Part I
Chemical Pulping

Handbook of Pulp. Edited by Herbert Sixta

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1
Introduction

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1.1
Introduction

Industrial pulping involves the large-scale liberation of fibers from lignocellulosic plant material, by either mechanical or chemical processes. Chemical pulping relies mainly on chemical reactants and heat energy to soften and dissolve lignin in the plant material, partially followed by mechanical refining to separate fibers. Mechanical pulping involves the pretreatment of wood with steam (and sometimes also with aqueous sulfite solution) prior to the separation into fibrous material by abrasive refining or grinding. Depending on its end-use, the material recovered from such processes – the unbleached pulp – may be further treated by screening, washing, bleaching and purification (removal of low molecular-weight hemicelluloses) operations.

For any given type of production, the properties of the unbleached pulp are determined by the structural and chemical composition of the raw material. The variation in fiber dimension and chemical composition of some selected fibers is detailed in Tab. 1.1.

By far, the predominant use of the fiber material is the manufacture of paper, where it is re-assembled as a structured network from an aqueous solution. Fiber morphology such as fiber length and fiber geometry have a decisive influence on the papermaking process. A high fiber wall thickness to fiber diameter ratio means that the fibers will be strong, but that they may not be able to bond as effectively with each other in the sheet-forming process. Another property which is important to fiber strength is the spiral angle of the longitudinal cellulose micelle chains which constitute the bulk of the fiber walls. Moreover, certain chemical properties of the fibers and the matrix material in which they are embedded must also be taken into account.

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Tab. 1.1 Fiber dimensions and chemical composition of some selected agricultural and wood fibers (adopted from [1–6]).

Fiber type	Cell dimensions				Chemical Composition				
	Length [mm]		Diameter [µm]		Cellulose %	Pentosan %	Lignin %	Ash %	SiO_2 %
	average	range	average	range					
Stalk fibers (grass fibers)									
Cereal straw (wheat, corn, rice)	1.4	0.4–3.4	15	5–30	29–35[a]	26–32[a]	16–21[a]	4–9[a]	3–7[a]
Bamboo	2.7	1.5–4.4	14	7–27	26–43[a]	15–26[a]	21–31[a]	1.7–5[a]	1.5–3[a]
Sugarcane bagasse	1.7	0.8–2.8	34		32–44[a]	27–32[a]	19–24[a]	1.5–5[a]	0.7–3[a]
Bast fibers (single fibers)									
Flax	33.0	9–70	19	5–38	64.1[d]	16.7[d]	2[d]	2–5[a]	
Hemp	25.0	5–55	25	10–50	78.3[d]	5.5[d]	2.9[d]	0.5[d]	
Jute		2–5	20	10–25	59.4[d]	18.9[d]	12.9[d]	0.6[d]	<1[a]
Kenaf	3.4[d]	1.5–11[d]	24[d]	12–36[d]	31–39[a]	21–23[a]	15–18[a]	2–5[a]	
Leaf Fibers									
Abaca (long)		3–12[d]	10[d]	6–46[d]	61[a]	17[a]	9[a]	<1[a]	<1[a]
Sisal (long)	3.3[d]	0.8–8[d]	21[d]	7–47[d]	43–56[a]	21–24[a]	8–9[a]	0.6–1.0[a]	<1[a]
Seed and fruit fibers									
Cotton lint (raw)		20–50[c]		8–19[c]	88–96[e]			0.7–1.6[e]	<1[a]
Cotton linters (second cut, raw)		2–3[c]		17–27[c]	80[c]			2[c]	<1[a]
Wood fibers									
Softwood	3.3	1.0–9.0	33	15–60	40–44[b]	(25–29)[b]	25–31[b]		
Hardwood	1.0	0.3–2.5	20	10–45	43–47[b]	25–35[b]	16–24[b]		

Adopted from Refs. [1[a], 2[b], 3, 4[c], 5[d] and 6[e]].
Values in parentheses indicate total hemicellulase.

1.2
The History of Papermaking

The history of papermaking can be traced back to about AD 105, when Ts'ai-Loun created a sheet of paper using old rags and plant tissues. In its slow travel westwards, the art of papermaking reached Arabia in the middle of the eighth century, from where it entered Europe via Spain in the 11th century. By the 14th century, a number of paper mills existed in Europe, particularly in Spain, France, and Germany. For centuries, paper had been made from linen, hemp and cotton rags. After cleaning, sorting and cutting, these were boiled with potash or soda ash to remove the remaining dirt and color. The operation was continued in a "breaking engine" by adding fresh water until the cloth was separated into single fibers.

Until the paper machine was constructed in 1799 by Louis-Nicholas Robert, the final sheet-formation process was carried out manually.

