Chapter 2

Overview of Pulp and Papermaking Processes

The pulp and paper industry is very diversified, using many types of raw materials to produce very different kinds of paper by different methods in mills of all sizes. Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugarcane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal (Gullichsen, 2000).

The paper manufacturing process has several stages: raw material preparation and handling, pulp manufacturing, pulp washing and screening, chemical recovery, bleaching, stock preparation, and papermaking (Fig. 2.1).

Paper production is basically a two-step process in which a fibrous raw material is first converted into pulp, and then the pulp is converted into paper. The harvested wood is first processed so that the fibers are separated from the unusable fraction of the wood, the lignin. Pulp making can be done mechanically or chemically. The pulp is then bleached and further processed, depending on the type and grade of paper that is to be produced. In the paper factory, the pulp is dried and pressed to produce paper sheets. Postuse, an increasing fraction of paper and paper products is recycled. Nonrecycled paper is either landfilled or incinerated.

Pulp mills and paper mills may exist separately or as integrated operations. Figure 2.2 shows a simplified flow diagram of an integrated mill. Manufactured pulp is used as a source of cellulose for fiber manufacture and for conversion into paper or cardboard.

2.1 RAW MATERIAL PREPARATION AND HANDLING

Pulp manufacturing starts with raw material preparation, which includes debarking (when wood is used as raw materials), chipping, chip screening, chip handling and storage, and other processes such as depithing (e.g., when bagasse is used as the raw material) (Biermann, 1996a; Gerald, 2006; Gullichsen, 2000).
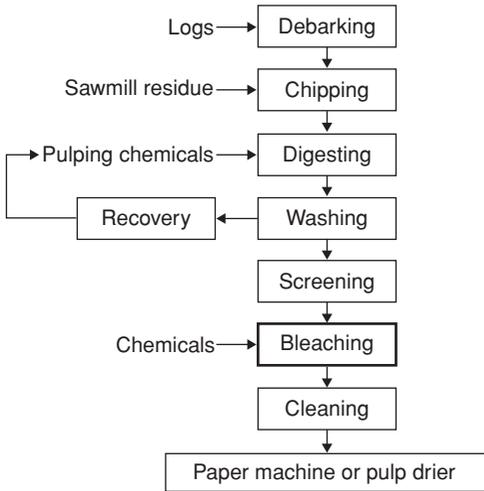
Figure 2.1   Pulp and papermaking processes.

Log debarking is necessary to ensure that the pulp is free of bark and dirt. Both mechanical and hydraulic bark removal methods are in common use. The barking drum is the most common form of mechanical debarking. Bark is removed from the logs by friction created from the rotating drum action as the logs rub against each other. In wet drumbarkers, water is added to the early solid steel portion of the drum to help loosen the bark. The remaining portion of the drum has slots to permit the
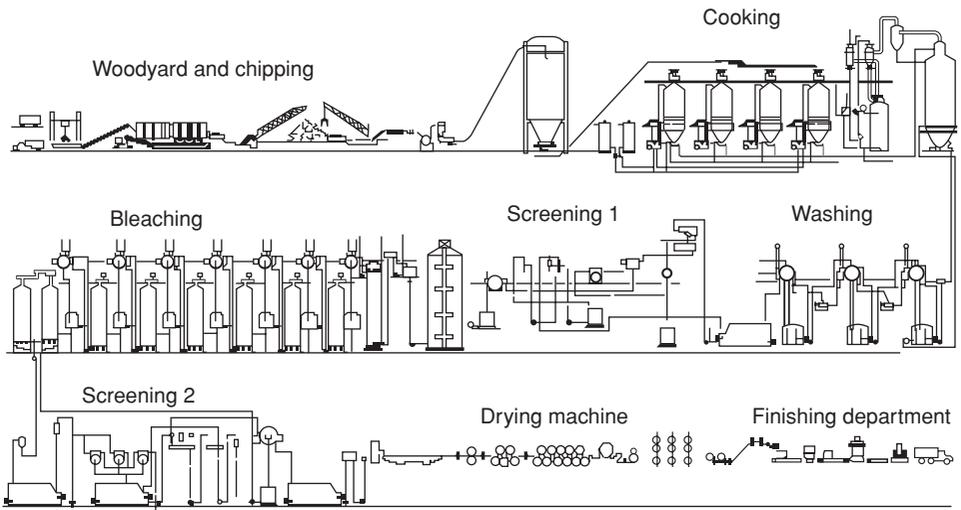
Figure 2.2   A simplified flow diagram of an integrated mill (chemical pulping, bleaching, and paper production). Based on Smook (1992b).

removed bark to fall out while the log continues on through. In dry drumbarkers, the entire length of the drum has slots for bark removal. Dry drumbarkers are longer in length and rotate much faster than wet-type drumbarkers. The bark from dry drumbarking can be fired directly into bark-burning furnaces, while bark from a wet system must be collected in a water flume, dewatered and pressed before burning. Drumbarkers usually create about 4–5% wood waste and cause broomed ends on the logs that produce inferior wood chips for pulping. They are relatively low-cost devices but have high power consumption (Russel, 2006).

After debarking, the logs (or portions of logs) are reduced to chip fragments suitable for the subsequent pulping operations. Several designs of chippers are in use, the most common being the flywheel-type disk with a series of blades mounted radially along the face. The logs are usually fed to one side of the rotating disk at an optimum angle (about 45 degrees) through a vertical directing chute. The logs can also be fed horizontally to a disk mounted at the proper angle. Generally, the horizontal feed provides better control but is less suitable for scrap wood pieces. Off-size chips adversely affect the processing and quality of pulp.

Acceptable-size chips are usually isolated from fines and oversized pieces by passing the chips over multistage vibratory screens. The oversized chips are rejected to a conveyor, which carries them to a "rechipper." The fines are usually burned with the bark (unless special pulping facilities are available).

Conventional screening segregates chips only on the basis of chip length. More recently, the greater importance of chip thickness has been recognized, and a few recently designed screens now segregate according to this parameter. Also, new design "rechippers" that slice the chip lengthwise to reduce thickness cause far less damage to the fibers than the old-style crushers.

Within mill areas, most chips are transported on belts or in pipes, using an airveying system. Chips are readily handled by air over distances of 300–400 m, but power consumption is high and chip damage can be significant. By contrast, a belt conveyor system has a much higher initial cost. Other systems such as chain and screw conveyors are also used to move chips, but usually for relatively short distances. Bucket elevators are used for vertical movement.

Chip storage is widely utilized primarily because chips are more economical to handle than logs. Some disadvantages are apparent, for example, blowing of fines and airborne contamination, but it has been only recently that the significant loss of wood substance from respiration, chemical reactions, and microorganism activity has been quantified. It is now recognized that losses of 1% wood substance per month are typical. Considerable research has already been carried out to find a suitable chip preservative treatment, but so far, a totally effective, economical, and environmentally safe method has not been identified. In the meantime, it makes good sense to provide a ground barrier of concrete or asphalt before building a chip pile to reduce dirt contamination and inhibit the mobility of ground organisms. Chips should be stored on a first-in/first-out basis to avoid infection of fresh chips by old chips; the ring-shaped pile facilitates the complete separation of "old" and "new" chips. Wind-blown concentrations of fines should be avoided because they reduce the dissipation of heat that builds up in the pile from various causes. Thermal degradation and even spontaneous

combustion can result from localized heat buildup. Optimum chip handling depends partly on pulping requirements. Because loss of extractives is high for the first 2 months of outside storage, all chips for sulfite pulping should go to storage (to reduce resin problems). If by-product recovery is important (as for some kraft pulping operations), fresh chips should bypass storage wherever possible to maximize yield.

A number of reclaiming methods are in use. Older installations employ a belt or chain conveyor along the side of the pile, which is fed by a bulldozer that pushes chips down the side of the pile onto the conveyor. This arrangement is labor-intensive (necessitating a full-time bulldozer operator) and inevitably results in damage to the chips. Modern installations work automatically, some employing augers or chain conveyors on rotating platforms at the base of the pile.

With respect to a given wood source, the quality of chips is measured by uniformity of size (i.e., length and thickness) and by the relative absence of "contaminants." All chips of 10–30 mm long and 2–5 mm thick are usually considered to be of good quality. Contaminants are considered to be oversized chips (either length or thickness), pin chips (passing 3/8 in. screen), fines (passing 3/16 in. screen), bark, rotten wood (including burned wood), and dirt and extraneous.

Oversized chips represent a handling problem and are the main cause of screen rejects in chemical pulping (Smook, 1992a). Size reduction of the oversize fraction is difficult to accomplish without generation of fines. Pin chips and (especially) fines and rotten wood cause lower yields and strengths in the resultant pulps and contribute to liquor circulation problems during cooking of chemical pulps. Bark mainly represents a dirt problem, especially in mechanical and sulfite pulping. The kraft pulping process is much more tolerant of bark because most bark particles are soluble in the alkaline liquor. Figure 2.3 illustrates the chip creation process.

2.2 PULP MANUFACTURING

The manufacture of pulp for paper and cardboard employs mechanical (including thermomechanical), chemimechanical, and chemical methods (Table 2.1).

Mechanical Pulping

There are three main categories of mechanical pulp: groundwood pulp, refining pulp, and chemimechanical pulp. Figure 2.4 shows the steps in the two first categories. In
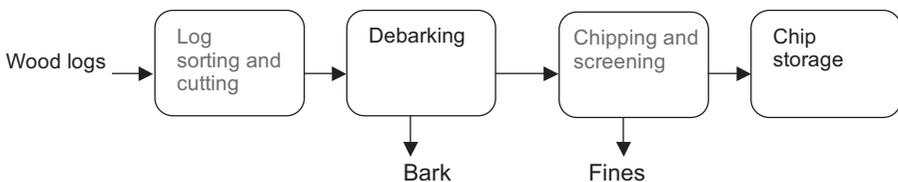

Figure 2.3 A flow diagram for wood preparation.

