Evaluation of profitability of processing sawmill by-products into ecological fuels and energy may be carried out in determining their value using the formula (3) [55], and then comparing it with the price of unprocessed "wooden residue." Transformation of the formula given below (Eq. (3)), which allows to set down the maximum possible margin, costs of processing, or the price level of the "residue" up to which purchasing of it will still be profit-making:

$$W_{pub} = \frac{1}{a}\left[c_j\left(1-\frac{m_j}{1-p}\right)-k_{jp}-k_{jt}\right] \qquad [\mathrm{EUR/m^3}] \tag{3}$$

where W_{pub} is the value of wooden residue being processed into any wooden fuel [EUR/m^3], A is the amount of basic material necessary to generate one unit of a given wooden fuel [m^3/t, mp/t].[2] c_j is the sales price per unit of a given wooden fuel [EUR/t], m_j is the target net profit margin m_j: {0.01; 0.05; … 0.15}, P is the Corporate Income Tax (CIT), in 2015 = 0.19, k_{jp} is the cost per unit of processing wooden residue into a given wooden fuel [EUR/t], and k_{jt} is the cost of transporting a unit of wooden residue [EUR/t].

Comparative analysis used the data related to the prices of sawmill wood by-products, which was obtained via questionnaire carried out at wood processing plants (sawmills) in Poland in 2015. Analysis has embraced both companies (wood processing) which generated their own wood by-products as well as those which have to buy those (wooden) by-products (**Table 5**). Analysis of the juxtaposed values indicates that the most profitable form of processing wooden by-products is briquettes production and the highest margin level: 37.3% in case of the entrepreneurs who are in possession of those by-products may be obtained utilizing wood chips. The least profitable material for the production of briquettes is paper chips of 50% moisture content, due to their high price in the unprocessed form.

9. Conclusion

The formula rationalizing the utilization of the stream of sawmill by-products via determining the value of their individual types facilitates the selection of the most profitable, from the sawmill perspective, and the way of utilizing its post-production by-products. At the same time, it gives their owners the basis for choosing a versatile structure of their utilization. The above presented method may also be used when evaluating the profitability of production adopted as the main commercial activity by the entrepreneurs using the product available on the market.

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[1] For comparison, the current average exchange rate is 1 EUR = 4.2705 PLN (Table No. 078/A/NBP/2017 of April 21, 2017; Source: http://www.nbp.pl/homen.aspx?f=/kursy/ratesa.html [Accessed: April 21, 2017]).

[2] The symbol "mp" means spatial meter in [mp/t] and [EUR/mp].

The following conclusions and recommendations were formulated:

1. The study showed that significantly higher increase in the value of further processed sawmill by-products is achieved by those entrepreneurs who process them at the place of their conversion without bearing any additional cost of transport.

2. Preferred and the most efficient way of utilizing wood by-products would be the sales of this raw material for further processing into paper and other derivatives (for example defibered chips), or alternatively direct utilization of solid pieces of wood assigned for a specific product which allows to gain added value, recycle, and reuse.

3. Only definite lack of resources primary usage should determine an optimum method of processing.

4. The highest value is characteristic for wooden by-products processed into briquettes, slightly lower for those processed into pellet. The least profitable is converting wooden by-products into energy.

   In detail, it was identified that:

   - The highest level of threshold margin is reached by the production of wooden briquettes utilizing wood chips (37.3%). The producer—who does not incur transport cost—may reach a higher margin, from 4.7% (wood chips) up to 9% (sawdust with 50% moisture content).
   - The maximum margin of net profit—determined for wooden pellet—is on average between 7.6 and 8% (including or excluding cost of transport) lower than in case of processing wooden by-products into briquettes.
   - Recommended for processing into pellet are: dry sawdust and paper chips—for which the average sales price may be higher.
   - The most profitable material—for briquettes production—constitutes de-fibered chips and wood chips (with moisture content of 25%), due to lower quality requirements concerning final product.

5. The descriptive analysis showed that significantly higher increase in the value of further processed sawmill by-products is achieved by those entrepreneurs who process them at the place of their conversion without bearing any additional cost of transport.

6. Investigating the further processed sawmill by-products (i.e. the wooden by-products into ecological fuels) is of essential importance for the economic development of regions, especially for industries characterized by high territorial fragmentation, e.g., the forest and wood-based sector in Poland.

   It needs to be highlighted that Polish wood market and derivative markets are determined by quasi-monopolistic organization of the market of wooden raw material. Institutional conditions of inter-municipal and inter-sectoral cooperation in Poland are concurrently an opportunity and a barrier for the establishment of partnerships with the participation of wood industry. Functioning of a secondary wood market, dispersed and territorially diversified, is a subject to market mechanisms. It creates a new market for sawmill wood by-products, which is an opportunity for the development of small- and microenterprises in the forest- and wood-based sector in Poland.

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Section 3

Environmental Friendly Method of Fibre Processing

Chapter 6

Environmentally Friendly Method for the Separation of Cellulose from Steam-Exploded Rice Straw and Its High-Value Applications

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Additional information is available at the end of the chapter

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Abstract

Separation of cellulose from agricultural straw is one of the key bottlenecks hindering the application of such kind of biomass resources. In this chapter, we provide three environmental-friendly ways for separation of cellulose from agricultural straw pretreated with steam explosion, which include delignification with recyclable water-polar aprotic organic solvent, selective bio-degradation of the lignin component, and extraction of cellulose with imidazolium-based ionic liquids from the steam-exploded rice straw. The isolated rice straw celluloses have been adopted as an enhancement for all-cellulose composites (ACCs) and cellulose/cement composites. Ultra-high tensile strength (650.2 MPa) can be achieved for the ACCs containing the activated straw cellulose fiber (A-SCF). The cellulose/cement composites show a significant promotion in the flexural strength and fracture toughness. The new nonderivative solvent for cellulose, tetrabutylammonium hydroxide (TBAH) aqueous solution with urea as additives has been proved to be manipulable for dissolving cellulose.

Keywords: rice straw, steam explosion, cellulose, ionic liquids, all-cellulose composites, cellulose/cement composites, cellulose solvent

1. Introduction

Due to the ever-growing demand for energy, environmental impact caused by pollution, and the depletion of fossil fuel reserves, the demand for materials from renewable resources has become an important matter [1, 2]. Lignocellulose biomass is considered one of replacing chemicals as well as fuels based on oil [3]. Agricultural residues is one of the most valuable and renewable lignocellulosic biomass as well as a promising alternative for cellulosic materials. Among different sources of agricultural residues, rice straw has been extensively investigated because it is one of the most consumed cereals in the world, about 650–975 million tons per year all over the world [4, 5]. Rice straw is composed of approximately 35% cellulose, 18% hemicellulose, and 15% lignin [6]. It can be used as raw material for conversion to high value-added products through chemical, biochemical and physical processes. However, cellulose is usually accompanied by other structural biopolymers, saying hemicellulose, and lignin. Therefore, determination of methods for the efficient separation of the constitutive biomass components has long been the major obstacles to its utilization.