Throughout the 18th century the papermaking process remained essentially unchanged, with linen and cotton rags furnishing the basic fiber source. However, the increasing demand for paper during the first half of the 19th century could no longer be satisfied by the waste from the textile industry. Thus, it was evident that a process for utilizing a more abundant material was needed. Consequently, major efforts were undertaken to find alternative supplies for making pulp. As a result, both mechanical and chemical methods were developed for the efficient production of paper from wood. Mechanical wood pulping was initiated in 1840 by the German Friedrich Gottlob Keller. The wood-pulp grinding machine was first commercialized in Germany in 1852 (Heidenheim) on the basis of an improved technology developed by Voelter and Voith. However, mechanical pulping did not come into extensive use until about 1870 when the process was modified by a steam pretreatment which softens the inter-fiber lignin. Paper made from mechanical wood pulp contains all the components of wood and thus is not suitable for papers in which high brightness, strength, and permanence are required.

The clear deficiencies compared to paper made from cotton rags made it necessary to strengthen the development of chemical wood pulping processes, focusing on the removal of accessorial wood components such as lignin and extractives.

The first chemical pulping process was the soda process, so-named because it uses caustic soda as the cooking agent. This process was developed in 1851 by Hugh Burgess and Charles Watt in England, who secured an American patent in 1854. A year later, the first commercial soda mill using poplar as raw material was built on the Schuylkill River near Philadelphia under the direction of Burgess, who served as manager of the mill for almost 40 years. Because this process consumed relatively large quantities of soda, papermakers devised methods for recovering soda from the spent cooking liquor through evaporation and combustion of the waste liquor and recausticizing of the sodium carbonate formed. To compensate for the losses, sodium carbonate had to be added to the causticizing unit. Since the preparation of sodium carbonate from sodium sulfate was rather expensive by using the Leblanc process, Carl Dahl in Danzig tried to introduce sodium sulfate directly in place of soda ash in a soda pulping recovery system. This substitution produced a cooking liquor that contained sodium sulfide along with caustic soda. Fortunately, the pulp so produced was stronger than soda pulp and was called “kraft” pulp, so named from the Swedish word for “strong”. The process, which was patented in 1884 by Dahl, has also been termed the sulfate process because of the use of sodium sulfate (salt cake) in the chemical make-up. As a consequence, many soda mills were converted to kraft mills because of the greater strength of the pulp. Kraft pulp, however, was dark in color and difficult to bleach compared to the competing sulfite pulp. Thus, for many years the growth of the process was slow because of its limitation to papers for which color and brightness were unimportant. With the development of the Tomlinson [7,8] combustion furnace in the early 1930s, and with the discovery of new bleaching techniques, particularly using sodium chlorite (1930) and later chlorine dioxide (1946), bleached kraft became commercially important. The availability of pulp of high brightness and high strength and the expanding demand for unbleached kraft in packaging resulted in rapid growth of the process, making kraft the predominant wood-pulping method.

In 1857, shortly after the discovery of the soda pulping process, Benjamin Tilghman, a US chemist, invented acid sulfite pulping. In 1867, the US patent was granted to Tilghman on the acid sulfite cooking process, using solutions of sulfur dioxide and hydrogen sulfite ions at elevated temperature and pressure. Tilghman observed that the presence of a base such as calcium (to form hydrogen sulfite ions) was important in preventing the formation of burned or discolored pulp. His invention, however, did not result in commercial use due to severe technical difficulties (leakages, etc.), although the product he obtained was satisfactory.

In 1870, Fry and Ekman in Sweden carried these studies further and their improved process, which came into use in 1874, used rotary digesters and indirect heating to produce magnesium-based sulfite pulp. This process was applied in the first American mill, the Richmond Paper Co., built in 1882 at East Providence, Rhode Island, with a capacity of about 15 tons of book and newsprint per day.

Immediately after the German/French war of 1870/1871, Alexander Mitscherlich began to work on the development of calcium hydrogen sulfite cooking with an excess of dissolved sulfur dioxide. The process was characterized by its low temperature (ca. 110 °C), low pressure and long retention time, thus producing rather strong fibers. Heating was carried out indirectly by means of steam in copper coils within the digester. The German sulfite pulping industry was built 1880 on the basis of the Mitscherlich process. In 1887, the first commercially successful sulfite mill in America was built by G. N. Fletcher in Alpena, Michigan. This mill continued in active production until 1940.

Between 1878 and 1882, the Austrians Ritter and Kellner developed an acid calcium-based hydrogen sulfite process using upright digesters with direct steaming. The time of cooking was considerably reduced by applying high temperature and high pressure (“quick cook” process). The patent rights for the Ritter–Kellner process which covered the digester, the method of making the acid cooking liquor, and all features of the system were acquired about 1886 by the American Sulfite Pulp Co.

Following the introduction of the upright digesters, progress was rapid and sulfite pulping became the leading cooking process using spruce and fir as the preferred species. The good bleachability and low costs of the applied chemicals were the main reasons for the advantage over the soda and kraft processes. In 1925, the total production of chemical wood pulp showed a distribution of 20% soda, 20% kraft and 60% unbleached and bleached sulfite pulps. While for sulfite pulp manufacture, a single-stage treatment of pulp at low consistency, using calcium hypochlorite satisfied most requirements, this simple bleaching treatment was not practical for kraft that is difficult to bleach, nor can it retain maximum strength.

