Kraft Pulping

PEDER J. KLEPPE

Abstract: Present knowledge concerning the kraft pulping process is evaluated from the point of view of industrial application. Reported influences of pulping variables on delignification rate, pulp yield, and pulp properties are examined. Special emphasis is placed on methods for increasing pulp yield and the feasibility of adopting these methods by industry. Water and air pollution problems related to kraft pulping and possible solutions are discussed. Recent developments in process technology and process control are described.

Keywords: Sulfate pulping · Processing · Processes · Delignification · Yield · Carbohydrates · Kappa number · Pulps · Properties · Pollution · Reviews

THE origin of the kraft pulping process dates back to two U. S. patents granted to Eaton in 1870 and 1871 for the delignification of wood with a mixture of sodium hydroxide and sodium sulfide (*1*). The beneficial effect of adding sulfur or sulfides to the cooking liquor for the soda pulping of straw was supposedly established about 60 years earlier in England (*2*).

Industrial application of the kraft process was, however, first made possible by an important discovery by Dahl in 1879. He found that the chemical losses resulting from the recovery of cooking chemicals from soda pulping of straw could be compensated for by the addition of sodium sulfate to the combustion furnace (*3*). The sulfate was reduced to sulfide in the reduction phase of the soda recovery system. The recovery of sulfide from alkaline pulping liquor was thereby accomplished.

The new pulping and recovery method, called the sulfate process, was at once adopted for pulping of coniferous wood in Scandinavia. It was there that the "super" strength of paper made from these sulfate pulps was recognized in 1885 (*2*), and the new types of paper products were therefore called kraft papers. Kraft is the Swedish word for strength. The term "kraft" has by now become standard for identifying the sulfate pulping process, i.e., the pulping of the wood, as well as the chemical recovery process. Economical recovery of pulping chemicals in the kraft process was a necessity in order for it to compete with the sulfite process, which from the very beginning, in 1874, required no recovery system because of the cheap cooking chemicals (*4*).

Progress in the kraft process has been dominated to a very high de e by technical innovations in the unit operations of collection, evaporation, and burning of the black liquor, and of final recovery of the pulping chemicals. The greatest advance came in the 1930's by the introduction of the Tomlinson recovery furnace where final evaporation and burning of black liquor, heat recovery, and chemical recovery were incorporated in one unit. The most important developments in the kraft process during the last two decades have probably been the continuous digester, the diffusion washing of cooked chips in the digester, the continuous diffuser, the fluidized reburning of lime mud, the oxidation of black liquor, the collection of effluents, and process control of various production units. Production capacities of the various unit operations have increased tremendously, often tenfold or more, and this has become one of the most important economical factors in pulping.

The kraft process has, during the last 30 years, become the dominant pulping process. Its present status is illus-

Peder J. Kleppe is Associate Professor of Wood and Paper Science at North Carolina State University at Raleigh with the responsibility of teaching and doing research on pollution abatements in the forest products industry. He graduated in 1961 from the Technical University at Darmstadt, Germany, majoring in wood chemistry under Dr. Georg Jayme. From 1962 to 1965, Dr. Kleppe was Research Chemist at the Norwegian Pulp and Paper Research Institute, where he did applied research and development work on polysulfide pulping. In 1965 he joined Westvaco at the Charleston Research Laboratory and conducted research on industrial wood and pulp chemistry problems until he became Research Associate at North Carolina State University in 1968. Dr. Kleppe is author and co-author of a number of papers and several patents in the area of polysaccharide and pulping chemistry, and pulping technology. He is a member of TAPPI, the Technical Association of the Norwegian Pulp and Paper Industry, the Norwegian Chemical Society, and Sigma Xi.

trated in Table I, which shows the estimated production capacity of different types of pulps in North America and Scandinavia in 1969. About 78% of the chemical pulp capacity and about 55% of the total wood pulp capacity in this area are in kraft mills. About half of the kraft pulps are made into bleached or semibleached products.

The major reasons for the success of the kraft pulping process can be summarized as follows:

1. An efficient and economical recovery process has been developed for the pulping chemicals.
2. All commercially available woods can be pulped by the process.
3. The discovery of chlorine dioxide as a bleaching agent for pulps, and methods to produce it cheaply and to use it very efficiently in the bleaching of kraft pulps.
4. Kraft pulps produce paper and board products with generally superior strength properties compared to products made from other pulps.