Thus, novel environmental-friendly processes have been developed continuously, which include steam explosion [7], organosolv processing [8], the chlorine-free method [5], biological treatment [9], and ionic liquid isolation [10]. In this chapter, a brief review on the separation of rice straw cellulose in sustainable ways and the related utilization of the cellulose enhanced composites are systematically presented.

2. Steam explosion as pretreatment of rice straw

2.1. Introduction

Steam explosion (SE) has been a well-known technology for the pretreatment of straws during the separation of cellulose [11–13]. The critical process is the high-temperature hydrothermal treatment followed by a sudden exposure to atmospheric pressure [14].

During processing, the major hemicelluloses are partially hydrolyzed (autohydrolysis) due to high temperature transforming the acetyl groups connected with hemicellulose into acetic acid. Part of lignin can be depolymerized and leaving on the cellulose [15]. It is reported that the hydrolysis of hemicellulose separation was related to the reaction time and the pressure in the reactor [16]. For example, with the optimum condition (215°C, 7.5 min), a high-yield of sugar (81%) and ethanol (12.4%) can be obtained [17]. Therefore, the critical issue is a suitable condition of parameters, such as cooking time and the pressure, for efficient removal of hemicelluloses during the steam explosion which has been optimized by Zhou et al. [18]with a regression method in statistics.

2.2. Optimizing of conditions for steam explosion

Naturally dried rice straw was cut into pieces of about 2–3 cm in length and then shredded in a high-speed pulverizing mill. The crushing process was necessary for the effective infiltration of steam into the cell. The rice straw was then put into the reactor with a solid to liquid ratio of 3:1 (w/w). The high-temperature steam was poured in by opening a valve and cooked for a specified time, followed by explosion procedure.

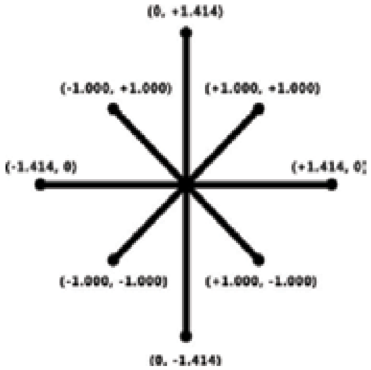

Figure 1. Spatial distribution of these two factors.

Normalized	Pressure *X1* (MPa)	Cooking time *X2* (min)
1.414	3.2	32
1.000	3.0	30
0.000	2.5	25
−1.000	2.0	20
−1.414	1.8	18

Table 1. Parameter table.

A series of experiments were designed to investigate the effects of pressure *X1* (corresponding to temperature) and cooking time *X2* on the final product of hemicelluloses (γ-Cellulose) and cellulose (α-Cellulose) in the process of steam explosion by using a regression method in statistics. The number of the experiments (N) meets the equation below:

$$N = 2^m + 2m + 3 \tag{1}$$

where, m is the number of independent factors and "3" is the number of experiments in the central point, which could improve the accuracy of the regression.

The spatial distribution of these two factors (*X1*, *X2*) in this regression design is illustrated in **Figure 1**. According to the earlier works of exploratory, the interval factors have been determined, as shown in **Table 1**.

The details of the experimental plan as well as the content of hemicelluloses and cellulose of the steam-exploded straw are shown in **Table 2**. The sample 11 of steam explosion in **Table 2** is selected for the comparison of the main components with the original rice straw. It is clear that most of the hemicelluloses can be hydrolyzed and extracted at the proper set of conditions for the steam explosion.

No.	*X1*	*X2*	Treatment severity lgR_o[a]	γ-C (%)[b]	α-C (%)[b]	DP[c]
Rice straw	—	—	—	17.98	35.06	1123
1	1.000	1.000	6.19	3.01	70.43	229.5
2	−1.000	1.000	5.60	8.66	69.85	303.3
3	1.000	−1.000	6.01	3.84	65.03	198.4
4	−1.000	−1.000	5.42	3.25	67.58	272.7
5	0	1.414	5.92	6.29	72.96	360.2
6	0	−1.414	5.67	6.68	70.51	276.2
7	1.414	0	6.25	2.72	61.77	246.0
8	−1.414	0	5.37	8.46	70.49	418.6
9	0	0	5.81	1.45	64.80	268.3
10	0	0	5.81	1.38	64.72	266.0
11	0	0	5.81	1.10	64.65	270.9

[a] Refers to the strength of the steam explosion and could be calculated by Eq. (2).

[b] The contents of α-Cellulose and γ-Cellulose, respectively, which are determined according to Tappi method T203 cm-99.

[c] The intrinsic viscosity of α-Cellulose ([η]) that is measured in cupriethylenediamine (CED) solution, and from which the DP (degrees of polymerization) could be calculated by the equation below, according to SCAN-CM 15:88 standard.

Table 2. Effect of reaction time and pressure on the final content of hemicelluloses and cellulose [18].

The value of lgRo is proportional to the strength of steam explosion. Additional hydrolysis of α-Cellulose may happen along with higher lgRo, as indicated by sample 7 in **Table 2**.

$$R_0 = \int_0^{t[min]} \exp\left(\frac{T[^\circ C] - 100}{14.75}\right) \bullet dt \tag{2}$$

$$DP^{0.76} = [\eta]/2.28 \tag{3}$$

Experimental data in **Table 2** have been fitted to the following second-order polynomial:

$$Y_i = a + bX_1 + cX_2 + dX_1^2 + eX_2^2 + fX_1X_2 \tag{4}$$

where Y_i refers to α-Cellulose, γ-Cellulose and SCAN viscosity, respectively. The symbols of *a*, *b*, *c*, *d*, *e* and *f* are the corresponding estimated parameters. Regression has been carried out using a nonlinear method with the SPSS software, and the result data are as shown in **Table 3**. R^2 values of α-Cellulose and γ-Cellulose are close to 0.9, which indicate good models for these factors. However, the model of SCAN viscosity is not well fitted, as indicated by the low value of the R^2.

Since the regression has established good models (Eqs. 5 and 6) describing the relationships between independent factors (referring to *X1* pressure and *X2* cooking time of the steam explosion process) and the responses (referring to Y_i, final content of γ-Cellulose and α-Cellulose).

Symbols	γ-Cellulose (%)	α-Cellulose (%)	SCAN viscosity
a	1.31	64.72	268.42
b	−1.65	−1.79	−48.76
c	0.50	1.34	26.80
d	1.80	0.54	14.93
e	2.25	3.28	4.85
f	−1.56	0.78	6.95
R^2	0.896	0.861	0.332

Table 3. Characteristic constants and R^2 of the regression [18].