Since 1937 the sulfite cooking technology lost ground to the kraft process despite the introduction of soluble sodium and ammonium bases and the recovery of cooking chemicals in case of magnesium (e.g., the Lenzing [9], the Babcock & Wilcox [10], and the Flakt [11] Mg base systems) and sodium (e.g., the Stora [12], the Rauma [13–15] and the Tampella [16] systems) bases. As previously mentioned, advances in kraft pulping technology comprising the introduction of the modern combustion furnaces by Tomlinson, the improvement of the white liquor recovery system and the development of continuous multi-stage bleaching using chlorination (C), alkali extraction (E) and hypochlorite (H) bleaching and later chlorine dioxide (D) were the key elements of achieving the predominant position in chemical wood pulping. Kraft pulping enables the use of practically all species of wood to produce pulps with high degrees of purification and brightness while maintaining high strength.

Until the end of the 19th century, the exclusive role of pulp production was to supply the paper industry with raw materials. At that time, the first patents were applied for the production of cellulosic products involving chemical conversion processes. The most important technology for the production of regenerated cellulose fibers, the viscose process, was developed by Charles F. Cross and Edward J. Bevan who, with C. Beadle, received a patent on the process in 1892 [17]. The discovery of cellulose diacetate by Miles [18] in 1904 and Eichengrün [19] in 1905 marked the breakthrough of cellulose acetate production, which subsequently developed as the second highest consumer of dissolving pulp until the present time.

Dissolving pulp refers to pulp of high cellulose content which was produced until World War II solely from purified cotton linters or, in case of lower demands on purity (as for viscose), according to the acid sulfite process using somewhat higher temperature and acidity together with prolonged cooking to remove the greater part of the hemicelluloses. The regular kraft pulping process is not capable of removing hemicelluloses completely; in particular, residual pentosans interfere with the chemical conversion of cellulose to either viscose, cellulose ethers or acetates. The hemicelluloses can only be effectively solubilized when exposing wood chips to acid hydrolysis prior to alkaline pulping. The prehydrolysis-kraft (PHK) process was finally developed during World War II in Germany, with the first mill operating in Königsberg (Kaliningrad). In the prehydrolysis step, the wood chips are treated either at temperatures between 160 and 180 °C for between 30 min and 3 h with direct steaming, or in dilute mineral acid (0.3–0.5% H_2SO_4) at temperatures between 120 and 140 °C. This pretreatment liberates organic acids (e.g., acetic, formic) from the wood, and these hydrolyze the hemicelluloses selectively to produce water-soluble carbohydrates. Since the 1950s, the PHK process, with its various modifications, has been installed, particularly in the United States and South America. One of the advantages of this process is its applicability to most wood species; in contrast, sulfite pulping has been restricted to spruces, hemlock, fir, and a few hardwoods. The latest development of the PHK – the Visbatch® and VisCBC processes – combine the advantages of both steam hydrolysis and displacement technology [20].

1.3
Technology, End-uses, and the Market Situation

Today's pulping processes have advanced significantly since their emergence during the second half of the 19th century, and have progressed towards more capital-intensive and increasingly large-scale automated production processes, with continuous emphasis on improvements in product quality, production efficiency and environmental conservation. Thus, the pulp and paper industry has become a very important sector of the economy.

At present, more than 90% of the pulp (virgin pulp fiber) produced worldwide is wood pulp. The first species of trees to be used in great quantities for papermaking were pine and spruce from the temperate coniferous forests located in the cool northern climates of Europe and North America. However, during the past few decades a gradual shift to hardwood species has occurred, mainly driven by lower costs, better availability and advances in pulping and papermaking processes. Today the main species comprise birch, beech, aspen and maple, in the United States and central and western Europe, pine in Chile, New Zealand and United States, eucalyptus in Brazil, Spain, Portugal, Chile and South Africa. Eucalyptus pulp was first introduced as a market pulp during the early 1960s. Brazilian eucalyptus shows a seven-year growth cycle; this is the shortest of all trees worldwide, and translates into very high forest productivity. Eucalyptus plantations yield an average of 45 m^3 ha^{-1} $year^{-1}$ of wood, whereas the average for North American forests is 2–4 m^3 ha^{-1} $year^{-1}$. A shorter growth cycle means lower investments and wood production costs, and thus a more rational utilization of natural resources and more available space for other equally important land uses.

Worldwide, the largest stock of hardwood undoubtedly exists in South America, and that of softwood in Russia, Canada and in the South of the United States, respectively. It may be expected that, in the long run, South America and Russia are promoted to the dominating pulp producers. A gradual shift from today's dominating bleached softwood kraft pulp to cheaper bleached hardwood kraft pulp will take place for the years to come, due mainly to the higher growth rate and the better delignifying properties of the latter.