Table 2.1   Types of Pulping

Process	Pulp color	Yield (%)	Uses
Thermomechanical pulping	Brown	>95	Boxboard, newsprint, paper bags
Chemithermomechanical pulping	Light brown	85–95	Newsprint, specialty papers
Semichemical	Beige–brown	60–80	Newsprint, bags
Chemical—kraft, sulfite	Light brown	40–55	Newsprint, fine papers

both the grinding and refining processes, the temperature is increased to soften the lignin. This breaks the bonds between the fibers (Casey, 1983b; Gullichsen, 2000). Groundwood pulp shows favorable properties with respect to brightness (≥85% International Organization for Standardization (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. Groundwood pulp has been the quality leader in magazine papers, and it is predicted that this situation will remain unchanged (Arppe, 2001). The most important refiner mechanical pulping process today is thermomechanical pulping (TMP). This involves high-temperature
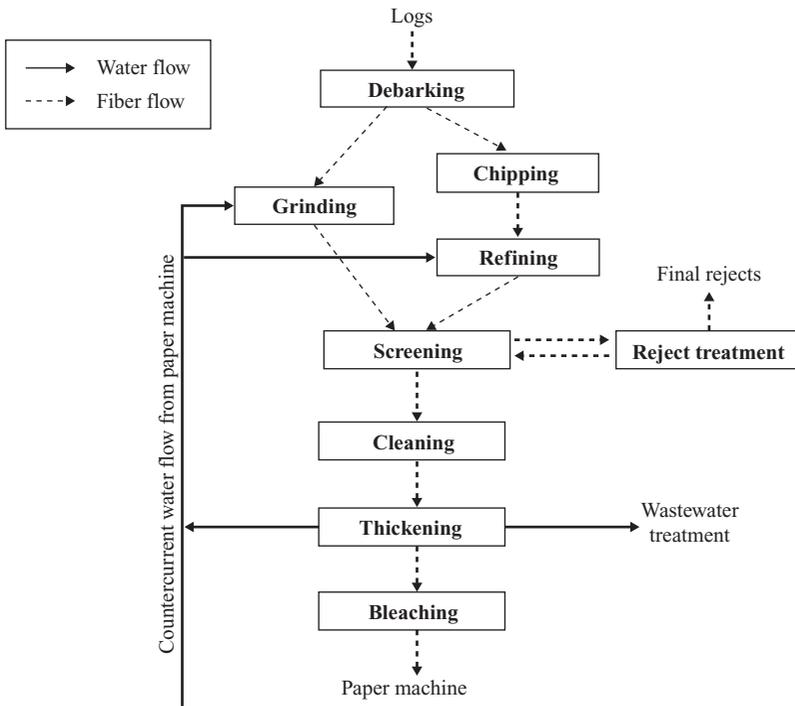

Figure 2.4   The mechanical pulping process.

steaming before refining; this softens the interfiber lignin and causes partial removal of the outer layers of the fibers, thereby baring cellulosic surfaces for interfiber 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 result in easier liberation of the fibers in subsequent refining. The chemithermomechanical 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) and are generally obtained in the yield range of 85–95%. Currently, mechanical pulps account for 20% of all virgin fiber materials. 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.

Semichemical Pulping

Semichemical pulping processes are characterized by a mild chemical treatment preceded by a mechanical refining step (Fig. 2.5) (Biermann, 1996b). Semichemical pulps, which apply to the category of chemical pulps, are obtained predominantly from hardwoods in yields of between 65% and 85% (∼75%). The most important semichemical process is the neutral sulfite semichemical (NSSC) process, in which chips undergo partial chemical pulping using a buffered sodium sulfite solution, and
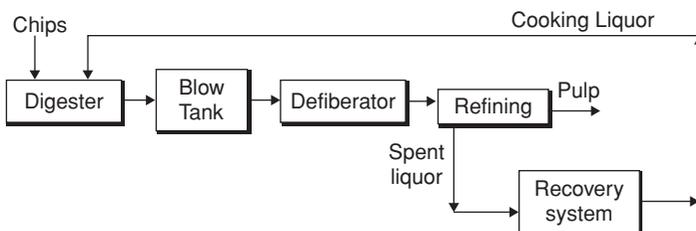
Figure 2.5   The semichemical pulping process.

are then treated in disk 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, 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 makeup (Na, S) for the kraft process. However, with the greatly improving recovery efficiency of modern kraft mills, the NSSC makeup is no longer needed so that high-yield kraft pulping develops as a serious alternative to NSSC cooking. Semichemical pulp is still an important product category, however, and accounts for 3.9% of all virgin fiber materials.

Chemical Pulping

Chemical pulping dissolves the lignin and other materials of the interfiber matrix material, and also most of the lignin that is in the fiber walls. This enables the fibers to bond together in the papermaking process by hydrogen bond formation between their cellulosic surfaces. Chemical pulps are made by cooking (digesting) the raw materials, using the kraft (sulfate) and sulfite processes (Casey, 1983a).

Kraft Process

The kraft process produces a variety of pulps used mainly for packaging and high-strength papers and board. Wood chips are cooked with caustic soda to produce brown stock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy (Biermann, 1996b). Figure 2.6 shows a simplified schematic diagram of the kraft pulping process and the corresponding chemical and energy recovery process. The kraft process dominates the industry because of advantages in chemical recovery and pulp strength. It represents 91% of chemical pulping and 75% of all pulp produced. It evolved from an earlier soda process (using only sodium hydroxide as the active chemical) and adds sodium sulfide to the cooking chemical formulation. A number of pulp grades are commonly produced, and the yield depends on the grade of products. Unbleached pulp grades, characterized by a dark brown color, are generally used for packaging products and are cooked to a higher yield and retain more of the original lignin. Bleached pulp grades are made into white papers. Nearly half of the kraft production is in bleached grades, which have the lowest yields. The superiority of kraft pulping has further extended since the introduction of modified cooking technology in the early 1980s. In the meantime, three generations of modified kraft pulping processes (modified continuous cooking, isothermal cooking, and compact cooking as examples for continuous cooking and cold blow, SuperBatch/rapid displacement heating, and continuous batch cooking for batch cooking technology) have emerged through continuous research and development. The third generation includes black liquor impregnation, partial liquor exchange, increased and profiled hydroxide ion concentration, and low cooking

Figure 2.6 The kraft pulping process and the chemical and energy recovery cycle. Based on Smook (1992b).
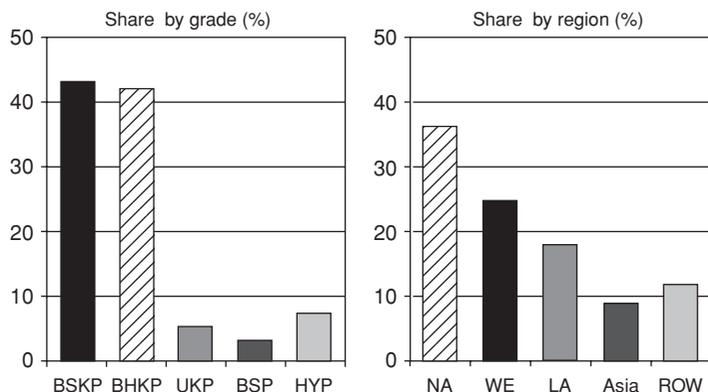
Figure 2.7   Global market pulp capacity of bleached kraft pulp: percent share by grade and percent share by region (Johnson et al., 2008). Reproduced with permission from Beca AMEC.

temperature (elements of compact cooking); also the controlled adjustment of all relevant cooking conditions in that all process-related liquors are prepared outside the digester in the tank (as realized in continuous batch cooking). 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 by-products (Annergren and Lundqvist, 2008; Marcoccia et al., 2000; McDonald, 1997).

In 2005, the global market pulp capacity was approximately 54 million tonnes; bleached kraft pulp accounted for 85% of capacity (Johnson et al., 2008). North America has the majority share by region, followed by Western Europe and Latin America (Fig. 2.7). Bleached hardwood kraft pulp capacity has grown at a faster rate than bleached softwood kraft pulp.

Many of the developments in kraft pulp production have been driven by severe environmental concerns, especially in Central Europe and Scandinavia during the 1980s and 1990s. 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 products during the 1980s caused a rapid development of alternative, environmentally benign bleaching processes (Bajpai, 2005a). 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, since numerous field studies have shown that ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic substances. ECF pulp, bleached with chlorine dioxide, continues to dominate the world bleached chemical pulp market (Pryke, 2003). In 2007, ECF production reached more than 88 million tonnes, totaling more than 89% of world market share. Total ECF production increased by 12.6 million tonnes compared to 2005 levels (AET, 2007). In contrast, TCF production continued to decline, maintaining a small niche market at less than 5% of world bleached chemical pulp production.
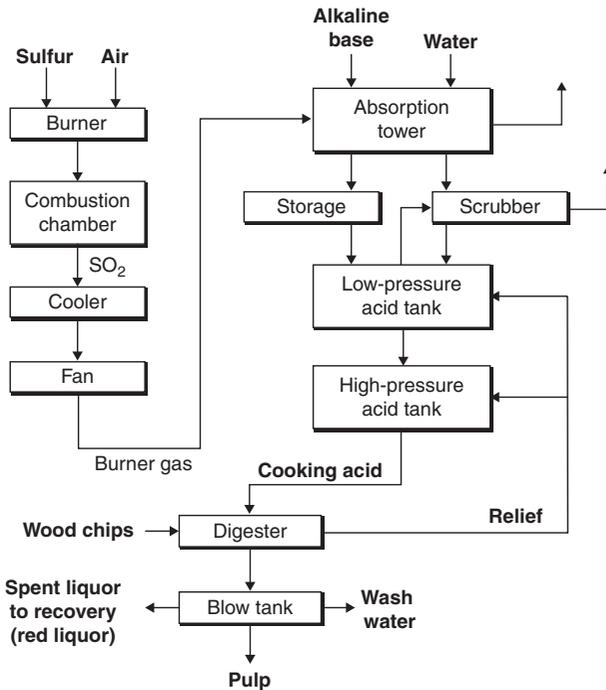
Sulfite Process

This process uses different chemicals to attack and remove lignin. Compared to kraft pulps, sulfite pulps are brighter and bleached more easily, but are weaker. Sulfite pulps are produced in several grades, but bleached grades dominate production (Sixta, 2006). Yields are generally in the range of 40–50%, but tend toward the lower end of this range in bleached grades. Compared to the kraft process, this operation has the disadvantage of being more sensitive to species characteristics. The sulfite process is usually intolerant of resinous softwoods, tannin-containing hardwoods, and any furnish containing bark. The sulfite process produces bright pulp, which is easy to bleach to full brightness, and produces higher yield of bleached pulp, which is easier to refine for papermaking applications.

The sulfite process is characterized by its high flexibility compared to the kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulfite pulping by changing the dosage and composition of the chemicals (Biermann, 1996b; Smook, 1992b). Thus, the use of sulfite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulfite process can be distinguished according to the pH adjusted into different types of pulping. The main sulfite pulping processes are acid (bi)sulfite, bisulfite (Magnefite), neutral sulfite (NSSC), and alkaline sulfite.

A typical sulfite pulping process is shown in Fig. 2.8 (Smook, 1992b). The sulfite cooking process is based on the use of aqueous sulfur dioxide and a base—calcium, sodium, magnesium, or ammonium. The specific base used will impact on the options available within the process in respect of chemical and energy recovery system and water use. The dominating sulfite pulping process in Europe is the magnesium sulfite pulping, with some mills using sodium as a base. Both magnesium and sodium bases allow chemical recovery. The lignosulfonates generated in the cooking liquor can be used as a raw material for producing different chemical products.