These relationships can be visualized, as shown in **Figure 2**. The values of coordinates of their nadirs are given in **Table 5**.

$$Y_{\gamma-C} = 1.31 - 1.65 \times X_1 + 0.50 \times X_2 + 1.80 \times X_1^2 + 2.25 \times X_2^2 - 1.56 \times X_1 \times X_2 \tag{5}$$

$$Y_{\alpha-C} = 64.72 - 1.79 \times X_1 + 1.34 \times X_2 + 0.54 \times X_1^2 + 3.28 \times X_2^2 + 0.78 \times X_1 \times X_2 \tag{6}$$

As discussed earlier, the aims of the steam explosion maximizing the removal of the γ-Cellulose and the loss of α-Cellulose. From the observation, there is no serious contradiction between these two aims, since the nadir of γ-Cellulose and α-Cellulose locates at the center and the edge, respectively. Therefore, the optimal condition for the steam explosion is 2.74 MPa and 25.3 min, according to the data in **Table 4**. Under the optimal condition, the structure of steam-exploded rice straw showed the characteristics of soft, loose and porous with different sizes distributed though all of the fiber (as shown in **Figure 3a**), which supported further separation of cellulose and lignin. The most of hemicelluloses could be efficiently hydrolyzed,

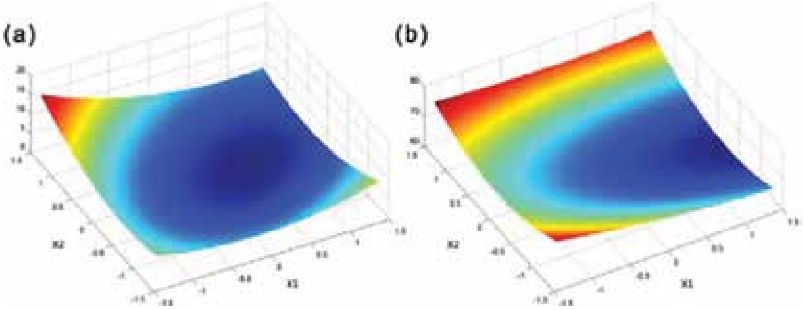

Figure 2. A 3D graphic of dependent factor (referring to final content of γ-cellulose Y_i) vs. independent factors (referring to pressure *X1* and reaction time *X2* of the steam explosion process), (a) according to Eq. (5), and (b) according to Eq. (6).

	γ-Cellulose		α-Cellulose	
	Scaled factor	Factor	Scaled factor	Factor
Pressure $X1$ (MPa)	0.481	2.74	1.414	3.20
Reaction time $X2$ (min)	0.056	25.3	−0.374	23.1
Content of cellulose Y_i (%)	0.93		62.82	

Table 4. Factor values for the minimum of the content of γ-cellulose and α-cellulose.

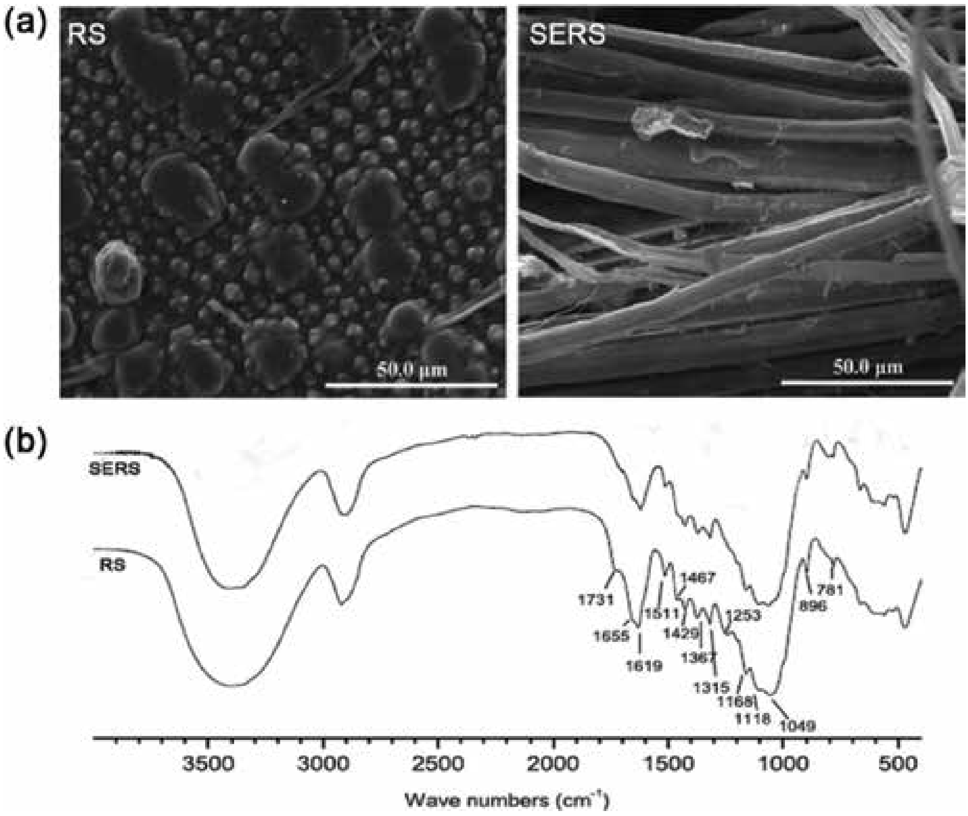

Figure 3. (a) SEM images and (b) FT-IR spectra of rice straw (RS) and steam-exploded rice straw (SERS) [18].

leaving only 1% residual hemicelluloses. However, the majority of cellulose, as well as the fragmentized lignin, were retained in the size, which could be identified by the SEM observations (**Figure 3a**) and the FTIR spectra (**Figure 3b**) [18].

3. Posttreatment of steam-exploded rice straw

3.1. Selective dissolution of cellulose using ionic liquids

Ionic liquids (ILs) are emerging as promising solvents for treatment of lignocelluloses [19–23], due to its low vapor pressures. These solvents are made up of large organic cations and small inorganic anions, which have the following key properties: (a) they are liquids below 100°C or even at room temperature; (b) high thermal stability; and (c) high polarity [24]. These properties allow to be easily adjusted to dissolve diversity of lignocellulosic biomass [25–27]. Since several kinds of ionic liquids have been found to be non-derivatized solvents for cellulose, they have been applied in such research fields as capturing the portrait of single cellulose molecule [25], and chemical modification of cellulose [19]. In this section, ionic liquids are used in separation of cellulose from steam-exploded rice straw. It is proved to be an efficient and environmentally friendly way to selectively dissolve and then recover cellulose [6].

Four kinds of ionic liquids: 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-benzyl-3-methyl-imidazolium chloride (BnMIMCl) and 1-benzyl-3-methyl-imidazolium trifluoroacetate (BnMIMTFA) have been synthesized according to literature [20]. Their solubility for cellulose and lignin are shown in **Table 5**. The results indicate that BnMIMCl and BnMIMTFA are efficient for dissolving lignin. BMIMCl and AMIMCl are efficient for dissolving cellulose.

AMIMCl is selected as a selective solvent to separate cellulose from the steam-exploded rice straw. The contents of acid-insoluble lignin and celluloses of the steam-exploded rice straw are 14.76 and 64.80% respectively. After dissolving in AMIMCl, there is only 0.90% acid insoluble lignin contained in the recovered cellulose. With a procedure of bleaching by immersing the separated cellulose into hydrogen peroxide aqueous solution together with ozone blowing (about 3.4 g/h produced by SZH5 ozone apparatus, Peking) was needed for bleaching. The bleached cellulose was finally obtained with a yield of 30.73%. The component analysis according to TAPPI standard methods (T 222 om-06 and T 203 cm-09) indicated no detectable acid-insoluble lignin and only 0.85% of hemicelluloses left in the final cellulose. The average degree of polymerization (DP) was 484.