Wood pulps are categorized by the pulping process as either chemical or mechanical pulps, reflecting the different ways of fiberizing. Chemical pulping dissolves the lignin and other materials of the inter-fiber matrix material, and also most of the lignin which is in the fiber walls. This enables the fibers to bond together in the papermaking process by hydrogen bond formation between their cellulosic surfaces. As noted previously, kraft pulping has developed as the dominating cooking process, and today the kraft pulps account for 89% of the chemical pulps and for over 62% of all virgin fiber material (Tab. 1.2). In 2000, the annual global virgin pulp fiber production totaled 187 million tonnes, while only about 50 million tonnes or 27% accounted for market pulp [21]. The remaining 73% stems from integrated paper and cellulose converting mills (captive use).

Due to distinct disadvantages of the sulfite cooking process (including all its modifications) over the kraft pulping technology (see above), the share of sulfite

Tab. 1.2 Global pulp production by category, 2000 [21].

Pulp category	Pulp production [Mio t]
Chemical	131.2
Kraft	117.0
Sulfite	7.0
Semichemical	7.2
Mechanical	37.8
Nonwood	18.0
Total virgin fiber	187.0
Recovered fiber	147.0
Total fibers	334.0

pulps in total fiber production steadily decreased from 60% in 1925 [22] to 20% in 1967 [22], to 9.2% in 1979 [23], and finally to only 3.7% in 2000 [21] (see Tab. 1.2).

The superiority of kraft pulping has further extended since the introduction of modified cooking technology in the early 1980s [24]. In the meantime, three generations of modified kraft pulping processes (MCC, ITC and Compact Cooking as examples for continuous cooking and Cold-blow, Superbatch/RDH and Continuous Batch Cooking, CBC, for batch cooking technology) have emerged through continuous research and development [25]. The third generation includes black liquor impregnation, partial liquor exchange, increased and profiled hydroxide ion concentration and low cooking temperature (elements of Compact Cooking), as well as the controlled adjustment of all relevant cooking conditions in that all process-related liquors are prepared outside the digester in the tank farm (as realized in CBC). However, the potential of kraft cooking is not exhausted by far. New generations of kraft cooking processes will likely be introduced, focusing on improving pulp quality, lowering production costs by more efficient energy utilization, further decreasing the impacts on the receiving water, and recovering high added-value wood byproducts [25].

During the 1980s and 1990s, many of the developments in chemical pulp production of both sulfite and kraft processes were driven by severe environmental concerns, especially in Central Europe and Scandinavia [26]. Increasing pulp production resulted in increasing effluent loads. The need to reduce the amount of organic material originating mainly from bleach plant effluents was most pronounced in highly populated countries, where filtered river water was used as a source of drinking water. The biodegradability of the bleach plant effluents, particularly from the chlorination (C) and extraction stages (E), turned out to be very poor due to the toxicity of halogenated compounds. Finally, the detection of polychlorinated dioxins and furans in chlorination effluents and even in final paper

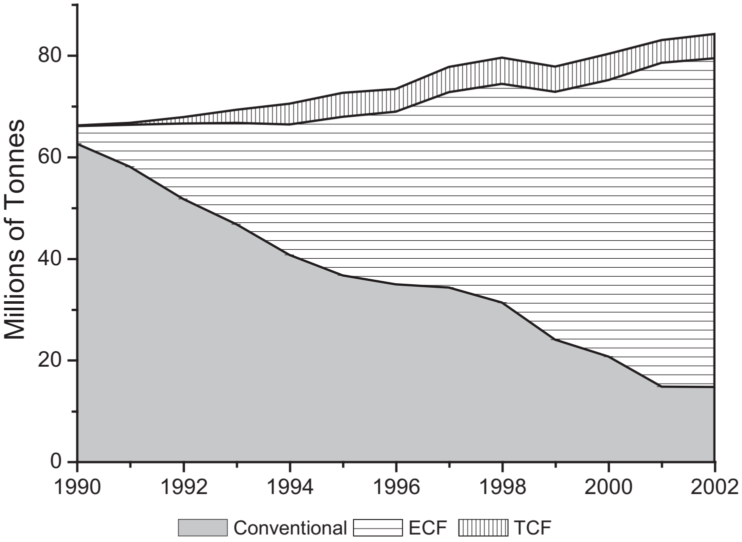

Fig. 1.1 World bleached chemical pulp production: 1990–2002 [29].

products during the 1980s caused a rapid development of alternative, environmentally benign bleaching processes [27]. The initial intention was the complete replacement of all chlorine-containing compounds, resulting in Totally Chlorine Free (TCF) bleaching sequences. This could be easily accomplished with sulfite pulps due to their good bleachability. Kraft pulp mills have been converted dominantly to Elemental Chlorine Free (ECF) bleaching rather than to TCF bleaching, because the latter, by using ozone or peracids to yield high brightness, deteriorates pulp quality. ECF bleaching, comprising chlorine dioxide (D) -containing bleaching sequences, such as DEOpDEpD, is acknowledged as a core component of the best Available Technology (BAT), since numerous field studies have shown that ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic substances [28]. ECF pulp, bleached with chlorine dioxide, continues to dominate the world bleached chemical pulp market. In 2002, ECF production reached more than 64 million tonnes (Fig. 1.1) [29]. Market data show that ECF production grew by 17% in 2001, whereas TCF pulp production remained constant, maintaining a small niche market at just over 5% of world bleached chemical pulp production. The transition to ECF is essentially complete in Europe, the United States and Canada, with ECF production now representing more than 96% of the whole bleached chemical pulp production.