2.3   PULP WASHING AND SCREENING

After pulp production, pulp processing removes impurities, such as uncooked chips, and recycles any residual cooking liquor via the pulp washing process (Smook,

Figure 2.8   The sulfite pulping process. Based on Smook (1992b).

1992b). Pulps are processed in a wide variety of ways, depending on the method that generated them (e.g., chemical and sulfite). Some pulp processing steps that remove pulp impurities include screening, defibering, and deknotting. Pulp may also be thickened by removing a portion of the water. At additional cost, pulp may be blended to ensure product uniformity. If pulp is to be stored for long periods, drying steps are necessary to prevent fungal or bacterial growth. Residual spent cooking liquor from chemical pulping is washed from the pulp using pulp washers, called "brown stock washers" for kraft and "red stock washers" for sulfite. Efficient washing is critical to maximize return of cooking liquor to chemical recovery and to minimize carryover of cooking liquor (known as washing loss) into the bleach plant because excess cooking liquor increases consumption of bleaching chemicals. Specifically, the dissolved organic compounds (lignins and hemicelluloses) contained in the liquor will bind to bleaching chemicals and thus increase bleach chemical consumption. In addition, these organic compounds function as precursors to chlorinated organic compounds (e.g., dioxins and furans), increasing the probability of their formation.

The most common washing technology is rotary vacuum washing, carried out sequentially in two, three, or four washing units. Other washing technologies include diffusion washers, rotary pressure washers, horizontal belt filters, wash presses, and dilution/extraction washers. Pulp screening removes remaining oversized particles such as bark fragments, oversized chips, and uncooked chips. In *open* screen rooms,

wastewater from the screening process goes to wastewater treatment prior to discharge. In *closed-loop* screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Centrifugal cleaning (also known as liquid cyclone, hydrocyclone, or centricleaning) is used after screening to remove relatively dense contaminants such as sand and dirt. Rejects from the screening process are either repulped or disposed of as solid waste (Gullichsen, 2000).

Brown Stock Washing

The objective of brown stock washing is to remove the maximum amount of liquor-dissolved solids from the pulp while using as little wash water as possible. The dissolved solids left in the pulp after washing will interfere with later bleaching and papermaking and will increase costs of these processes. The loss of liquor solids due to solids left in the pulp means that less heat can be recovered in the recovery furnace. Also, makeup chemicals must be added to the liquor system to account for lost chemicals (Gullichsen, 2000).

It would be easy to achieve very high washing efficiencies if one could use unlimited amounts of wash water. As it is, one has to compromise between high washing efficiency and a low amount of added wash water. The water added to the liquor during washing must be removed in the evaporators prior to burning the liquor in the recovery furnace. This is a costly process and often the bottleneck in pulp mill operations. Minimizing the use of wash water will therefore decrease the steam cost of evaporation.

In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or freshwater. Then, the liquor is extracted by thickening the pulp, either by filtering or pressing. This procedure must be repeated many times in order to sufficiently wash the pulp.

In displacement washing, the liquor in the pulp is displaced with weaker wash liquor or clean water. Ideally, no mixing takes place at the interface of the two liquors. In practice, however, it is impossible to avoid a certain degree of mixing. Some of the original liquor will remain with the pulp, and some of the wash liquor will channel through the pulp mass. The efficiency of displacement washing then depends on this degree of mixing and also on the rate of desorption and diffusion of dissolved solids and chemicals from the pulp fibers.

All pulp washing equipment is based on one or both of these basic principles. Displacement washing is utilized in a digester washing zone. A rotary vacuum washer utilizes both dilution/extraction and displacement washing, while a series of wash presses utilize dilution\extraction. Most pulp washing systems consist of more than one washing stage. The highest washing efficiency would be achieved if freshwater were applied in each stage. However, this approach would require large quantities of water and is therefore not used. Countercurrent washing is the generally used system design. In countercurrent washing, the pulp in the final stage is washed with the cleanest available wash water or freshwater before leaving the system. The drained

water from this stage is then sent backward through each of the previous stages in a direction opposite to the pulp flow (Smook, 1992b).

Screening

Screening of the pulp is done to remove oversized and unwanted particles from good papermaking fibers so that the screened pulp is more suitable for the paper or board product in which it will be used (Biermann, 1996b; Ljokkoi, 2000). The biggest oversized particles in pulp are knots. Knots can be defined as uncooked wood particles. The knots are removed before washing and fine screening. In low-yield pulps they are broken down in refiners and/or fiberizers; they are also removed in special coarse screens called "knotters."

The main purpose of fine screening is to remove shives. Shives are small fiber bundles that have not been separated by chemical pulping or mechanical action. Chop is another kind of oversized wood particle removed in screening. It is more of a problem when pulping hardwoods because it originates mostly from irregularly shaped hardwood vessels and cells. Chop particles are shorter and more rigid than shives. Debris is the name for shives, chop, and any other material that would have any sort of bad effect on the papermaking process or on the properties of the paper produced.

2.4 PULP BLEACHING

Pulps prepared by most pulping processes are too dark to be used for many paper products without some form of bleaching. This is particularly true of pulps derived from alkaline processes, such as the kraft process, which are brown. Unbleached pulps from these processes are used mainly for packaging grades. Pulps from mechanical and sulfite processes are lighter in color and can be used in products such as newsprint. The sulfite process produces chemical pulps with the lightest color (Smook, 1992c). The brightness of pulp is widely used as an indication of its whiteness and provides a convenient way of evaluating the results of bleaching processes. Brightness is calculated from the reflectance of sheets of paper made from the pulp, using a defined spectral band of light having an effective wavelength of 457 nm. A disadvantage of this measurement is that the wavelength lies in the violet–blue region of the spectrum and does not adequately measure the optical properties of unbleached and semibleached pulps. Two standard procedures have been developed for the measurement of pulp brightness, the main differences between them being related to the geometry and calibration of the measuring instruments. The results of optical measurements are dependent on the geometry of illumination and viewing. Technical Association of the Pulp and Paper Industry (TAPPI) or (General Electric) GE brightness is measured with an instrument in which the illumination of the sample is directional, oriented at 45 degrees to the surface. The most common standard, developed by the ISO, requires the use of a photometer with diffuse sample illumination. The GE standard uses magnesium oxide as the reference standard, to which a reflectance value of

100% is assigned. The ISO standard uses an absolute reflecting diffuser with a 100% reflectance value. Brightness values obtained from these two methods are expressed as percent GE and percent ISO, respectively. Because of the differences in geometries of the specified instruments, there is no method for interconverting the brightness values obtained by the two methods. However, there is usually no more than about 2 brightness units difference between the two systems (Bristow, 1994). Brightness levels of pulps can range from about 15% ISO for unbleached kraft to about 93% ISO for fully bleached sulfite pulps.

Bleaching of pulp is done to achieve a number of objectives. The most important of these is to increase the brightness of the pulp so that it can be used in paper products such as printing grades and tissue papers. For chemical pulps, an important benefit is the reduction of fiber bundles and shives as well as the removal of bark fragments. This improves the cleanliness of the pulp. Bleaching also eliminates the problem of yellowing of paper in light, as it removes the residual lignin in the unbleached pulp. Resin and other extractives present in unbleached chemical pulps are also removed during bleaching, and this improves the absorbency, which is an important property for tissue paper grades. In the manufacture of pulp for reconstituted cellulose such as rayon and for cellulose derivatives such as cellulose acetate, all wood components other than cellulose must be removed. In this situation, bleaching is an effective purification process for removing hemicelluloses and wood extractives as well as lignin. To achieve some of these product improvements, it is often necessary to bleach to high brightness. Thus, high brightness may, in fact, be a secondary characteristic of the final product and not the primary benefit. It is therefore simplistic to suggest that bleaching to lower brightness should be practiced based on the reasoning that not all products require high brightness.

The papermaking properties of chemical pulps are changed after bleaching. Removal of the residual lignin in the pulp increases fiber flexibility and strength. On the other hand, a lowered hemicellulose content results in a lower swelling potential of the fibers and a reduced bonding ability of the fiber surfaces. If bleaching conditions are too severe, there will be fiber damage, leading to a lower strength of the paper. The purpose of bleaching is to dissolve and remove the lignin from wood to bring the pulp to a desired brightness level (Farr et al., 1992; Fredette, 1996; McDonough, 1992; Reeve, 1989, 1996a). Bleaching is carried out in a multistage process, that is, alternate delignification and dissolved material extracting stages. Additional oxygen- or hydrogen peroxide-based delignification may be added to reinforce the extracting operation. Since its introduction at the turn of the century, chemical kraft bleaching has been refined into a stepwise progression of chemical reaction, evolving from a single-stage hypochlorite (H) treatment to a multistage process, involving chlorine (Cl_2), chlorine dioxide (ClO_2), hydrogen peroxide, and ozone (O_3). Bleaching operations have continuously evolved since the conventional CEHDED sequence and now involve different combinations with or without chlorine-containing chemicals (Rapson and Strumila, 1979; Reeve, 1996a).

The introduction of Cl_2 and ClO_2 in the 1930s and early 1940s, respectively, increased markedly the efficiency of the bleaching process (Rapson and Strumila, 1979; Reeve, 1996a). Being much more reactive and selective than hypochlorite, Cl_2

had less tendency to attack the cellulose and other carbohydrate components of wood, producing much higher pulp strength. Although it did not brighten the pulp as hypochlorite, it extensively degraded the lignin, allowing much of it to be washed out and removed with the spent liquor by subsequent alkaline extraction. The resulting brownish kraft pulp eventually required additional bleaching stages to increase brightness, which led to the development of the multistage process. Chlorine dioxide, a more powerful brightening agent than hypochlorite, brought the kraft process efficiency one step further (Rapson and Strumila, 1979; Reeve, 1996a). Between the 1970s and 1990s, a series of incremental and radical innovations increased again the efficiency of the process, while reducing its environmental impacts (Reeve, 1996b). Development of oxygen delignification, modified and extended cooking, improved operation controls, for example, improved pulp and chemical mixing, multiple split chlorine additions, and pH adjustments increased the economics of the process and led to significant reduction of wastewater (Malinen and Fuhrmann, 1995; McDonough, 1995). In addition, higher ClO_2 substitution brought down significantly the generation and release of harmful chlorinated organic compounds. Table 2.2 details different considerations that have affected the development and use of the main bleaching chemicals over time. The information contained in the table provides an overview of economic and product quality considerations associated with pulp bleaching techniques and chemicals.