The SEM image and XRD profile of the bleached cellulose are shown in **Figure 4**. As seen in **Figure 4a**, cellulose fibers could be observed clearly with average lengths more than 100 μm. The prominent peak at 22.13° denotes the (002) reflection (as shown in **Figure 4b**). However, the characteristic (101) and (101) peaks (2θ between 15 and 17°) are not as distinct as those in cotton [24], but combine into one broad peak at 15.728°.

The FTIR spectra of the original rice straw, steam-exploded rice straw as well as the bleached cellulose had been provided, **Figure 5a**. The peaks at 1510, 1465 and 1423 cm^{-1} in the sample RS, corresponded to the skeleton stretch of the benzene ring, mainly contributed by lignin. These peaks reduced in steam-exploded sample and disappeared in the bleached cellulose, indicating that the lignin could be removed by selective dissolving of IL. The ^{13}C CP/MAS solid-state NMR spectrum of the bleached cellulose shown in **Figure 5b** suggests that highly purified cellulose is obtained. The chemical shifts at 62 and 64 ppm are assigned to C6 of the primary alcohol group

Ionic liquid	**AMIMCl (%)**	**BMIMCl (%)**	**BnMIMTFA (%)**	**BnMIMCl (%)**
Cellulose	5.2	4.9	-	-
Lignin	-	-	4.9	3.9

"-" represents nearly no sample can be dissolved.

Table 5. Solubility of the four ILs for cellulose and lignin [6].

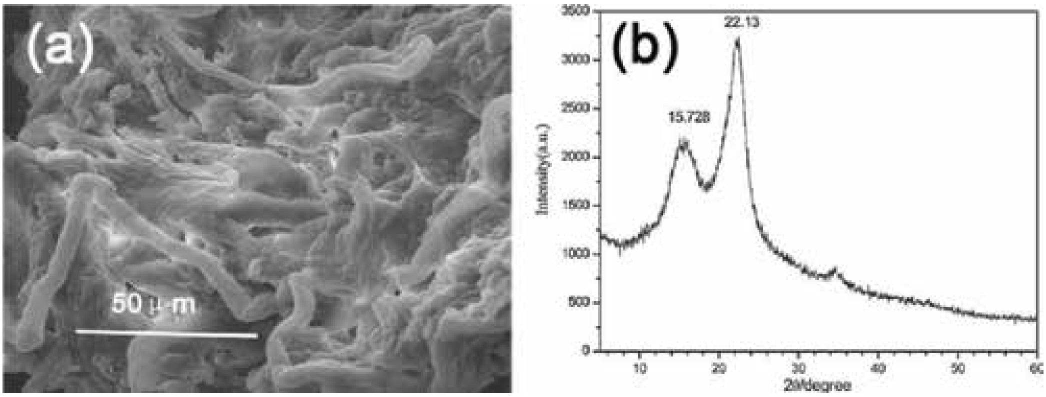

Figure 4. (a) SEM image and (b) XRD profile of bleached cellulose [6].

of cellulose, 71 and 74 ppm attributed to C2, C3 and C5, the ring carbons of cellulose. The peaks at 83 and 88 ppm associated with C4, and 104 ppm associated with C1. The feeble signals at 173 and 20 ppm attributed to the carbonyl and the methyl resonances, respectively.

3.2. Organosolve dissolution of lignin from the steam-exploded straw size

The organosolv process can effectively degrade lignin, which is mainly used osmosis to break and decompose the internal chemical bonds of cellulose and hemicellulose [28–30]. It is considered to be an environmentally friendly way because it can be recycled conveniently, which demonstrates its potential utilization in isolation of lignocellulosic biomass [8]. Moreover, the structure of the dissolved component will be protected from degrading under such moderate conditions, which is benefit for further utilization. The efficient solvent for delignification combined with steam explosion treatment has been realized as the separation of the three components that are cellulose, hemicellulose and lignin. However, few organosolv process

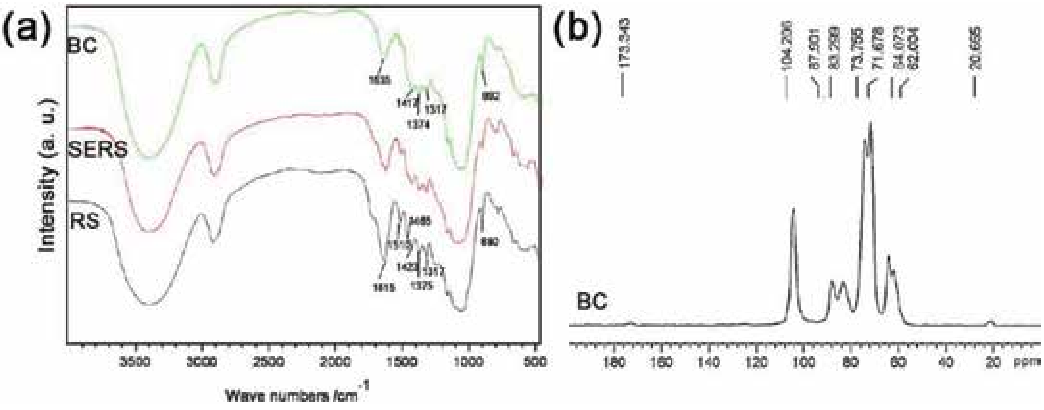

Figure 5. (a)FT-IR spectra and (b) ^{13}C CP/MAS solid-state NMR spectrum of rice straw (RS); steam-exploded rice straw (SERS); bleached cellulose (BC) [6].

have been proved attractive as regards efficiency and selectivity, even though intensive researches have been done [31, 32]. In this section, consideration has given on the effect of delignification with mixed solvent from steam-exploded rice straw under ambient pressure [18].

First, the rice straw is pretreated by steam explosion as the optimal conditions mentioned above. The steam-exploded rice straw was then washed with hot water (1:20 g/mL). After that, the residue was delignified by different mixed solvent to obtain crude cellulose. Finally, it was bleached with aqueous solution (1:30 g/mL, pH 11, 55°C) of 2% hydrogen peroxide and 0.2% TAED (tetraacetylethylenediamine) for 5 h.

The mixed solvent system and its results were summarized in **Table 6**. Comparing the delignification efficiency of H_2O-Dimethyl Sulfoxide (DMSO) (sample 7, 63.27%), H_2O-*N*-methylpyrrolidone (NMP) (sample 8, 75.14%) and H_2O-*N*, *N*-dimethylformamide (DMF) (sample 9, 84.78%) solvent systems to H_2O-methanol (sample 1, 57.13%), one could conclude that water-aprotic solvent system was better than water-protic solvent system for delignification. The delignification efficiency of H_2O-methanol could be further improved to 79.99% with aniline additive as the catalyst (sample 6). Similarly, aniline additive as a catalyst in the H_2O-DMF solvent system resulting in the efficiency improvement of delignification from 84.78 (sample 9) to 95.04% (sample 10).

Conclusively, the H_2O-DMF-aniline solvent system (in a volume ratio of 20:10:1) demonstrated to be the most efficient solvent for removing lignin from the steam-exploded rice straw because the DMF and aniline included amino groups might improve the dissolution of lignin.