Dissolving pulps represent specialty pulps within the chemical pulp segment. They are chemically refined bleached pulps composed of more than 90% pure cellulose (α-cellulose). As mentioned above, two basic processes are used to produce dissolving pulp. The sulfite process produces pulp with an α-cellulose content of 90–92%, whereas the PHK process typically produces pulp with an α-cellulose content of 94–96%. Special alkaline purification treatments can yield even higher cellulose levels of up to 96% for the sulfite and up to 98% for the PHK processes. The low-level α-cellulose pulps are predominantly used to manufacture viscose staple fibers, whereas the high-level α-cellulose pulps are converted to viscose yarn for industrial products such as tire cord, high-purity cellulose ethers, various cellulose acetates and other specialty products.

Although world production of dissolving pulp has been reduced constantly since the mid-1970s, the developments of the past two years have signaled a slight change in this trend. With an annual global production averaging 3.65 million tonnes in 2003, dissolving pulp accounted for only 2.8% of the total wood pulp production. However, the high demands for cellulose purity and reactivity, as well as its manifold routes of utilization, are the main reasons for the advanced state of technology within the pulp industry.

Viscose staple fibers and viscose filaments (both textile and technical) had the lion's share of the total production, at 2.2 million tonnes (60%), while 0.53 million tonnes (15%) stemmed from the manufacture of a variety of cellulose acetate products (cigarette filters, filaments, plastics, etc.). The remaining 25% were accounted for by the production of cellulose ethers, cellophane, microcrystalline cellulose (MCC), specialty papers and nitrocellulose (Tab. 1.3).

Tab. 1.3 World production of dissolving pulp by end-use in 2003 [30].

Cellulose product	End-use	Mio t
Regenerated fibers	Staple, filaments	2.20
Cellophane	Incl. sponges, casings	0.10
Cellulose acetate	Tow, filament, plastic	0.53
Cellulose ether	Non-ionic, ionic (CMC)	0.47
MCC	Incl. moulding powder	0.09
Others	Nitrocellulose, speciality papers	0.26
Total		**3.65**

Unlike paper-grade pulping the acid sulfite process is the dominant process for the production of dissolving pulps, and accounted for 60–63% of the total production, while 22–25% originated from PHK process in 2003. The remaining 12–16% was produced from cotton linters which, for purification and viscosity control, is treated by alkaline cooking and subsequent hypochlorite bleaching. Purified cotton linters represents the dissolving pulp of highest cellulose purity particularly used for manufacturing acetate plastics and high-viscosity cellulose ethers. However, in China cotton linters is used as a raw material for the manufacture of viscose fibers, both staple and filaments.

Similar to paper-grade pulps, a gradual shift from softwood to hardwood can be observed. This development is mainly driven by better availability and lower costs. The slight increase in the world's dissolving pulp production predicted for the next five years is mainly attributed to new installations of viscose fiber plants in Asia and to the continuous growth of the cellulose ether and acetate tow markets.

Semichemical pulping processes are characterized by a mild chemical treatment preceded by a mechanical refining step. Semichemical pulps, which apply to the category of chemical pulps, are obtained predominantly from hardwoods in yields of between 65 and 85% (average ca. 75%). The most important semichemical process is the neutral sulfite semichemical process (NSSC), in which chips undergo partial chemical pulping using a buffered sodium sulfite solution, and are then treated in disc refiners to complete the fiber separation. The sulfonation of mainly middle lamella lignin causes a partial dissolution so that the fibers are weakened for the subsequent mechanical defibration. NSSC pulp is used for unbleached products where good strength and stiffness are particularly important; examples include corrugating medium, as well as grease-proof papers and bond papers. NSSC pulping is often integrated into a kraft mill to facilitate chemical recovery by a so-called cross-recovery, where the sulfite spent liquor is processed together with the kraft liquor. The sulfite spent liquor then provides the necessary make-up (Na, S) for the kraft process. However, with the greatly improving recovery efficiency of modern kraft mills, the NSCC make-up is no longer needed so that high-yield kraft pulping develops as a serious alternative to NSCC cooking. Semichemical pulps is still an important product category, however, and account for 3.9% of all virgin fiber material (see Tab. 1.2).

The second category of pulping procedures – mechanical pulping processes – can be classified as stone grinding (groundwood pulping: stone groundwood, SGW, and pressure groundwood, PGW) and refiner pulping processes (refiner mechanical pulp, RMP, pressurized refiner mechanical pulp, PRMP, thermomechanical pulp, TMP, chemigroundwood, CGW, chemi-refiner mechanical pulp, CRMP, and the chemi-thermomechanical pulp, CTMP).

Groundwood pulp shows favorable properties with respect to brightness (≥85% ISO after bleaching), light scattering and bulk, which allows the production of papers with low grammages. Moreover, the groundwood process also offers the possibility of using hardwood (e.g., aspen) to achieve even higher levels of brightness and smoothness [31]. Groundwood pulp has been the quality leader in magazine papers, and it is predicted that this situation will remain [31].