It is astonishing to recognize how much of the important progress in the kraft process has been built on empirical approaches. However, in order to modify and optimize the various unit operations further, we need fundamental knowledge of what occurs in the process. This is particularly true for the kraft pulping operation, where approximately the same pulping conditions have been used during the last 50 years.

I will summarize the present knowledge on kraft pulping from the point of view of industrial application. However, it is impossible within the scope of this paper to refer to all the contributions made in this area. Extensive coverage of the literature on the chemistry of kraft pulping can be found in recent publications of Rydholm (5, 6) and Clayton (2).

RATE OF DELIGNIFICATION

The kinetics of kraft pulping seem very complex. No general formula has yet been published which exactly describes the rate of delignification over the whole range of practical pulping conditions. The present picture of the reaction mechanisms is that the swollen lignin in the wood chip is split into fragments at the solid–liquid interface by the hydroxyl and hydrosulfide ions present in the pulping liquor (7, 8). The fragments are dissolved as phenolate or carboxylate anions. They can undergo

condensation reactions with themselves (9), the undissolved lignin (9), and possibly also with the carbohydrates (10). The condensed lignin is more difficult to remove from the fibers (11, 12). There are strong indications that an important function of the sulfide or hydrosulfide ions in kraft pulping is to reduce condensation of lignin fragments by blocking reactive groups such as hydroxyl in benzyl alcohols (13).

The influence of the pulping temperature on the rate of delignification can be expressed quantitatively according to the Arrhenius equation:

$$\ln k = B - \frac{E}{RT}$$

where

k = reaction rate
B = constant
E = energy of activation
T = temperature, °K
R = gas constant

By arbitrarily setting the reaction rate as $k = 1$ at 100°C, a method has been developed for expressing the cooking time and the temperature as one single variable (14). The relative reaction rate corresponding to the temperature at a given time is plotted vs. the cooking time in hours. The area under the curve is characterized as the H factor (14). The activation energy, E, has been found to be about 33,000 cal/mole for the main mass (bulk) of lignin removed (12, 15). The application of the H factor is very useful both in the laboratory and in the mill to correct the cooking time so as to obtain a given lignin content if the temperature varies during the cooking period.

The delignification appears as a first order reaction with respect to lignin (11, 16) if the logarithm of residual lignin in the wood residue is plotted vs. cooking time at constant temperature or vs. the H factor. However, the delignification seems to proceed in three distinct phases, as shown in Fig. 1. Even at low temperature (<140°C), part of the lignin is removed from the wood. This early lignin removal is about 10 times as fast as would be expected on the basis of the corresponding H factor. The type of lignin removed is therefore characterized as extracted lignin (17) and corresponds to about 20% of the total lignin for pine and about 30% for birch. The

Table I. Approximate Capacity[a] (Million Short Tons per Year) of Wood Pulp in 1969 for North America and Scandinavia

| Place | Total wood pulp | Paper and board grade pulps | | Sulfite Total | Dissolving[b] grade pulps | Semi-chemical pulps | Ground-wood pulps |
| | | Kraft | | | | | |
		Total	Bleached and semibleached				
U. S. A.	44.19	28.77	12.50	2.61	1.78	4.02	4.70
Canada	20.84	7.70	5.94	3.21	0.46	0.35	8.94
Scandinavia	19.33	9.96	4.68	4.14	0.86	1.00	5.30
*U. S. A. Canada, and Scandinavia	84.36	46.43	23.12	9.96	3.10	5.37	18.94

[a] Literature source: *Pulp & Paper* Vol. 43, No. 7, 1969.   [b] About half of the dissolving grade pulps in the U. S. A. are prehydrolyzed kraft pulps (3). In Scandinavia and Canada, most of the dissolving grade pulps are sulfite pulps.

removal of the bulk of the lignin proceeds at a practicable rate only above temperatures of 150°C. The rate of the bulk delignification is dependent on the concentration of hydroxyl and hydrosulfide ions in the cooking liquor (11, 12, 15, 18).