The FTIR spectrum of the original rice straw, the steam-exploded rice straw, the delignified sample with H_2O-DMF-aniline and bleached cellulose shown **Figure 6a** indicated that the

No.	Solvent system[a]	Additives	Lignin residue (wt%)	Delignification[b] (%)
1	H_2O-methanol	—	7.52	57.13
2	H_2O-methanol	Formic acid	5.09	70.98
3	H_2O-methanol	Terephthalic acid	5.10	73.93
4	H_2O-methanol	Salicylic acid	2.89	77.33
5	H_2O-methanol	Sodium hydroxide	3.92	69.25
6	H_2O-methanol	Aniline	3.51	79.99
7	H_2O-DMSO	—	6.45	63.27
8	H_2O-NMP	—	4.36	75.14
9	H_2O-DMF	—	2.67	84.78
10	H_2O-DMF	Aniline	0.87	95.04

[a] Represents the residual cellulose-enriched fractions obtained with water, organic solvent and additives in ratios of 20:10:1 (v: v: v).

[b] The acid-insoluble lignin content in the steam-exploded rice straw is measured to be 12.75%.

Table 6. Influence of the composition of mixed solvent on the delignification process [18].

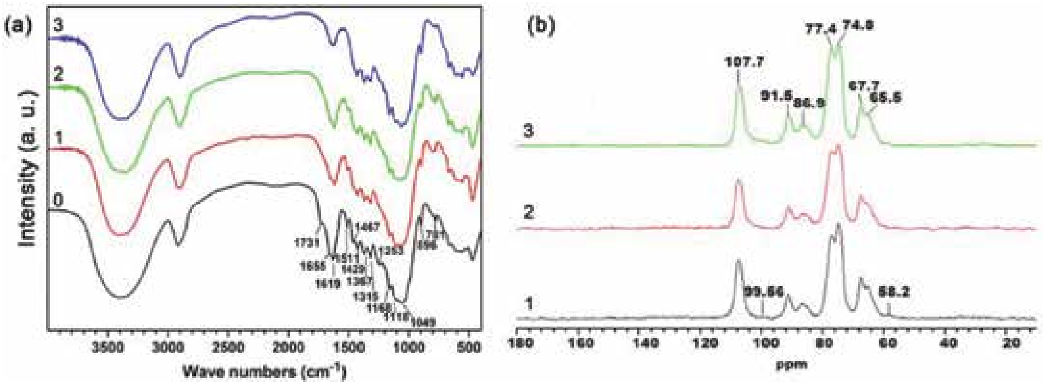

Figure 6. (a) FTIR spectra and (b) ^{13}C-NMR spectra of different samples (0, original rice straw); steam-exploded rice straw (1, SERS); H_2O-DMF-aniline delignified rice straw (2, DERS); bleached cellulose (3, BC) [18].

lignin in straw could be removed and obtained pure cellulose because the absorptions at 1511 and 1429 cm^{-1} assigned to the aromatic C=C stretch from aromatic ring in lignin became weak after the steam explosion (spectrum SERS) and delignification (spectrum DERS), and finally disappeared in the bleached cellulose (spectrum BC) [18].

Figure 6b indicated the ^{13}C CP/MAS solid-state NMR spectra of the steam-exploded rice straw (SERS), delignified rice straw (DERS) and bleached cellulose (BC).All of these spectra were dominated by the resonances attributable to cellulose. Notably, two small peaks at 99.5 and 58.2 ppm in the spectrum of steam-exploded rice straw (pattern SERS) were assigned to lignin and they nearly disappear in spectrum DERS, BC, which were the delignified cellulose with the water-DMF-aniline solvent system and bleached cellulose, respectively.

3.3. Biological removal of lignin from the steam-exploded straw size

Biological treatments employ microorganisms and their enzyme systems to break down the lignin present in lignocellulosic biomass. This approach has recently attracted increased attention because of its mild condition, low energy consumption, and the absence of pollution [33, 34]. Among the microorganisms those are capable of degrading lignocelluloses, white rot fungi has a higher selectivity toward lignin with lower energy input, as well as being environmentally friendly [35].

One white rot fungus, *Phanerochaete chrysosporium* (*P. chrysosporium*), harbors at least 10 lignin peroxidases (LiP), five manganese peroxidases (MnP), and several copper oxidases in its lignin-degrading system [36, 37]. Combinatorial treatment of steam explosion and biological treatment has been considered as an effective method of separating components for various kinds of biomass. Chen et al. [38] reported the effects of the solid-state fermentation (SSF) conditions on biodegradation of steam-exploded wheat straw with *P. chrysosporium*. Under the optimum conditions of SSF, the degradation amount of lignin reached 60% on the 5th day. Zhang et al. [39] indicated that steam explosion is an important pretreatment method for biodegradation of lignin in rice straw. After steaming under 2.5 MPa for 25 min, then completely decompressed within 3 min, the steam-exploded straw was collected and dried for biodegradation treatment. In their study, the degradation rate of lignin was 31.23% without steam explosion, and 55.40%

lignin loss rate had been found on day 30 after steam explosion pretreatment. A two-stage process proposed by Zhou et al. [40] was based on the pretreatment of steam explosion and followed by a *P. chrysosporium* post-treatment for the isolation of cellulose.

As the above processes, the orthogonal experiments (using L_{16} $(4)^5$ orthogonal table) were designed (**Table 8**) to investigate the relationship between the delignification in SERS and the five factors. Each factor had been set based on the pretest results and a literature review (**Table 7**). Curves of the factors vs. the delignification was shown in **Figure 7**.

According to **Table 8**, the maximum lignin loss rate, 64.25%, was obtained with the conditions of 1% spore suspension, 70% moisture content, 0.1% T-80, initial pH of 5.0, and 28 days of fermentation. The experimental outcomes could not be used as the best SSF conditions, so the orthogonal analysis should be performed. **Table 8** shows the results of orthogonal analysis for five factors used in the fermentation process and the order of importance of these factors on lignin removal was E > C > B > D > A. Based on the *k* value of the testing factors, the optimum process for fermentation is $A_3B_3C_2D_3E_4$, corresponding to 1.5% spore suspension, 0.3% T-80, 70% moisture, initial pH of 5.0, and 28 days of SSF.

According to the analysis presented above, the most important factor for delignification was SSF time. However, there was no top value of SSF time vs. delignification unlike the other four factors as shown in **Figure 7**. Hence, the effect of SSF time required further study.

Moisture was found to be significant to the delignification by *P. chrysosporium*. Water in SSF systems shows functions of transporting the nutrients and metabolites, which can contribute to the stability of the cellular and molecular structures. As displayed in **Figure 7**, until the moisture levels (70 and 75%), the delignification increased with increase of moisture. However, the delignification decreased after moisture exceeded 75% because the high moisture hampered the diffusion of oxygen into the liquid and solid phases thus limited aerobic SSF.

Figure 8 shows the effect of SSF time on the removal of lignin. The experimental results satisfactorily fitted the Boltzmann model with the decisive coefficient $R^2 = 0.9983$. The lignin content of the steam-exploded rice straw was efficiently degraded after a prolonged period. Nearly half of the highest lignin removal rate was obtained on the 7th day of fermentation. When the treatment time of using *P. chrysosporium* was 10 days, the lignin removal increased to 50.13%. Thereafter, the lignin removal rate decreased and tends to stabilize after 12 days.