Until recently, it was believed that a 90-degree brightness could not be achieved without the use of chlorine and chlorine-containing chemicals as bleaching agents. The implementation of modified cooking and oxygen-based delignification impacted on the entire process by lowering the kappa number of the pulp prior to bleaching, thereby further reducing the amount of bleaching chemicals needed. Under tightening regulations and market demands for chlorine-free products, the industry eventually accelerated the implementation of ECF and TCF bleaching processes, by substituting oxygen-based chemicals to hypochlorite, Cl_2 and ClO_2, although the timing and scale of these trends have varied between regions (Bajpai, 2005a; McDonough, 1995).

2.5   STOCK PREPARATION

Stock preparation is conducted to convert raw stock into finished stock (furnish) for the paper machine. The pulp is prepared for the paper machine including the blending of different pulps, dilution, and the addition of chemicals. The raw stocks used are the various types of chemical pulp, mechanical pulp, and recovered paper and their mixtures. The quality of the finished stock essentially determines the properties of the paper produced. Raw stock is available in the form of bales, loose material, or, in case of integrated mills, as suspensions. Stock preparation consists of several process steps that are adapted to one another as fiber disintegration, cleaning, fiber modification, and storage and mixing. These systems differ considerably depending on the raw stock used and on the quality of furnish required. For instance, in the case of pulp being pumped directly from the pulp mill, the slushing and deflaking stages

Table 2.2 Functions and Economic and Technological Implications of Bleaching Agents

Oxidant symbol	Code/form	Function	Advantages	Disadvantages
C	Cl_2, Gas	Oxidize and chlorinate lignin	Effective, economical	Can cause loss of pulp strength
O	O_2, gas used with NaOH solution	Oxidize and solubilize lignin	Low chemical cost, provide chloride-free effluent for recovery	Large amount required, expensive equipment, can cause loss of pulp strength
H	$Ca(OCl)_2$ or NaOCl	Oxidize, brighten, and solubilize lignin	Easy to make and use	Can cause loss of pulp strength if used improperly, expensive
D	ClO_2	Oxidize, brighten, and solubilize lignin	Achieve high brightness without pulp degradation, good particle bleaching	Expensive, must be made on-site
P	H_2O_2, 2–5% solution	Oxidize and brighten lignin	Easy to use, high yield, and low capital cost	Expensive, poor particle bleaching
Z	O_3, gas	Oxidize, brighten, and solubilize lignin	Effective, provide chlorine-free effluent for recovery	Expensive, poor particle bleaching
E	NaOH, 5–10% solution	Hydrolyze and solubilize lignin	Effective and economical	Darken pulp

Based on Gullichsen (2000) and Reeve (1996a).

are omitted. The following operations are practiced in the paper mills (Biermann, 1996e; Paulapuro, 2000):

- Dispersion
- Refining
- Metering and blending of fiber and additive

A number of new concepts have been introduced by Kadant Lamort with regard to virgin pulp stock preparation.

Dispersion

Pulpers are used to disperse dry pulp into water to form a slush or a slurry. The stock in the pulper is accelerated and decelerated repeatedly, and hydrodynamic shear forces

are produced by the severe velocity gradients. The resulting forces serve to loosen fibers and reduce any flakes into individual fibers.

Beating/Refining

Pulp produced in a mill without mechanical treatment is unsuitable for most paper grades. Paper made from unbeaten virgin pulp has a low strength, is bulky, and has a rough surface. In good-quality paper, the fibers must be matted into a uniform sheet and must develop strong bonds at the points of contact. Beating and refining are the processes by which the undesirable characteristics are changed (Baker, 2000).

Mechanical treatment is one of the most important operations when preparing papermaking fibers. The term "beating" is applied to the batch treatment of stock in a Hollander beater or one of its modifications. The term "refining" is used when the pulps are passed continuously through one or more refiners, whether in series or in parallel. Refining develops different fiber properties in different ways for specific grades of paper. Usually, it aims to develop the bonding ability of the fibers without reducing their individual strength by damaging them too much, while minimizing the development of drainage resistance. So, the refining process is based on the properties required in the final paper. Different types of fiber react differently because of differences in their morphological properties (Baker, 2000, 2005). The refining process must take into account the type of fibers.

Most of the strength properties of paper increase with pulp refining because they rely on fiber–fiber bonding. However, the tear strength, which depends highly on the strength of the individual fibers, decreases with refining. After a certain point, the factor limiting the strength is not the fiber–fiber bonding, but the strength of the individual fibers.

Refining beyond this causes a decrease in other strength properties besides tear. Refining a pulp increases the fibers' flexibility and results in denser paper, which means that bulk, opacity, and porosity values decrease during the process (Lumiainen, 2000). Mechanical and hydraulic forces are employed to alter the fiber characteristics. Shear stresses are imposed by the rolling, twisting, and tensional actions, occurring between the bars and in the grooves and channels of the refiner. Normal stresses (either tensional or compressive) are imposed by the bending, crushing, and pulling/pushing actions on the fiber clumps caught between the bar-to-bar surfaces. During beating and refining, fibers randomly and repeatedly undergo tensile, compressive, shear, and bending forces. They respond in three ways

1. Fibers develop new surfaces externally through fibrillation and internally through fiber wall delamination.

2. Fibers deform, resulting in changes in their geometric shape and the fibrillar alignment along their length. Overall, the fibers flatten or collapse. Fiber curl changes and kinks are induced or straightened. On the small scale, dislocations, crimps, and microcompressions are induced or diminished.

3. Fibers break, resulting in changes in length distribution and a decrease in mean fiber length. A small amount of fiber wall material also dissolves. All

these changes occur simultaneously and are primarily irreversible. The extent of the changes depends on the morphology of the fibers, the temperature, the chemical environment, and the treatment conditions. The conditions depend on the design of the equipment and its operating variables such as the consistency, intensity, and amount of treatment. Each pulp responds differently to a given set of conditions, and not all fibers within it receive the same treatment (Lumiainen, 2000).

As different types of fibers have different lengths and cell wall thicknesses and also vary in the width of their central lumen (canal), some fibers are fibrillated more by one kind of beating than another. Fibers that have thick cell walls and narrow central canals, such as linen, are less prone to cutting but readily fibrillate. So, choosing the right type of fiber to produce the refining effect appropriate to the desired paper properties is important. The problem in producing paper with the required properties is that cutting and fibrillation are not independent of one another. Cutting is necessary to produce smaller fibers that pack to give a good, smooth paper, while fibrillation is required for strength. The degree to which each of these is achieved depends on the characteristics of refining. Moreover, increasing fibrillation to impart strength and stiffness also increases the surface area of the fiber mat and reduces permeability.

The characteristics built into a paper by refining are a compromise. Cutting is different from fibrillation. Beating the fiber in an aqueous environment forces water into the cell walls. This is necessary for fibrillation. However, cutting does not require the cell walls to be swollen and should be conducted early in the refining process so that it does not introduce additional fibrillation—too much water retention by the fiber may result in drainage difficulties. While cutting can be distinguished from fibrillation in the refining process, fibrillation cannot be achieved without cutting some fibers.

There is a difference in drainage properties between cut and fibrillated fibers. Because of the difference, papermakers use the terms "free beaten" and "wet beaten," respectively. The difference in papermaking properties between the free-beaten and wet-beaten are

- Wet-beaten produces strong, dense, less porous, less absorbent, and dimensionally unstable papers.
- Free-beaten produces weak, bulky, porous, absorbent, and dimensionally stable papers.

The swollen cell walls in wet-beaten stock will collapse and shrink when the final paper is dried. However, if they come into contact with water again, such as in the lithographic printing process, they will readily reswell because damage to the cell walls makes them susceptible to water ingress. Wet-beaten stocks experience a large shrinkage in web width on drying but quickly expand again, which may cause registration problems during printing on rewetting. However, maximum burst tensile and fold strength can only be achieved by extended refining. This causes swelling and fibrillation at the cost of stability and bulk.

The degree of fibrillation imposed during refining also affects the rate at which the dilute suspension of pulp dewaters on the machine. The rate of dewatering is important because once the wet paper web has been formed, water must be removed

as quickly and efficiently as possible (starting from 99% water in the pulp fed on to the papermaking wire down to about 7% in the finished paper). The freeness of the pulp is important to the papermaker, with the rate of drainage giving an indication of the degree of beating or refining. The freeness is a measure of intentional beating and of any changes in fiber morphology during the mixing and dispersion of fibers.

Different refiners are used in refining and these differ in their design and operating conditions (Bajpai, 2005b; Baker, 2000; Biermann, 1996d; Stevens, 1992). While machine configurations have undergone changes, all have a similar action and work by an arrangement of cutting edges, brushing surfaces, contact pressures, and peripheral speeds. Within certain limits, when a refiner is properly applied, there is not a great difference between the ability of conical and disk refiners to develop fibers. A fiber is only aware of how many times it is hit and how hard it is hit.

The first refining machine was a Hollander beater. It was invented in the 1700s and operates in a batchwise mode. It was phased out in the late 1970s because it is slow and expensive to run. These days it is only used in small mills and in special applications, for example, cutting long cotton/rag fibers before the refining process. The Hollander beater comprises a large open vessel, a rotating bar-equipped drum, and two or three bar-equipped counter bed plates. It is energy-intensive, but produces a gentle and quite uniform treatment. Its refining energy and intensity can be independently controlled, which is an advantage. The beater suits small-capacity mills and short runs and is more versatile than other refiners, because different treatments can be obtained by changing the pressure during the beater cycle.

Two types of continuous refiner are used for stock preparation: conical refiners and disk refiners. Conical and disk refiners have almost completely replaced beaters in stock preparation systems. They occupy less space at similar levels of production and are more efficient in developing fiber strength. Conical refiners can be split into low-angle types (Jordan) and high-angle types (Claflins). They have been manufactured in a range of sizes and capacities. Their operation is similar to that of a disk refiner, except in geometry. In conical refiners, the refining surfaces are on a tapered plug. These surfaces consist of a rotor that turns against the housing and the stator, both of which contain metal bars mounted perpendicularly to rotation. The Jordan refiner, patented by Joseph Jordan in 1858, is a low-angle conical refiner. It achieves different levels of refining by moving a rotating plug into a stationary shell to change the distance between the two surfaces. There are many sizes and capacities of this type of refiner. The Jordan refiner is still found in many fine paper mills but has a number of shortcomings when compared to the more modern conical and double-disk refiners (Lumiainen, 2000). The no-load power is high, which equals low operating efficiency; typically, in many installations the efficiency is less than 50%.