The most important refiner mechanical pulping process today is thermomechanical pulping (TMP). This involves high-temperature steaming before refining; this softens the inter-fiber lignin and causes partial removal of the outer layers of the fibers, thereby baring cellulosic surfaces for inter-fiber bonding. TMP pulps are generally stronger than groundwood pulps, thus enabling a lower furnish of reinforcing chemical pulp for newsprint and magazine papers. TMP is also used as a furnish in printing papers, paperboard and tissue paper. Softwoods are the main raw material used for TMP, because hardwoods give rather poor pulp strength properties. This can be explained by the fact that hardwood fibers do not form fibrils during refining but separate into short rigid debris. Thus, hardwood TMP pulps, characterized by a high-cleanness, high-scattering coefficient, are mainly used as filler-grade pulp. The application of chemicals such as hydrogen sulfite prior to refining causes partial sulfonation of middle lamella lignin. The better swelling properties and the lower glass transition temperature of lignin results in easier liberation of the fibers in subsequent refining. The CTMP pulps show good strength properties, even when using hardwood as a fiber source, and provided that the reaction conditions are appropriate to result in high degrees of sulfonation. Mechanical pulps are weaker than chemical pulps, but cheaper to produce (about 50% of the costs of chemical pulp [31]) and are generally obtained in the yield range of 85–95%. Currently, mechanical pulps account for 20% of all virgin fiber material (see Tab. 1.2). It is foreseen that mechanical paper will consolidate its position as one major fiber supply for high-end graphic papers. The growing demand on pulp quality in the future can only be achieved by the parallel use of softwood and hardwood as a raw material.

The largest threat to the future of mechanical pulp is its high specific energy consumption. In this respect, TMP processes are most affected due to their considerably higher energy demand than groundwood processes. Moreover, the increasing use of recovered fiber will put pressure on the growth in mechanical pulp volumes.

Almost 10% of the total pulp production is made from nonwood plant fibers, including stalk, bast, leaf and seed fibers (see Tab. 1.1). In view of the enormous annual capacity of nonwood fiber material (mostly as agricultural waste) as a potential source for pulp production of 2.5 billions tons, the current nonwood pulp annual production of only 18 million tons is rather low [32,33]. Assuming an average pulp yield of 50%, the utilization of nonfiber material as a source for pulp production accounts only for 1.4%. In 1998, the major raw material sources for nonwood pulp were straw, sugar cane bagasse and bamboo, with shares of 43%, 16%, and 8% of the total nonwood pulp capacity, respectively [32]. With regard to the fiber length, the nonwood pulps can be divided into three groups: (a) those with fiber length >4 mm, represented by cotton lint, abaca, flax and hemp; (b) those with fiber lengths of 1.5–4 mm, represented by bamboo, bagasse, kenaf and reed; and (c) those with a fiber length <1.5 mm, represented by all kinds of straw pulps [34]. Technically, the nonwood pulps belong to the group of chemical pulps, and are predominantly produced according to the soda cooking process. Kraft cooking processes are applied using selected substrates such as bamboo, kenaf, sisal, or others.

The complex logistics of harvesting, transporting and storing a bulky seasonal commodity, particularly in regions of the world where wood supplies are adequate, has prevented the emergence of nonwood plant fibers as a source of cost-competitive pulp for both printing/writing and cellulose products. The use of nonwood fibers, however, is common in wood-limited countries, such as China and India, which are the two largest producers of nonwood pulp. In China, the nonwood pulping capacity amounts to approximately 80% of the country's total pulping capacity, while in India it is 55% [21]. In Western countries, nonwood pulp has established niches in specialty paper production. Flax, hemp and abaca have confirmed good results as reinforcing pulps for thin applications such as cigarette paper, bank notes, and bibles. Cotton papers are known to be superior in both strength and durability to wood-based papers, and this favors their use as acid-free, high-end fine papers. In general, the higher costs of nonwood pulps limit their use to high-end products often marketed as "eco-friendly" papers. Even bigger players are now beginning to enter the market for eco-papers more seriously, and are positioning themselves in the as yet tiny niche of eco-friendly nonwood printing/writing grades. Small (but growing) niches have been developed for "tree-free" papers. The most popular fiber sources for these papers are kenaf, hemp, flax, bamboo, wheat straw and other grasses. The emerging use of blends from nonwood and deinked fibers increasingly blurs the border between tree-free and other eco-friendly papers. In order to expand the use of nonwood pulps in applications beyond the current niche markets, it will be necessary to develop cost-effective pulping processes, and particularly innovative recovery methods to handle the high silica content.

Mastering the technological and logistical requirements of harvesting, storing and processing large quantities of bulky fibers will continue to be a major challenge.