Several equations have been published (15, 17, 19) for describing the bulk delignification rate at constant temperature, and one of the latest ones is as follows (18):

$$-\frac{dL}{dt} = k_1 \cdot L\,[OH^-] + k_2 \cdot L\,[OH^-]^a \cdot [SH^-]^b$$

where k_1, k_2, a, and b are constants and L is the concentration of lignin in wood residue.

$$-\frac{d[\ln L]}{dt} = k_1[OH^-] + k_2[OH^-]^a[SH^-]^b.$$

The use of the present equations for determining the degree of delignification or Kappa No. at given pulping conditions is complicated by changes in [OH⁻] and [SH⁻] during industrial pulping. It is also difficult to determine the exact [OH⁻], [SH⁻], and [S⁻] concentration because the equilibria between them are not known at practical pulping temperatures (18). Another complicating factor is the fact that part of the lignin, the residual lignin, is removed at a much lower rate than the bulk lignin (12). The transition point between bulk and residual delignification is known to shift to higher lignin contents when either the cooking temperature (12), the

effective alkali charge, or the sulfidity (12) of the liquor is decreased. The influence of temperature on the rate of residual delignification can be calculated from the Arrhenius equation by using an activation energy of about 21,000 cal/mole (12). The rate of lignin removed during this last stage is about the same for both kraft and soda pulping.

More basic research is needed in order to develop a general kinetic equation which can be used in process control. Today, in the industry, an empirical approach is used to control the degree of delignification. It is known that by keeping constant the active alkali charge based on wood, the H factor, and the liquid-to-wood ratio, very little variation in the lignin content of the pulp is observed in a sulfidity range of about 15–35% (20). A change in the hydrosulfide ion concentration is compensated for by a simultaneous change in the hydroxyl ion concentration. It is, however, important to keep the effective alkali charge high enough to prevent lignin precipitation at the end of the cook. In the industry, it is therefore common to keep the residual effective alkali in the range of 5–10 g as NaOH per liter. If the white liquor sulfidity is above about 35%, a constant effective alkali charge gives the best control of Kappa number (20).

It was possible for a Finnish mill (21) to obtain a total correlation of 0.98 with their observed Kappa numbers by the use of a simple empirical regression equation given below:

$$Kappa\ No. = K_0 - K_1 A + K_2 A^2 - K_3 H + K_4 AH$$

where K_0, K_1, K_2, K_3, and K_4 are constants, A is the active alkali charge (16–18% Na₂O), H is the H factor, and the Kappa number range is 26–45.

Chip size can influence the rate of delignification. The prevailing theory is that if the chip is too thick, the delignification in the center of the chip will be controlled by diffusion of hydroxyl ions to the reaction sites. The delignification will thus proceed faster at the surface than toward the center of the chip. The result will be nonuniform pulping.

It has been shown that the diffusion rates of hydroxyl ions are about the same in all directions of the wood chips under the prevailing temperature of a kraft cook (22, 23). The chip thickness is therefore the critical dimension (24). The thickness at which the chemical transport step is not influential will depend on the pulping temperature (24). The rate of diffusion is proportional to the absolute temperature (°K) The delignification rate more than doubles for every 10°C increase. The density and morphology of the wood is a factor which influences the rate of diffusion and thereby the critical chip thickness. The optimal thickness of chips is thus dependent on cooking conditions and type of wood. Mill chips are commonly 3–5 mm thick. This is usually above the thickness which eliminates the influence of the chemical transport step (15). Uniform chips and complete penetration of the chips with liquor is important for good control of pulping.
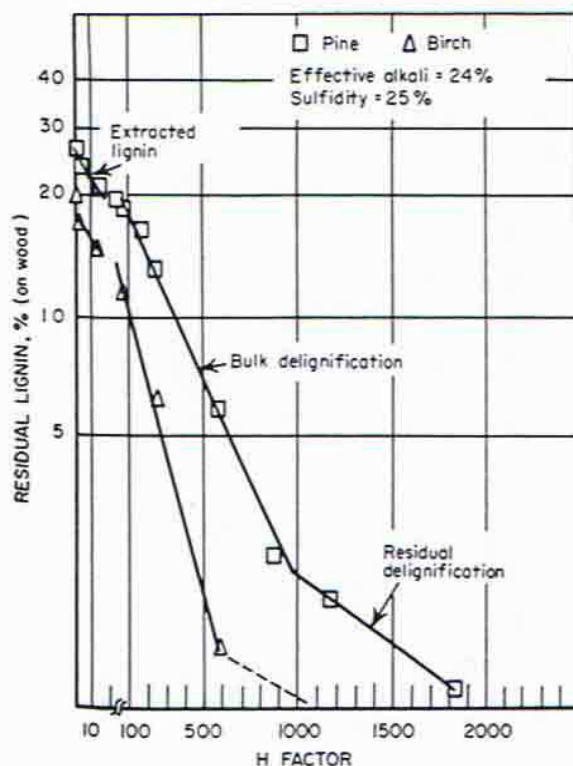

Fig. 1. Removal of lignin in kraft pulping of pine and birch as a function of the H factor (based on data from Aurell-Hartler, 26).