Although the lignin degradation of steam-exploded rice straw is very important, too much weight loss is unexpected. The relationship between the SSF time and weight loss is shown

No.	Factor	Level 1	Level 2	Level 3	Level 4
A	Spore suspensions concentration (%)	0.5	1.0	1.5	2.0
B	T-80 concentration (%)	0.1	0.2	0.3	0.4
C	Moisture content (%)	65	70	75	80
D	Initial pH	3	4	5	6
E	SSF time (day (d))	7	14	21	28

Table 7. Factors levels for the orthogonal experiments [40].

Test no.	Factors					Delignification (%)
	A	**B**	**C**	**D**	**E**	
1	0.5	0.1	65	3	7	16.63
2	0.5	0.2	70	4	14	49.68
3	0.5	0.3	75	5	21	56.37
4	0.5	0.4	80	6	28	37.92
5	1.0	0.1	70	5	28	64.25
6	1.0	0.2	65	6	21	52.78
7	1.0	0.3	80	3	14	28.75
8	1.0	0.4	75	4	7	17.02
9	1.5	0.1	75	6	14	48.43
10	1.5	0.2	80	5	7	8.65
11	1.5	0.3	65	4	28	62.65
12	1.5	0.4	70	3	21	53.46
13	2.0	0.1	80	4	21	39.15
14	2.0	0.2	75	3	28	57.97
15	2.0	0.3	70	6	7	24.06
16	2.0	0.4	65	5	14	43.06
K_1	160.60	168.46	175.81	156.81	66.36	
K_2	162.80	169.08	191.45	168.50	170.61	
K_3	173.19	171.83	179.79	173.02	201.76	
K_4	164.93	152.15	114.47	163.19	222.79	
k_1[a]	40.15	42.12	43.95	39.20	16.59	
k_2[a]	40.70	42.27	47.86	42.12	42.65	
k_3[a]	43.30	42.96	44.95	43.25	50.44	
k_4[a]	41.23	38.04	28.62	40.80	55.70	
R[b]	3.15	4.92	19.24	4.05	39.11	

[a] k_1, k_2, k_3, and k_4 are the mean values of the sum of the evaluation indexes of all levels. By comparing k values, the optimal levels of the factors can be confirmed.

[b] The range of factors (R = Max(k_j)− Min(k_j)) indicates the function of the corresponding factor. The larger value of R means the greater impact of the level of the factor on the experimental index.

Table 8. Experimental setup together with results of *P. chrysosporium* delignification [40].

in **Figure 9**, which turned out to be a linear relationship with decisive coefficient $R^2 = 0.99843$. The weight loss of SERS is proportional to the SSF time, differing from the results shown in **Figure 8**. Weight loss of SERS might be attributed to the removal of lignin and hemicellulose over 10 days of fermentation, after which the degradation of cellulose gradually became a major factor of SSF.

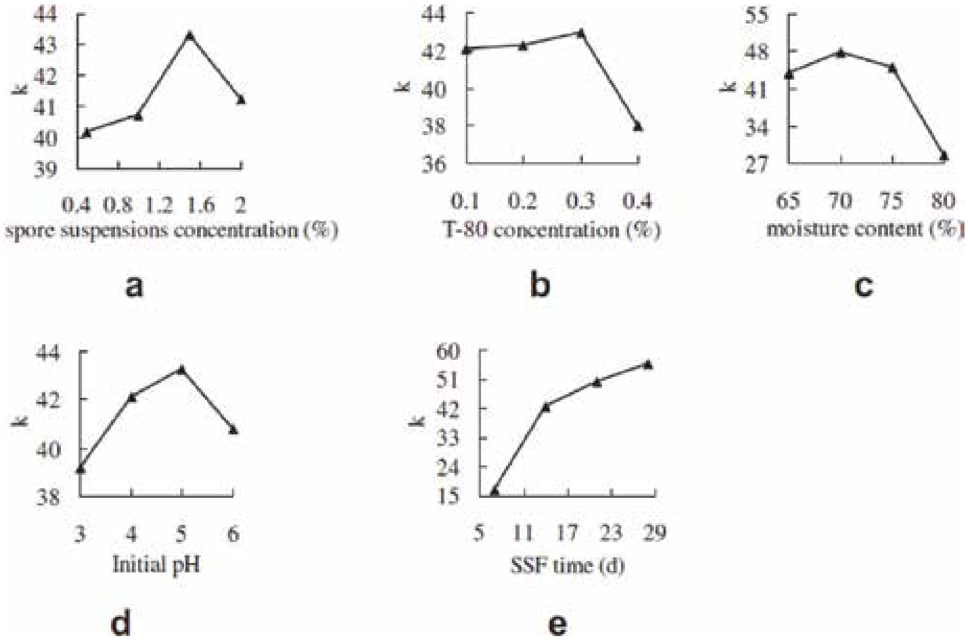

Figure 7. Curves of the factors vs. delignification [40].

In comparison with the FTIR spectrum of untreated SERS (**Figure 10a**), prominent changes could be obtained in the samples degraded after different SSF timings. The increase in the intensity of peak at 1650 cm^{-1} showed higher abundance of C=O groups of lignin, demonstrating the aromatic lignin moieties altered by oxidation with lignin biodegradation. In addition, peaks at 1510 and 1431 cm^{-1} turned weakening with increasing treatment time, implying the

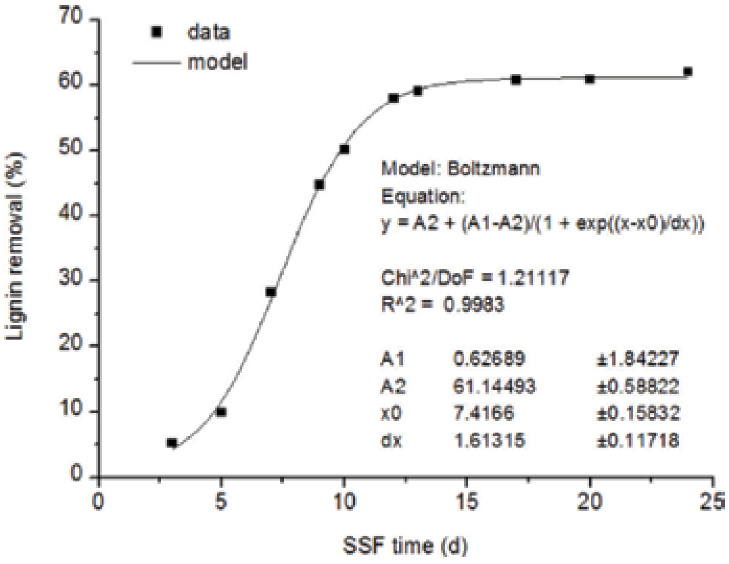

Figure 8. The effect of SSF time on the removal of lignin [40].