1.4
Recovered Paper and Recycled Fibers

After wood, the second largest share of pulp produced worldwide is pulp made from recovered paper (see Tab. 1.2). Apart from good economic reasons, a major force in this drive to recycling is derived from public pressure to reduce the amount of used paper that is landfilled as waste. In the recycling process, recovered paper is reduced to pulp principally by mechanical means, followed by separation and removal of inks (de-inked paper, DIP), adhesives, and other contaminants, through both chemical and mechanical processes. Recovered fibers generally differ from virgin wood fibers in terms of their fiber morphology and physical properties. Strength, as well as swelling and optical properties, tend to deteriorate due to the recycling process. To a large extent, modern processing technology can compensate for the inherent disadvantages of recovered fibers which, however, contribute to higher costs. Modern mechanical refining is used, for example, to resurrect surface fibrils, and modern papermaking machines and coatings can enhance sheet strength and surface properties, while the efficiency of contaminant removal has been improved by modern deinking systems.

The proportion of recovered fiber has grown substantially during the past few years, and continues to expand. Its share of the global fiber flow increased from 22.5% in 1978 to 33.5% in 1992, and to 44% in 2000. The extent to which recovered paper is used varies greatly from country to country. In Central Europe, where there is a fiber deficiency, it accounts about half of the total fiber raw material (utilization rate 47%, collection rate 57.3% in 2003 [35]), whereas in countries

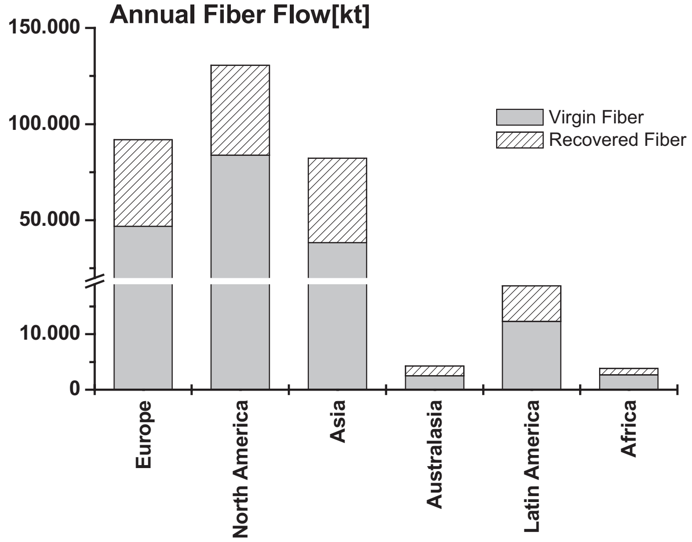

Fig. 1.2 Global annual flow of virgin and recovered fibers by region in 2000 [21].

such as Scandinavia and Canada, recycling levels are much lower. The share of virgin and recovered fiber by region is illustrated in Fig. 1.2.

On a European level, about 50% of the collected volumes are derived from trade and industrial sources, 40% from households, and the remaining 10% from offices. These proportions differ greatly between countries as well as collection systems. The future potential clearly lies in households, but as these consist of numerous small sources, the costs and quality of recovered paper are placed under pressure.

Among users of recovered paper, packaging grades are the major user at almost two-thirds of the total recovered paper. In Europe, case materials represent 23% of total paper and board production, have a utilization rate of 90%, and use 45% of the total recovered paper consumption [35]. The utilization rate of newsprint, representing about 12% of total paper and board production, has increased steadily over the years and reached 74% in 2003. The challenge for the future is certainly the use of recycled fiber for the manufacture of printing and writing papers. Currently, the utilization rate of these grades is slightly below 9% [35].

1.5
Outlook

Recoverable raw materials undoubtedly will play a decisive role in the future. Nature is producing an enormous amount of plant biomass, approximately 170 billion tons per year [36]. Although renewable raw materials offer many opportunities for use, they have been only rarely applied so far. In particular, the increased use of renewable raw materials for the production of chemical products would promote future developments towards a lasting supply of resources. Renewable raw materials are advantageous because they are part of the closed cycle of the biosphere. Therefore, using renewable raw materials is an opportunity to supply all substances needed without polluting the biosphere with foreign and hazardous substances.

With an estimated average annual growth rate of 2.2%, the world's consumption of pulp fibers is expected to rise from 334 million tons in 2000 to over 400 million tons in 2010 [37]. New pulp and paper capacities are now shifting to Asia and South America, where many new mill are currently under construction. By comparison, very few mills have been built in North America and Europe over the past few years.

Within the past three decades, enormous efforts have been devoted to the development of new pulping processes in an attempt to overcome the shortcomings of alkaline cooking, which mainly comprise air and water pollution as well as high investment costs. A serious alternative to kraft pulping could be possible, if a new process were available that had the following characteristics [38]:

- Selective delignification to increase pulp yield and preserve pulp strength properties.
- Pulp quality at least equal to that of kraft pulps.
- Low energy input and even temperature profile throughout whole fiber line processes in order to minimize energy demand.
- Low chemical consumption to enable an efficient and simple chemical recovery system.
- The possibility of closing the chemical cycle of the process (closed-loop operations) without impairing processability and pulp quality.
- Selective bleaching without chlorine-containing compounds.
- Minimum restriction in the use of raw material sources.
- Minimum air and water pollution; to avoid any malodorous emissions, the process should be totally sulfur-free.
- Recovery of valuable byproducts with competitive costs.
- Profitable smaller production units requiring lower set-up costs.