The next conical-type refiner is a wide-angle refiner with a 60-degree angle rather than 16 degrees. The most widely used version of this type of refiner is the Bematec Claflin refiner (Bajpai, 2005b). These refiners operate with a large working area at low speeds, having relatively little power installed for the throughput capacity. Fillings are available that produce anything from extreme cutting to almost pure fibrillation and do so, without sacrificing efficiency. Wide-angle refiners are adaptable and work economically under a variety of conditions. This type of refiner is found in many mills

and has a deserved reputation for robustness and long filling life. Another type of conical refiner is the shallow-angle refiner, for example, Conflo. It is well established worldwide. The advantages for this refiner are a low no-load power and a long refining zone (Lumiainen, 1991). The shallow-angle refiner is an energy-efficient replacement for older types of low-angle conical refiners and offers a range of fillings suitable for softwood and hardwood pulps.

In the mid-1990s, Pilao S.A. of Brazil, a manufacturer of disk-type refiners, began a project to improve on the available designs of conical refiners (Anonymous, 1998a, b). The goals were to develop a unit that combined the fiber development and reduced energy characteristics of the new conical refiners with higher capacity and energy efficiency. The result of the project was a conical refiner with three refining cones. The refining system is a wide-angle, double-flow conical refiner with a double-sided conical rotor and two conical stators. Like a double-disk refiner, the rotor floats and is balanced by stock flow and hydrodynamic pressure on both sides. In concept, the refiner can be thought of as a double-disk refiner folded back over itself. The new type of conical refiner provides more complete and homogeneous fiber treatment and improved fiber development. The hydrodynamic forces in a conical refiner may force more fibers across the bar intersections.

Disk refiners also operate continuously. These refiners became available for papermaking in the 1930s, after the conical refiners. Disk refiners are able to operate at high consistency, which favors fiber fibrillation with minimal fiber cutting. They have lower no-load energy requirements (an indication of energy that does not contribute to refining), are more compact, and are easier to maintain. The disk refiner group comprises three types: single-disk, double-disk, and multi-disk-type refiners. Single-disk refiners are almost entirely used only in high-consistency refining because their efficiency in low-consistency refining does not meet today's requirements. Multi-disk refiners are intended for very low-intensity refining with extremely fine plate pattern and are most suitable for the postrefining of mechanical and hardwood pulps (Baker, 2005).

Another type of refiner is cylindrical refiner called the "Papillon" developed by Andritz (Gabl, 2004; Lankford, 2001). It incorporates the Hollander beater principle—which integrates the production engineering requirements of a continuous refining process to some advantage. The pulp is refined on one-cylinder level, which yields the following advantages: the pulp transport and refining processes operate independently of one another. This means that refining conditions can be properly targeted over the entire refining gap. Same refining speed over the entire refining gap results in improved technological values and net energy consumption for refining, as well as a significant reduction in the no-load power compared to conventional refining units. The concept of the new refiner is based on market requirements in terms of improved use of the fiber strength potential available.

DoubleConifiner and ConiDisc are two advanced refiners available from Aikawa Iron Works KK (Aoshima, 2002). Both possess the combined characteristics of the double-disk refiner and conical refiner. DoubleConifiner achieves sufficient refining without causing damage to the pulp fibers, resulting in improvements in stretch resistance and intralayer strength. Thune Myren medium-consistency refiner

developed by Thune Myren, in conjunction with PFI, operates at between 10% and 22% consistency. The refiner is screw-fed, and the removed water can be re-added after refining or into the refiner casing (the preferred method).

The changes that take place in fibers during beating profoundly affect the character of the paper, which can be made from them. Some of the changes can be seen when the fibers are examined under a microscope, but in many instances, there is a marked change in the papermaking properties with no commensurate visible change. In general, it may be said that the outer surface of a fiber consists of a network of fibrils, while the inner, secondary wall has parallel bundles of fibrils of the same general dimensions. Beating tends to remove that portion of the outer surface which remains after the processes of cooking, bleaching, and purification. As beating proceeds further, the inner wall of the fiber starts to swell and disintegrate. Beating for most grades of paper involves only the first of the process, but for glassine papers it goes nearly to completion.

Blending/Chemical Addition

The various fibrous and additive components are combined and blended to make the furnish (Biermann, 1996e; Paulapuro, 2000). The pulp components are supplied from a high-density storage tower. Therefore, a series of controlled dilution steps and mixing stages are necessary to achieve a uniform consistency. Accurate proportioning of pulps and additives into a blend is the major task of this stage. Many chemical additives are added to the stock at different points before the paper machine. The chemical additions are made at points right up to the wire, known as "stock additives" or "wet-end additives." For the majority of these additives, there are alternative points of addition, but some are much more effective if added at the right place. Routine additions at the beater or paper machine wet-end stage include sizing agents, mineral fillers, starch, and associated products and dyes (Krogerus, 2007; Smook, 1992d). Chemicals to give special effects, for example, wet strength, and to control such machine problems as foam, slime, and pitch. Fillers, or loading materials, were originally considered as adulterants used chiefly to cheapen the paper. It was not long, however, before they were recognized as serving perfectly legitimate purposes by increasing the opacity of the paper, aiding in obtaining a good finish on calendering, and improving printing qualities by reducing "showthrough" and "strikethrough" of the ink. Today, fillers are used in the great majority of printing papers, though there are some bulky papers and specialties in which they are not employed. Fillers increase the weight more than the bulk of a paper; they also affect adversely the strength of the paper and make it much more difficult to size with rosin. These facts must be remembered when setting specifications for a paper. Commonly used fillers are discussed in the following sections (Biermann, 1996e; Krogerus, 2007).

China Clay

China clay has the benefit of being chemically inert and therefore can be used in its natural state with any type of sizing agent, acidic or alkaline. Commercial quantities

are available in a wide range of particle sizes and brightness levels, the finer and brighter grades being used in high-quality papers. The use of china clay provides a smooth receptive surface that easily accepts printing ink, and although not as opaque as some more expensive fillers, it is satisfactory for many types of paper.

Chalk

Naturally occurring chalk tends to be of coarser particle size than china clay; hence, it increases matt surface to the paper. However, as it reacts with the acidic alum used in conventional sizing, its use as a filler is restricted. Commercially, calcium carbonate is available to the papermaker as ground, naturally occurring calcium carbonate or as synthetically prepared "precipitated calcium carbonate." The precipitated calcium carbonate is produced in various ways, most common being the passing of carbon dioxide through milk of lime (calcium hydroxide) or by the reaction of soda ash (sodium carbonate) with milk of lime. Another source of calcium carbonate is from the alkali recovery stage in the sulfate process. These so-called protected chalks are coated with starch and a polymer. As chalk is inexpensive compared to china clay, and with the introduction of "neutral" or "alkaline" sizing, this has led to an increased use of chalk as a filler.

Titanium Dioxide

Titanium dioxide with its high refractive index provides excellent opacity and brightness to paper, especially useful for thin bible papers, laminate base papers, and waxed papers. Titanium dioxide is also used in combination with other fillers, such as china clay, whereby in order to reduce costs, the proportion of titanium dioxide is kept to a minimum. Thus, a typical addition to a white lining for boxboards is 10% china clay, 3% titanium dioxide. The use of fillers in such liners is to make the brown shade of inner piles of waste paper from which the board is formed. The comparatively high cost of titanium dioxide has led to the use of synthetically prepared fillers, for example, sodium aluminum trihydrate. These can be used to replace a proportion of the titanium dioxide with virtually no loss of opacity, thereby reducing costs. They are however not suitable for such partial substitution of titanium dioxide in waxed papers. Titanium dioxide absorbs ultraviolet radiation to a much greater extent than other fillers. It is therefore not economical to use fluorescent brightening agents in papers in which titanium dioxide is the only filler. The synthetically prepared fillers referred to above are often incorporated with titanium dioxide in such cases, because by reducing the absorption of the ultraviolet radiation they enhance the effect of the brightening agent.

Other Additives

Other additives used are slimicides, antifoaming agents, filler retention aids, pitch control agents, and wet-strength agents (Krogerus, 2007). Urea-formaldehyde and

melamine formaldehyde resins are commonly used wet-strength agents and have a range of qualities, most of which require curing on the machine and running under acid conditions. Other chemical types can operate under neutral conditions, for example, in tissues, such as, polymide resins, modified starches, and emulsified elastomers. It is important that the correct agent is used for particular papers.

Sizing Agents

Chemicals that are used in the process of sizing are known as sizing agents. The process of sizing can be accomplished in two principal ways: (1) internal sizing and (2) surface sizing (Davison, 1992; Hodgson, 1997; Latta, 1997; Luukkonen et al., 1995; Neimo, 2000; Roberts, 1996, 1997). Internal sizing plays an important role in controlling the absorption and penetration of liquid such as water and ink into the paper, paperboard, and sheet material. The purpose of internal sizing is to inhibit penetration of liquids into the internal structure of paper. Internal sizes are introduced at the wet end of the papermaking system, usually as colloidal suspensions, which are retained in the fiber network during sheet formation. Adequate sizing maintains consistent runnability through the size press and helps to provide uniform printability in uncoated papers. For coated paper base stock, adequate sizing helps to control binder migration. Many factors influence the degree to which paper will resist penetration by liquids. These may include such paper properties as porosity and hydrophobicity (Bajpai, 2004).

Internal sizing agents are hydrophobic substances, which must attach to the paper (through the use of an appropriate functional group) to present a hydrophobic surface. On the basis of the pH, the internal sizing can be categorized into three types: (1) acid sizing, (2) neutral sizing, and (3) alkaline sizing. The three most common internal sizing agents currently being used are rosin systems, alkene ketene dimers (AKD), and alkenyl succinic anhydrides (ASA). A papermaker chooses the appropriate sizing agent by observing the processing conditions in the wet end of the paper machine and the particular grade being produced. For paper being made with acidic conditions in the wet end, a papermaker would choose to use a rosin size as an internal sizing agent. In the past, mills used to prepare their own rosin size. But nowadays, readymade fortified rosins either in powder or in liquid form are available for use. In acid sizing, the alum chemistry plays a very important and critical role in imparting sizing property to the paper/board. At low pH (<4.0), the aluminum exists as a soluble ionic species, but as the pH is raised, a colloidal hydroxylated alum floc forms. At higher pH values (>7.0), the alum flocs tend to redissolve and soluble aluminate is formed. As alum floc is a cationic material, it has affinity for anions such as anionic rosin particles, and fiber, fines, and fillers. Thus, alum serves as a precipitating and anchoring agent for the size and also serves as a retention aid for fine fillers, and dyes, improves drainage etc. Extensive studies have been carried out on rosin sizing at neutral/alkaline pH, which include substitution of alum by other chemicals or with other retention aids. For effective sizing, alum may be replaced with polyaluminum chloride, which increases the efficiency of rosin sizing significantly at pH greater than 5.5. Some polyaluminum phosphate sulfate compounds can get

good sizing results using rosin size at neutral/alkaline pH. Similarly, polyamines are known to improve rosin-sizing efficiency at neutral/alkaline pH because of their large charge densities in the neutral region and high molecular weight.