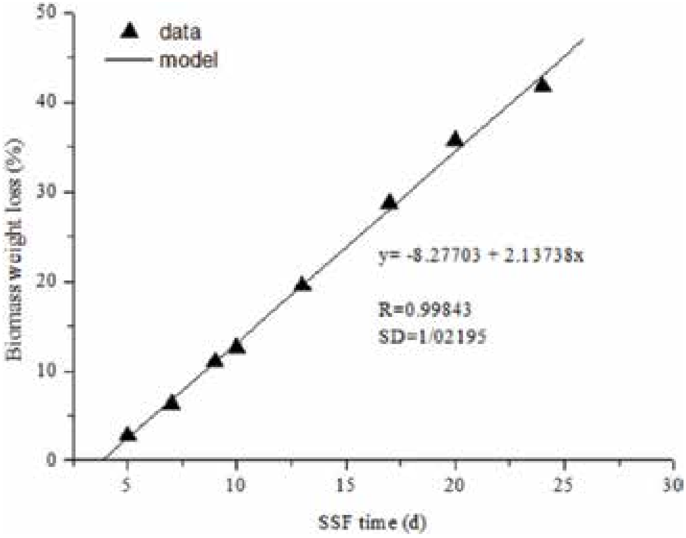

Figure 9. The effect of SSF time on the weight loss of SERS [40].

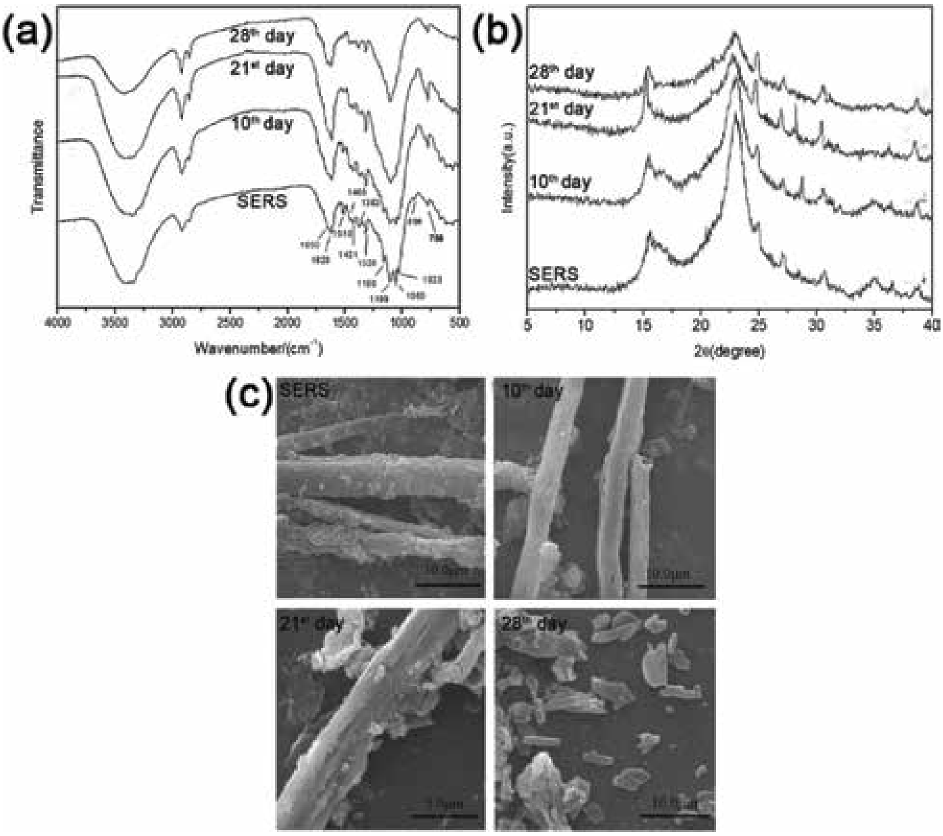

Figure 10. (a) FTIR spectra, (b) XRD patterns, and (c) morphologies of SERS before and after SSF with *P. chrysosporium.*

aromatic skeletal carbon of lignin was destroyed by *P. chrysosporium*. The peaks at 896, 1060, and 1160 cm^{-1} disappeared with increasing SSF time, showing that the structure of cellulose has been degraded after longer treatment time. Peaks observed near 23.11° (**Figure 10b**) represent diffractions of the (002) crystal plane, indicating that the crystal type of cellulose in SERS is cellulose type-I in nature (as shown in **Figure 10b**). Fermentation appeared not to change the crystal type of cellulose. With increasing SSF time, the peak height of the (002) crystal plane decreased and the peak width at half height increased compared with untreated SERS. The morphologies of the samples before and after bio treatment had been examined by SEM (**Figure 10c**) to visually demonstrate the process of delignification and cellulose degradation by *P. chrysosporium*.

4. High-value applications of cellulose isolated from straw

All-cellulose composites (AACs) have been proposed to meet the interfacial problem in the cellulose-based composites, where both the reinforcement phase and matrix are cellulose [41–43]. Zhou et al. [44] reported that ACCs, with microcrystalline cellulose (MCC) as the matrix and the straw cellulose fibers (SCFs) as the reinforcement agent exhibited an ultra-high tensile strength (650.2 MPa, **Figure 11**).

The mechanism for the high performance of alkali-treated SCF (N-SCF) and activated SCF (A-SCF) reinforced ACCs are shown in **Figure 12**. For the ACCs/N-SCF sample (**Figure 12a**), the reinforcement mechanism is possibly related to the removal of impurities and the increase of aspect ratio. For the ACCs/A-SCF sample (**Figure 12b**), the reinforcement mechanism can be possibly attributed to the fact that both A-SCF and MCC experience the same activation process. Due to successively pre-swell with solvents (water, ethanol, *N*, *N*-dimethylacetamide) gradually reducing polarity, the

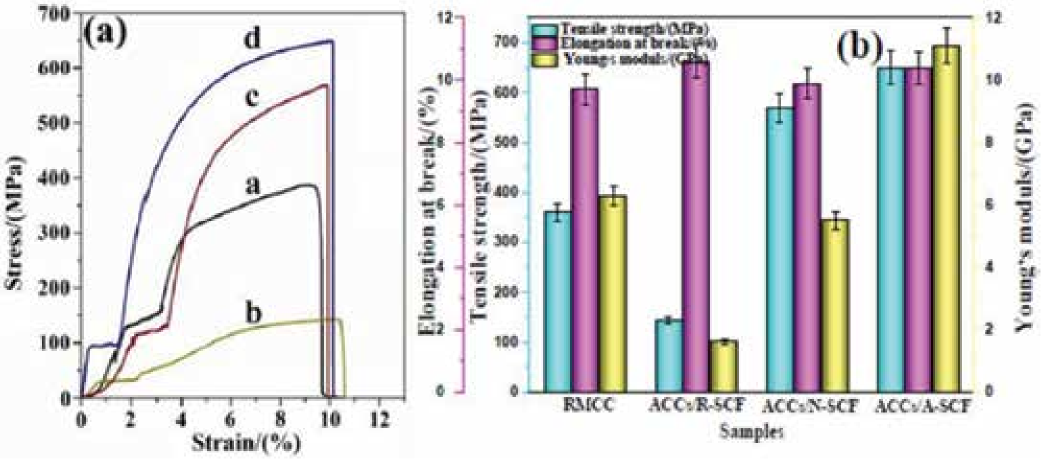

Figure 11. (a) Typical engineering stress–strain curves of the samples, (b) the corresponding tensile properties, where, a: Regenerated MCC, b: ACCs/activated SCF (A-SCF), c: ACCs/alkali-treated (N-SCF), and d: ACCs/activated SCF [44].