Organosolv pulping – that is, the process of using organic solvents to aid in the removal of lignin from wood – has been suggested as an alternative pulping route [39]. The pioneering studies on organosolv pulping began with the discovery in 1931 by Kleinert and Tayanthal that wood can be delignified using a mixture of water and ethanol at elevated temperature and pressure [40,41]. During the following years, a rather wide variety of organic solvents have been found to be suitable for pulp production. The intrinsic advantage of organosolv over kraft pulping processes seems to be the straightforward concept of recovering the solvents by using simple distillation. Furthermore, organosolv processes are predicated on the biorefining principle – that is, the production of high amounts of valuable byproducts. The advantage of small and efficient recovery units which could fulfill the demand for profitable smaller production units is, however, limited to very simple solvent systems such as ethanol-water derived from the Kleinert process. For example, the use of acid-catalyzed organosolv pulping processes such as the Formacell and Milox processes clearly complicates an efficient recovery of the solvents, and this in turn diminishes the advantage over existing pulping technologies [42]. The reason for this is the nature of the solvent system. The spent pulping liquor contains water, formic acid, and acetic acid which form a ternary azeotrope. The complexity of efficient solvent recovery, together with the limitation to hardwood species as a raw material and, moreover, the clearly inferior strength properties of organosolv pulps compared to kraft pulps, indicates that organosolv pulping processes are not ready to compete with the kraft process at this stage of development. [42]. The challenge of organosolv pulping for the future is to identify solvents with better selectivity towards lignin compared to those available today which simultaneously allow simple, but efficient, recovery.

Parallel to the research on alternative pulping processes, the kraft process has undergone significant improvements since the discovery of the principles of modified cooking during the late 1970s and early 1980s at the department of Cellulose Technology of the Royal Institute of Technology and STFI, the Swedish Pulp and Paper Research [43,44]. In the meantime, the third generation of modified cooking technology has been established in industry and, together with an efficient two-stage oxygen delignification stage prior "ECF-light" bleaching, the impact on the environment has been reduced dramatically within the past two decades. The specific effluent COD and AOX emissions after the biological treatment plant of today's state-of-the-art kraft pulping technology are at a level of about 7 kg adt^{-1} and <0.1 kg adt^{-1}, respectively [25]. Simultaneously, continuous effort on closing the loops led to a significant decrease in the total effluent flow from values higher than 100 m^3 adt^{-1} in the 1970s to about 16 m^3 adt^{-1} today. The successful technological improvements in the past, as well as the current developments focusing on new generations of alkaline cooking, clearly signal that kraft pulping will remain the dominant cooking process in the future.

It is commonly agreed [25,45] that the only serious alternative to kraft pulping is ASAM pulping (alkaline sulfite with anthraquinone and methanol) developed by Patt and Kordsachia [46,47]. In order to overcome the problem with the additional recovery of methanol, a new attempt was made to improve the efficiency of alkaline sulfite pulping, AS/AQ, in the absence of methanol [48]. The AS/AQ process, by using a split addition of alkali charge to ensure a rather even alkali profile throughout the cook, produces pulp with strength properties that are equal or even slightly superior to those of kraft pulp whilst revealing a distinct yield advantage, even at low kappa number [49,50]. Even though odor abatement is quite powerful in modern kraft mills, pulping processes based on AS/AQ are clearly advantageous in this respect. The principal stumbling block to implementing AS/AQ pulping has been the inability to regenerate sodium sulfite with the Tomlinson recovery cycle. An important prerequisite for the successful introduction of AS cooking is that a new chemical recovery technique based on black liquor gasification can be implemented.

It is most likely that, similar to the situation before 1930 when kraft pulping became the dominant cooking process through the development of the Tomlinson recovery boiler, a new generation of black liquor incineration combined with efficient energy and chemical recovery – namely black liquor gasification/combined cycle (BLGCC) – will mark a further breakthrough of alkaline pulping. BLGCC is certainly the key element to entering into a new era of pulping technology. Black liquor gasification technology is classified by operating temperature into high-temperature (~1000 °C) and low-temperature gasification (below 700 °C). The temperature level of the former is sufficient to convert the inorganic components into a smelt, whereas operating below 700 °C ensures that the inorganics leave as dry solids. If the gas is combusted in a combined cycle (as is the case in a BLGCC installation), there is the potential to produce at least twice more electric power from the same amount of black liquor than with a Tomlinson furnace – and this is the most compelling reason for pursuing this new technology [45]. Moreover, gasification also provides a significant separation of sulfur from sodium in that the reduced sulfur accumulates in the product gas in the form of hydrogen sulfide. The separation of sulfur from sodium is an important prerequisite for the application of modified alkaline cooking technologies including split sulfidity pulping, polysulfide pulping and AS/AQ pulping [51]. The prospects for commercializing BLGCC appear quite promising, and although a number of open technical issues have still to be solved, commercialization is expected within the next five to ten years [25].

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