For neutral/alkaline paper machines, a papermaker would prefer to use a synthetic sizing agents such as AKD and ASA. AKD is used as a sizing agent in pH range of 6–9 that is both in neutral and alkaline media. Internal sizing at neutral/alkaline pH gives the possibility to use calcium carbonate as a filler. Another benefit that neutral/alkaline sizing gives is that the paper gains an improved storage durability compared to rosin-sized paper, for example, archive papers. ASA is another type of cellulose-reactive sizing agent that has found wide domestic acceptance in recent years due to its advantages. ASA is preferred for many grades because of its on-machine sizing and size press holdout. Sizing with ASA is typically 80% to 100% developed on the machine, and paper can immediately be converted and shipped. ASA is found to be more reactive than AKD. ASA is typically used as an internal sizing agent for alkaline papermaking in the pH range of 7–9 with good sizing efficiency. The ASAs are quite reactive molecules and can promote sizing without heating. Therefore, alkaline papermaking with an ASA size offers the papermaker an opportunity for enormous saving in raw materials and production cost. AKD use is more common in Europe, while in the United States the application of ASA is growing and today surpasses that of AKD.

Several other compounds have been investigated for alkaline paper sizing and found to be successful at least on a laboratory scale. Some of these alternative chemistries include various forms of acid chlorides, acid anhydrides, enol esters, alkyl isocyanates, and rosin anhydrides (Hodgson, 1997). Polymers and copolymers of styrene and acrylates exhibit great promise as both an internal and surface sizing agent and offer some interesting effects from economic and technical aspects. The use of these products makes it possible to create a hydrophilic/hydrophobic matrix on the paper surface that improves copy, ink-jet, laser-jet, and offset printing results.

There seems to be some advantage to be gained in some grades of paper by using mixed sizing systems. A combined sizing system of AKD and a cationic rosin size used in conjunction with alum gives a synergistic improvement when used in liquid packaging board. Combinations of AKD and ASA when used in full or pilot-scale production of fine paper containing precipitated calcium carbonate have also been shown to give a better sizing response, less size reversion, and allowed the use of higher filler levels with higher specific surface area. There was also less migration, higher frictional resistance, and better ink-jet printability.

Nearly every paper contains coloring matter of some sort. Coloring is usually done by adding the necessary material to the stock in the beater. Even white papers generally contain small amounts of blue and pink to offset the naturally yellow tone of the fibers, and to give the blue tone, which is generally considered to be "white." Soluble dyes are used more generally than pigment colors and are always added to the stock after dissolving. Such dyes are of three types: the so-called acid, basic, and "direct" dyes, which have to be handled differently in the beater and which impart different characteristics to the paper. Acid dyes need to be applied on sized stock as they do not take well on unsized fibers. They give even colors of good fastness
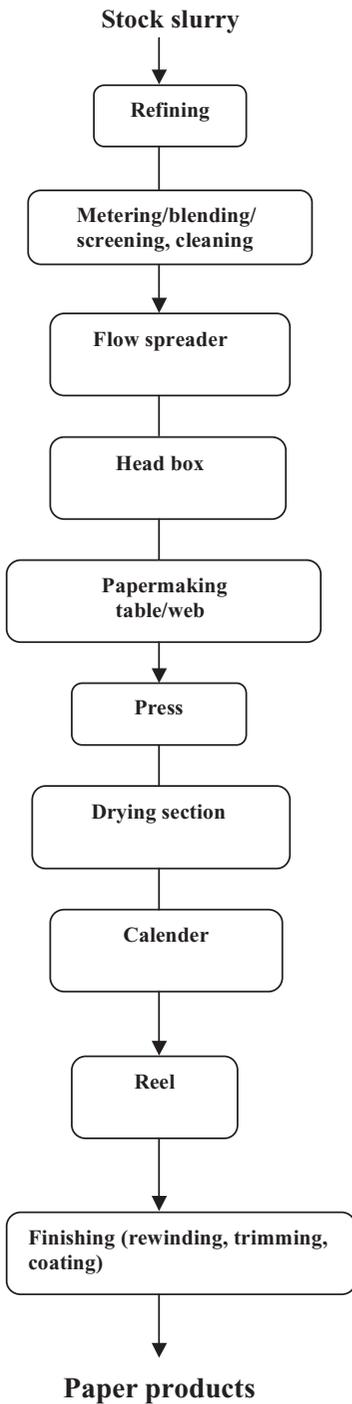
to light, but are not so intense or brilliant as the next class. Basic dyes give much brighter colors of greater depth, but most of them are not very fast to light, so are seldom used where great permanence of color is needed. Direct dyes take well on unsized fibers, but are not of great brilliance, and are used only where that property is unimportant. Different fibers take up the coloring matter differently, and if the fiber furnish contains both bleached and unbleached fibers uneven dyeing may result, some fibers being much more deeply colored than the rest.

Another characteristic that is developed by adding certain materials to the stock in the beater is known as "wet strength." A number of resins will cause this, among them being those formed from melamine and formaldehyde, or urea and formaldehyde, and others for the same purpose are being introduced frequently. These resins attach themselves to the fibers, and once the paper is dried it no longer becomes as weak when soaked in water as the untreated paper would be. While a paper with no resin will retain almost none of its dry strength on soaking, one treated to develop wet strength and correspondingly soaked may retain 30–40%. This difference is very appreciable in the use of the paper and makes it much more serviceable for blue prints, military maps, and all purposes where it might become wet.
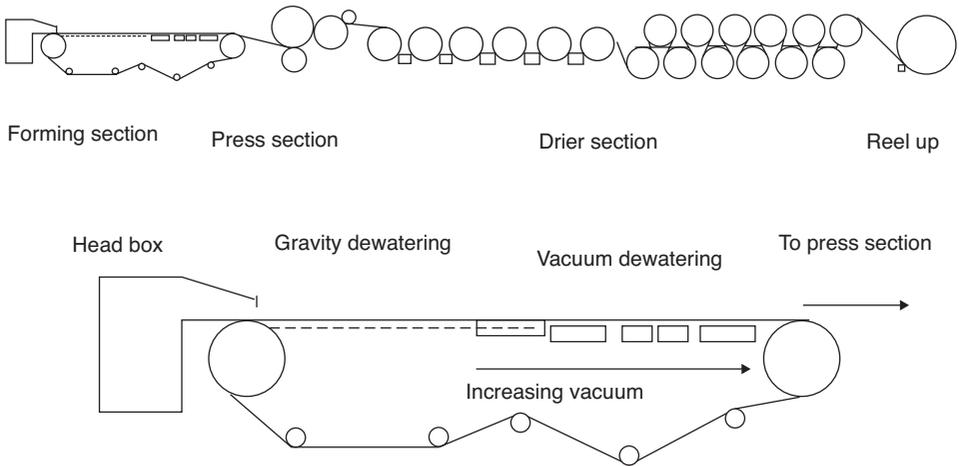
2.6 PAPERMAKING

A flow diagram for a typical papermaking process is shown in Fig. 2.9. The actual papermaking process consists of two primary processes: dry-end and wet-end operations. In wet-end operations, the cleaned and bleached pulp is formed into wet paper sheets. In the dry-end operations, those wet sheets are dried and various surface treatments are applied to the paper. The traditional Fourdrinier machine is still widely used but for many paper grades has been replaced with twin-wire machines or gap formers and hybrid formers (Atkins, 2005; Buck, 2006; Ishiguro, 1987; Lund 1999; Malashenko and Karlsson, 2000). Twin-wire formers have become the state-of-the-art design (Malashenko and Karlsson, 2000). In twin-wire formers, the fiber suspension is led between two wires operating at the same speed, and is drained through one or both sides. There are different types of twin-wire formers (e.g., gap formers). In gap formers, the diluted stock is injected directly into the gap between the two wires, and combinations of Foudrinier and twin wires (hybrid formers). Multiply papers can be made on a variety of formers, but recently two and three ply papers and liners are being made on multi-Fourdrinier wet ends. Whatever the forming device, the wet paper web is passed through presses to remove as much water as possible by mechanical means. More moisture is removed by evaporation on multiple drying cylinders.

The Fourdrinier papermaking machine is composed of three main sections: the forming section, the press section, and the drier section (Fig. 2.10). A paper slurry consisting of about 0.5–1.0% fiber is pumped into a box where it flows out through a slot onto a moving wire belt. Once on the belt, the water is removed by draining and suction, leaving the fibers to form a very wet and weak paper. The paper is then pressed, heated, and dried, resulting in a continuous roll or "web," which can be further finished as desired or required (Biermann, 1996f; Smook, 1992e).

Stock slurry

↓

Refining

Metering/blending/
screening, cleaning

Flow spreader

Head box

Papermaking
table/web

Press

Drying section

Calender

Reel

Finishing (rewinding, trimming,
coating)

↓

Paper products

Figure 2.9 A typical papermaking flow diagram.

Figure 2.10 A schematic diagram of a paper machine with a Fourdrinier forming section. Based on Smook (1992e).

Forming

The forming section of the Fourdrinier constitutes what is called the wet end of the machine. This section consists of the head box, the forming wire, foils, suction boxes, couch roller, breast roller, and dandy roll (Buck, 2006; Smook, 1992e). Pulp is pumped from the machine box through the screens and cleaners to the head box. The purpose of the head box is to deliver a uniform slurry to the forming wire. There are several different designs, but all incorporate a method to induce turbulence (deflocculation), while preventing crosscurrents, which would inhibit the uniformity of the stock. The simplest design is the gravity-fed head box. It uses height/weight-level difference to force the pulp through several baffles and a through a perforated rotating cylinder, before flowing through the apron and slice. A gravity-fed head box can deliver an 8 in.-stock depth at a rate of 400 ft/min. If faster production speeds are required, the stock must be fed under pressure. These machines can operate at speeds greater than 4000 ft/min. The pressurized head boxes are usually hydraulic, and the stock is forced through conical injectors, through a perforated plate and through a horizontally split apron and the slice. The apron height and the slice height, which control the jet of pulp, can be independently adjusted by hydraulics.