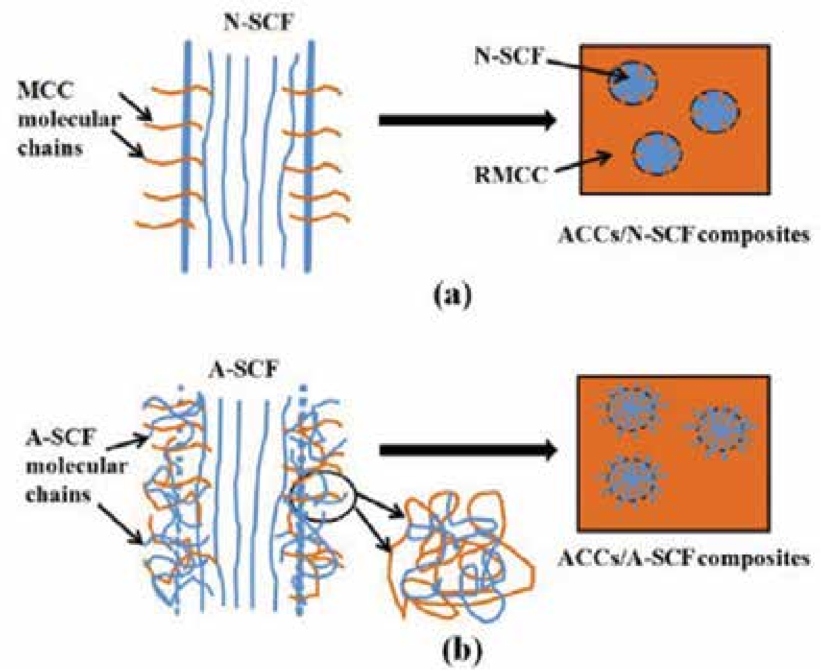

Figure 12. Schematic representations showing the reinforcement mechanism of the N-SCF (a) and the A-SCF (b) in the ACCs [44].

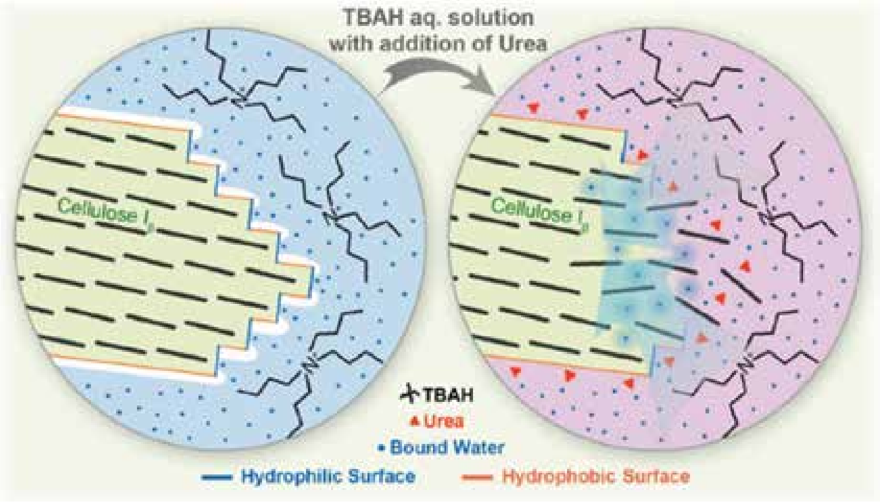

Figure 13. Schematic illustration for the mechanism of TBAH/urea aqueous solution dissolving cellulose. These two diagrams display various interfacial resistances between the crystal surface of natural cellulose and the solvent [49].

A-SCF and MCC molecular chains in SCF and MCC could be partially dissolved and penetrated into each other, resulting in improving entanglement density of molecular chains on the fiber surface.

Besides, the isolated cellulosic fibers of about 2–16 wt% can be introduced into the cement with a slurry vacuum de-watering technique [45]. It was found that the flexural strength and fracture toughness of the optimal sample were increased by 24.3% and 45 times, respectively.

Effective solvent system for cellulose dissolution is a long-standing goal due to the abundant hydroxyl groups on the cellulose chain form a strong, three-dimensional intermolecular and intramolecular hydrogen bonding network [46, 47]. Therefore, Zhou et al. [48] developed a new aqueous solvent for cellulose based on the quaternary ammonium hydroxide (TBAH). It was found that cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling condition. The mechanism for the dissolution is believed to be the match of amphiphilicity between the solvent and cellulose crystal. Then, Zhou et al. [49] studied the effects of urea to the dissolution of cellulose in TBAH. It was found that a hybrid hydrate of TBAH and urea formed. Urea can serve as a hydrophobic contributor, by which the amphiphilic property of the solvent system can be adjusted. With a suitable amphiphilicity, interfacial resistance between the solvent and crystal surface can be reduced so that the crystal of natural cellulose can be effectively infiltrated and subsequently dissolved by the solvent. The schematic dissolution process of the cellulose is shown in **Figure 13**.

5. Conclusions

The steam explosion process is realized as a promising pre-treatment for the separation of cellulose from natural biomasses. It can make most of the hemicellulose hydrolyze and part of the lignin degrade, which results in loose and porous structures, which could ultimately support further separation of cellulose and lignin. One kind of ionic liquids, 1-allyl-3-methylimidazolium chloride (AMIMCl), is selected for the extraction of cellulose, due to its especially selective solubility for cellulose rather than lignin. This process with ionic liquids shows advantages of efficiency, environmentally friendly, and recyclability character. Isolation of cellulose with the organic solvent system that composes of H_2O-DMF-aniline has proved that it also been considered as an environmental-friendly approach, and up to 95.04% lignin can be dissolved out from the steam-exploded rice straw, leaving quite a small amount of hemicellulose (<1%) and lignin (<0.85%). There is no obvious decrease in the degree of cellulose crystallinity during the delignification and bleaching processes. Approximately 58% lignin can be removed under selective delignification of the steam-exploded rice straw by *P. chrysosporium*. The isolated cellulose fiber from the rice straw can serve as a reinforcement material for the advanced mechanical property of composites. The prepared ACCs exhibit an ultrahigh tensile strength. The cellulose/cement composites show a remarkable improvement in the flexural strength and fracture toughness. Cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling process.

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This book gives emphasis to wood fiber raw materials, alternative sources of fibers for paper production, environmental issues, paper quality improvement and cost of paper production. Varieties of non-wood raw materials, including kenaf, rice straw, empty fruit bunches of palm trees, bamboo, bagasse, etc., are considered in this book. The process of fiber treatment also varied to meet paper quality improvement. Different organosolv processes of fiber treatment are discussed. Considering contemporary issues, one particular chapter analyzes the environmentally friendly way of processing non-wood fibers for paper production. The book also contains a chapter on the by-product raw materials of paper production and their profitable applications.

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