The pulp flowing onto the forming wire is approximately 0.5–1.0% fibers, with the makeup consisting of water. As the water is removed from the slurry, the fibers settle onto the surface of a traveling wire, forming a wet mat of paper. Therefore, the main objective of the forming section is the controlled removal of water. Originally, gravity allowed the water to drain through a brass forming wire 60–70 meshes/in., 40–50 ft length and 70–90 in. in width. But as production speeds increased, more efficient methods were developed. The forming wire, now a fine polymer screen with about 65 meshes/inch, carries the paper slurry over table rolls, foils, and suction

boxes, providing precise control over drainage and agitation control. As the slurry exits the slice onto the wire, the water starts draining from the suspension. Water jets are positioned over the edges of the forming wire to control the width of web, creating what is called the deckle edge. The first fibers forming the mat on the wire are oriented in the direction of the machine; this is, the wire side of the paper. If the rest of the fibers in the slurry were allowed to orient themselves in the same direction, the paper would have poor tear resistance and surface properties. If gravity was the main method of dehydration, the machine would have to be run at low speeds to overcome the orientation problem; the alternative is to remove the water quickly while the fibers are still agitated from the effects of the head box.

The first set of dewatering elements is a bank of table rolls. In earlier designs, table rolls were a series of small solid rollers. Now, they are much larger and are used as only the first water removal step. The rotation of the roll in contact with the covered wire causes a vacuum to form between the two, which pulls the water from the web.

With increasing speeds, the table rolls cause problems with paper uniformity and are not able to remove enough water before the presses. Foils have replaced most, if not all of the table rolls. Foils remove water using a doctor blade at the bottom of the forming wire. The blade causes a difference in pressures, which draws water from the web behind the blade. This method allows for more control over the removal process and is not significantly affected by machine speeds.

Water removal can be further enhanced by placing a vacuum on the foil drainage system. After the foils, water is further removed using flat suction boxes. The suction boxes remove the majority of the water, changing the stock consistency from 2% to 20% fiber content. Above the first couple of suction boxes, a skeleton roll covered with wire may ride at the top of the paper mat. This roll called a "dandy roll" compresses the paper, releasing any trapped air and improving the surface. The dandy roll can be covered with various wire patterns, which may simulate the forming wire and may have recessed or raised element designs, imparting a watermark onto the paper. In areas where the watermark elements, usually a wire design, are above the surface of the dandy roll, fewer fibers are allowed to settle, and the paper appears light. If the watermark elements are below the dandy roll surface, more fibers are allowed to settle than in the rest of the paper, and the paper appears darker in these areas. An alternative to using a dandy roll to create watermarks is the Molette. The Molette is a rubber stamp roll located before the wet press of the machine. This type of watermark actually embosses the paper and squeezes the fibers to the edges of the stamp.

A variation on the Fourdrinier was developed in the 1960s and employed the use of two forming wire, allowing the paper mat to be dried from both sides simultaneously. First, twin-wire machines were constructed so that the head box sprayed a vertical stream between the forming wires at the nip of twin breast rolls (Malashenko and Karlsson, 2000). The paper web was then further drawn vertically, while vacuum boxes operate from both sides. Newer designs returned to a horizontal feed system with both forming wires traveling horizontally and vacuum boxes drawing suction from below and above the web. Another variation is the use of a dewatering mat above the suction boxes on a Fourdrinier; this is referred to as a hybrid twin-wire machine.

In 1809, in England, John Dickinson invented another mechanical method of manufacturing paper, the cylinder mold machine (Smook, 1992e). Instead of pouring fibers through the forming wire, his machine dipped the forming wire into a vat, much in the same manner as handmade paper. This allowed him to create watermarks and four-sided deckled edges comparable to hand-couched paper. The modern cylinder mold machine, also known as "cylinder vat" or "mold made," is used to make fine bond paper with shadowed watermarks, currency and security papers, art papers, extremely heavy stock, corrugated cardboards, and multi-ply papers. The key to the cylinder mold machine is the use of a cylinder wire covered by the forming wire (now called the "cylinder blanket" or "cover"), partially submerged in a vat full of pulp. As the cylinder rotates into the paper stock, the slurry flows onto the surface of the cylinder, and the water flows through the wire cover to the inside of the cylinder where it is discharged. The fiber mat that accumulates onto the cylinder surface is removed or "couched" by a traveling felt belt. This traveling felt, "the cylinder felt," is sometimes referred to as the forming wire, even though the paper is already formed by the cylinder. If multiple-layer paper is desired, several vats and cylinders can be placed in series with the paper web acting as the cylinder felt for the additional paper mat. There are two main cylinder vat designs: contraflow and direct flow; and the cylinder felt can be above or below the drying stock.

Pressing

When the paper leaves the couch roll, it contains 80–85% of water, is very easily damaged, and will support its own weight for only a very short distance. It is therefore transferred to a traveling woolen felt, which supports it through the first of a series of presses whose function is to remove more water by squeezing and at the same time make the sheet denser and smoother. Two or three presses are used in series, and the paper may go directly through, or it may pass under one press and be reversed through its rolls so that the two sides of the sheet may be more nearly alike. The top roll of the press stands vertically over the lower roll, and it is connected with compound levers and weights, which permit regulation of the pressure applied and a maximum pressure much greater than that supplied merely by the weight of the top roll. Each press has a separate felt to carry the web, and just before the web reaches each set of rolls, the felt often passes over a suction box to aid in water removal. All felts are kept taut by a series of stretch rolls as they return to the point at which they picked up the paper web. Transferring the web from the couch to the first felt is done when starting by cutting a narrow strip by means of the squirt on the wire and blowing it onto the felt by an air blast; in slow machines it may be done by picking it off the couch by hand and lifting it onto the felt. At each press the web sticks to the top roll and has to be transferred to the next felt by hand or by air blast. After leaving the last press to go to the driers, the sheet will still contain about 71–74% of water, but it has gained enough in strength so that it can be handled to the driers without difficulty (Biermann, 1996f).

Many modern machines are equipped with a smoothing press whose function is not to remove water, but to smooth and flatten the sheet after it comes from the true

presses and before it goes to the driers. This aids in removing wire and felt marks and produces a superior paper, both for smoothness and for strength.

The felts used on the wet end of the paper machine are not true felts, which are made without weaving, but are actually heavy blankets woven from very high-grade woolen yarns. They must be strong to withstand the pull of the machine, but also of a texture loose enough to pass water readily. They are made in great variety to suit the speed of the paper machine and the grade of paper being made, and the surface of the paper is considerably influenced by the length of nap and the fineness of weave of the felt. Felts are easily damaged and must be handled carefully both off and on the machine.

Drying

After leaving the presses, the paper goes to the dry section of the machine, the purpose of which is the removal of the water, which cannot be taken out by pressing and which amounts to about 70% of the weight of the wet paper at this point (Biermann, 1996f). A paper machine drier is a cast iron drum with closed ends, very carefully made so that it may be in good running balance and supplied with a steam inlet and a device to remove condensed water continuously and without loss of pressure. The outer surface is turned and polished as smooth as possible. Driers are usually mounted in two rows, one above the other, but staggered, so that an upper drier is over the space between its two neighbors in the bottom row. At the back, end of each drier is a gear, which meshes with the gears on two driers in the row above or below, so that all turn at the same speed. A row of driers is usually broken into two banks with approximately an equal number of drums, and each bank is driven independently of the other. In some machines the driers are driven by an endless roller chain instead of gears; this is simpler in some respects and is desirable on high-speed news and kraft machines.

When the driers are arranged in two rows, each row usually has a long felt, which covers about one-half the surface of each drier and is kept tight by means of stretch rolls. These felts are also not true felts, and most of them are not wool, but a kind of heavy cotton duck; some are made of cotton and asbestos to withstand better the deterioration caused by the heat of the driers, which gradually rots the cotton. The purpose of the felts is to hold the paper firmly against the surface of the driers, except where it passes from one drum to the next, and thus produce a smooth sheet without cockles. The wet web is carried from the last press to the first drier and then in turn to the others until it emerges in a dry condition at the end of the two banks.

In passing the driers, about 2 lb of water must be evaporated for each pound of paper made. In cold climates, if this is allowed to escape directly into the room, it causes condensation on the ceiling and water drops all over the machine, so it is customary to cover the drier section with a hood from which the vapors are removed by fans.

From the driers the paper generally goes through calenders that consist of rolls of cast iron, chilled on the surface to make them hard, and ground and polished to a very smooth surface. A machine calender stack may have as many as 11 rolls, all

mounted in a housing at each end of the rolls, and all driven from the bottom roll by friction. The paper is fed in at the top, passes down through the stack and out at the bottom to the reel, where it is wound into large rolls, which are then rewound at full width or through slitter knives which allow the preparation of rolls of other desired sheet widths. The machine calender is designed to compact the sheet and give it a better finish. If this is not desired, the sheet coming from the driers may bypass the calender and go directly to the reel. Some paper machines use two calender stack sets so that the sheet passes the first one and then the other.

There are various modified paper machines for special purposes and products, but these need only brief mention. The "Yankee machine" dries the paper against a highly polished, single-drum drier, and this may be combined with the wet part of either a Fourdrinier or a cylinder. This produces the paper sometimes called "machine glazed." A modified Fourdrinier, known as the Harper machine, was built to handle very thin tissues, which were too light to be passed from the couch to the wet felt. Other modifications combine portions of the Fourdrinier and cylinder machines into various assemblies.

Finishing

After the drying section, the web is subjected to several finishing steps prior to shipping it as a final product. The web can be sized, giving the paper surface resistance, or if other properties are needed, the web can be surface-coated. The web can also be supercalendered, giving the surface a very smooth, uniform surface. In the final stages, the web is rewound and slit into two or more rolls and if needed sheeted.

Sizing

Sizing imparts resistance to liquids on the paper surface, a property necessary for paper used for writing or printing. Without external sizing, ink would bleed and feather. External or surface sizing can be performed either on the paper machine or on a stand-alone unit (Smook, 1992e). Machine sizing can be performed either by running the web through a size vat or by running the web through a size press. In the case of the size vat, the web, after exiting the drier section, is directed down into a vat and through another set of drying cans. Size presses are located after between the two drier sections and apply a coat of sizing by transference from rollers, and the metering is accomplished by the nip. The most common types of sizing consist of pigments and starches, although animal glue and glycerin can also be used (art and banknote papers).

Coating

Coating paper may be desirable or necessary to improve optical, printing/writing, and/or functional properties. Functional properties can be for protection from liquids,

oils, gases, and chemicals, improve adhesion characteristics, improve wear, or some other property. Coatings can be classified as aqueous, solvent, high solids, or extrusion. Aqueous coatings, used for commodity papers, contain water-soluble binders and are applied as a liquid. Common aqueous binders are casein, starch, protein, acrylics, and polyvinyl acetates. Solvent coatings are used in situations where the binders are not soluble in water and are used with specialty papers. High-solid and extrusion coatings are used for specialized papers, where chemical, gas, or liquid resistance is necessary. High-solid coatings are applied as a coating of monomers and are polymerized by UV or electron curing. Extrusion coatings are applied as a molten film of wax or polymer.

Supercalendering, Cockling, and Embossing

After the chemical processes have been completed, physical processes, such as supercalendering, cockling, and embossing, can be used to create the desired surface texture to the paper (Smook, 1992e). Supercalendering uses friction and pressure to create a very smooth and glossy paper surface. The supercalender consists of a stack of rollers having surfaces alternating between steel and cotton in construction. There is enough pressure between the steel and cotton rollers to slightly compress the cotton surface causing a drag. The difference in surface speed on either side of the nip creates friction, which polishes the paper surface. The cockle finish on many bond writing papers is created by the vat, sizing the web, then subjecting it to high-velocity air driers under high tension, and then under low tension. The finished paper is usually heavily sized and has the characteristic rattle associated with high-quality bond paper. Embossing is achieved by running the web through an off-line press, where it is subjected to an engraved cylinder. The concept is similar to the dandy roll, but because the paper fibers cannot be redistributed, the surface of the paper is raised or depressed.

Slitting, Sheeting, and Shipping

Once the paper roll (machine log) is reeled from the paper machine, it is removed and transferred to a rereeler or a machine winder (Biermann, 1996f). A rereeler unreels the web from the mandrels to create a full log. During this process any defects can be removed and the web spliced. A machine winder is similar to the rereeler, but is able to slit the web into multiple, narrower rolls. These rolls can be further finished by supercalendering, embossing, etc., sheeted or wrapped and shipped. If the finished product is sheeted paper, the rewound rolls are transferred to machines known as cutters. The cutters can slit the web to form multiple narrower webs and cut across the web creating sheets. The paper rolls are placed onto a stand at one end of the machine. As the web unwinds, it can be slit either adjusting the web width or creating several parallel webs. After the slitters, the web travels under a revolving knife, which cuts the web into sheets. After being cut, the sheets are jogged through an online inspection system, which checks caliper and dimensions. If the sheet does

not conform, it drops down into a sheeter for recycling as broke. After the cutters, the paper stacks are placed into guillotine trimmers, where the edges receive their final trim.

After trimming, paper rolls have inner headers (circular disks) applied to the ends, wrapped with a heavy moisture-resistant paper or plastic and sealed with outer headers. The sealed rolls are then placed flat, to prevent flat spots from forming, and shipped. Sheeted paper can be prepared for shipping in various ways depending on the size of the finished product. If the finished sheets are small, such as 8 1/2 in. × 11 in., the sheets are stacked in junior cartons, cross-stacked on pallets, strapped and wrapped. Similarly, larger sheets can also be carton-packaged, strapped and wrapped. Large orders, such as those for printers, can be bulk-packed on skids (slightly different dimensions and design than a pallet), wrapped, and strapped.

2.7 CHEMICAL RECOVERY

The chemical recovery system is a complex part of a chemical pulp and paper mill and is subject to a variety of environmental regulations. Chemical recovery is a crucial component of the chemical pulping process: it recovers process chemicals from the spent cooking liquor for reuse. The chemical recovery process has important financial and environmental benefits for pulp and paper mills. Economic benefits include savings on chemical purchase costs due to regeneration rates of process chemicals approaching 98%, and energy generation from pulp residue burned in a recovery furnace.

Environmental benefits include the recycle of process chemicals and lack of resultant discharges to the environment. The kraft and sulfite pulping processes use chemical recovery systems of some form; however, the actual chemical processes at work differ markedly.

Chemical Recovery (Kraft)

Although newer technologies are always under development, the basic kraft chemical recovery process has not been fundamentally changed since its patent issue in 1884. The stepwise progression of chemical reactions has been refined; for example, black liquor gasification processes are now in use in an experimental phase.

The schematic diagram of the kraft pulping process and the corresponding chemical and energy recovery process is shown in Fig. 2.6. The primary operations of the kraft recovery process are (Vakkilainen, 2000)

- Concentration of black liquor by evaporation.
- Combustion of strong black liquor to give the recovered inorganic chemicals in the form of smelt. The smelt, sodium sulfide, and sodium carbonate, dissolved in water, give green liquor.
- Causticizing sodium carbonate to sodium hydroxide, using calcium hydroxide that is recovered as sodium carbonate.

- Recovery of by-products such as tall oil, energy, and turpentine.
- Regeneration of calcium carbonate to calcium hydroxide in a limekiln.

Evaporation is done to produce black liquor of sufficiently high concentration with minimum chemical losses. Washing separates pulp and black liquor. The resulting weak black liquor contains 12–20% organic and inorganic solids. Burning this weak black liquor would require more heat than it would produce. The black liquor must therefore undergo concentration for efficient energy recovery. The evaporation of black liquor has following main unit operations: (1) separation of water from black liquor to generate concentrated black liquor and condensate, (2) processing of condensate to segregate clean and fouled condensate fractions, and (3) separation of soap from black liquor.

To decrease black liquor viscosity, a liquor processing stage such as a liquor heat treatment (LHT) unit can also be present. The LHT ensures high dry solids even with high-viscosity liquors. The LHT process treats the liquor at elevated temperature for an extended period, when high-molecular-weight polysaccharides and lignin are broken down and viscosity is permanently reduced (Rauscher et al., 2006). Another possible component could be a black liquor oxidation stage. Possible advantages to black liquor oxidation include improvement in multiple-effect evaporators through reduced scaling on heat transfer surfaces, reduced corrosion rates of metal evaporating surfaces, possible increases in tall oil yield, reduced chemical makeup requirements for Na_2SO_4 and CaO, increases in yield from higher white liquor sulfidities in the digester, and reduced total reduced sulfur emissions. In modern high solids evaporators, the mixing of recovery boiler electrostatic precipitator ash occurs with 30–45% dry solids black liquor. Noncondensable gases from evaporation require collection for processing. When using a direct-contact evaporator stage, efficient oxidation of black liquor is necessary to suppress release of odorous gases into the flue gas stream. Evaporation of black liquor uses direct or indirect heating and flashing of black liquor. Most industrial evaporators are the multiple-effect, steam-heated-type. Vapor recompression evaporation is often a component in the first stage of evaporation of weak black liquor as a capacity booster.

The properties of black liquor vary from mills to mills depending on many factors, including mill location, digester conditions, pulp yield, wood species, white liquor properties, chemicals-to-wood ratio, and brown stock washing efficiency. In general, hardwood pulping requires less chemicals, has a higher pulp yield, and consequently, generates less black liquor solids than softwood pulping (Tran, 2007). Harwood black liquor generally contains less organics, tall oil, and soap, and has a lower heating value (~5% lower) than softwood black liquor. In Brazil, Chile, and tropical countries, eucalyptus is the dominant wood species used in kraft pulping. Because the properties of eucalyptus black liquor are similar to those of other types of hardwood black liquor, the chemical recovery process in eucalyptus kraft mills is essentially the same as others.

When processing nonwood black liquors, small mills use direct-contact evaporation. Hot flue gas from the recovery boiler heats a film or spray of black liquor. This technique can only evaporate to a maximum 65% dry solid content due to the

sharply increasing liquor viscosity at higher dry solid contents. Unoxidized black liquor releases organic sulfur compounds on contact with flue gases. Oxidation of weak black liquor can partly avoid this. Economics favors the installation of in-direct heating as unit size increases. Then, all flue gas heat generates steam and electricity.

Concentrated black liquor contains dissolved wood residues (organic) and in-organic cooking chemicals. Combustion of the organic portion of liquor produces heat. The organic compounds in black liquor serve as a fuel for the production of steam, which is used to generate electricity. The heat released as a result of black liquor combustion is recovered as high pressure/temperature superheated steam in the recovery boiler. The efficiency in converting the fuel value in kraft black liquor (13,000–15,000 kJ/kg) to steam is typically lower than for fossil fuel combustion, because of the heat used to evaporate the water entering with the black liquor, the heat of reaction consumed in producing Na_2S, and the heat carried out with the molten smelt. The amount of steam produced is typically about 3.5 kg per kilogram of black liquor solids, but can range from 2.5 to about 3.8 kg steam per kilogram of black liquor solids, depending on the thermal efficiency of the recovery boiler (Tran, 2007). The high-pressure steam is passed through a steam turbine to generate electricity. Depending on the quality of the steam and the type of the turbine, a 1000 t/day kraft pulp mill can generate 25–35 MW of electricity by burning 1500 t/day black liquor dry solids in its recovery boiler. The lower pressure steam exiting from the turbine is used in various processes in the mill.

Combustion in the recovery furnace needs careful control. High concentration of sulfur requires optimum process conditions to avoid production of sulfur dioxide and reduced sulfur gas emissions. Besides environmentally clean combustion, efficient reduction of inorganic sulfur must occur in the char bed.

The process of the recovery boiler includes several unit processes: (1) combustion of organic material in black liquor to generate steam, (2) reduction of inorganic sulfur compounds to sodium suifide, (3) production of molten inorganic flow consisting primarily of sodium carbonate and sodium suifide, (4) recovery of inorganic dust from flue gas, and (5) production of a sodium fume to capture combustion residues of released organic sulfur compounds (Bajpai, 2008; Biermann, 1996c; Reeve, 2002; Vakkilainen, 2000).

A limekiln calcines lime mud to reactive lime (CaO) by drying and subsequent heating. The calcining process can use a rotary furnace or a fluidized-bed reactor (Adams, 1992; Biermann, 1996c; Venkatesh, 1992). The main unit processes of the limekiln are the following: drying of lime mud and calcining of calcium carbonate. Some additional operations can also be present. The limekiln combusts small amounts of odorous noncondensable gases. The limekiln process produces dust that requires capture. For larger amounts of oxidized sulfur gases, flue gas scrubbers are necessary. The drying of lime mud and the calcining of calcium carbonate to calcium oxide require heat. This heat comes from burning oil or natural gas in the limekiln. The limekiln can also use other fuels such as gasified biomass.

The causticizing process converts sodium carbonate in green liquor to caustic soda. The unit operations in causticizing include dissolving molten smelt to weak

white liquor to produce green liquor, green liquor clarification or filtration, mixing green liquor and lime in a slaker to form sodium hydroxide and lime mud with subsequent completion of the causticizing reaction in reaction tanks, white liquor clarification and filtration for lime mud separation, and lime mud washing (Arpalahti et al., 2000; Biermann, 1996c).

Molten smelt from the recovery boiler contains small amounts of unreacted carbon and nonprocess elements. The small undissolved particles in green liquor require separation for disposal. Separation can use settling or filtration. Washing the dregs minimizes chemical losses.

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