Another factor to consider in process control of kraft pulping is the variation in lignin content of both softwoods and hardwoods (5). Variation in the rate of bulk delignification at constant pulping conditions also occurs among wood species (25). At times this is caused by differences in the chemical structure of the lignin (25). It has been possible for some pulp mills to reduce the average standard deviation of the Kappa number to about 1–2 units (21), in spite of all the variables which influence the final lignin content of pulp. Prerequisite for this are control of the alkali charge, H factor, and liquid-to-wood ratio, and continuous correction for the observed variation in Kappa number, caused by changes in the wood quality.

PULP YIELD

The pulp yield becomes a very important economical factor as the cost of wood is a major part of the total production cost of kraft pulps. Consequently, knowledge of how process variables and changes in the raw materials influence the yield is essential for optimal return on investments. The general composition of woods and the degree to which the various wood constituents are dissolved during the kraft pulping process is fairly well known (2, 5, 6). The removal of the major wood components as a function of the degree of delignification is shown in Fig. 2 for Scotch pine (26). The hemicellulose content is reduced by approximately 40% during the extraction stage of the cook, at which stage about 20% of the lignin is dissolved. The loss is caused by dissolution of low molecular carbohydrates in alkali, removal of acid groups (acetyl, partially uronic acid), and also degradation of hemicelluloses by the so-called peeling reaction.

Carbohydrates with free carbonyl end groups are, according to accepted theory, not stable in alkali (27). About 60 monomer end groups will split off (28), mainly as isosaccharinic acids, before the molecules are
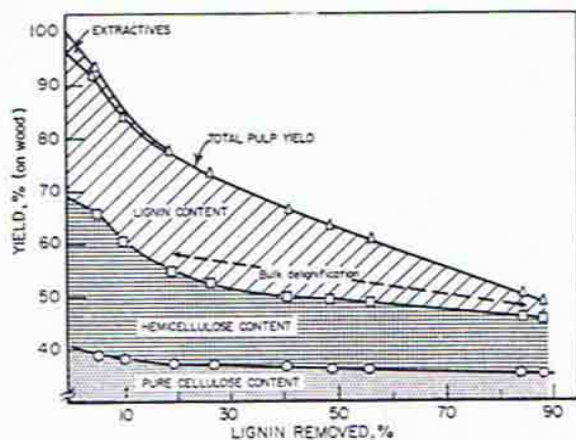

Fig. 2. Yield of the major wood components in pulping of pine at different stages of delignification (based on data from Aurell–Hartler, 26).

stabilized by formation of metasaccharinic acid end groups (27–30). The glucomannans and the hardwood xylans are especially susceptible to the peeling reaction (5). The former is the main hemicellulose component in softwoods (5) and the latter in hardwoods (5). A considerable yield loss is therefore caused by the peeling reaction. The xylans in softwoods are relatively stable in alkali, and only about 25–30% of it is removed from the wood residue during conventional kraft pulping. The reason for the relatively high alkali resistance of the softwood xylan has not been definitely established, but several theories exist (2, 5). The loss of cellulose during kraft pulping is relatively low, about 10–20%. An explanation for this is the average high degree of polymerization and the relatively low accessibility of hydroxyl ions in the crystalline region of the cellulose (5). At temperatures above about 150°C, random alkaline hydrolysis of accessible glucosidic linkages takes place (2, 5). The cleavage of these bonds result in new carbonyl end groups from where new peeling reactions are initiated (30). Additional yield loss results when the degraded carbohydrates reach a molecular size sufficiently small to make them alkali-soluble.

About 90% of the extractives in wood are removed during the extraction period of the cook. Fatty and resin acids are present as their respective sodium salts in the cooking liquor and are removed as tall oil. Volatile turpentine is recovered from vapor relief during pulping.

The acidic reaction products from the carbohydrates (5) consume a major part of the effective alkali in the pulping liquor.

The end use of the pulp determines the degree of delignification required. To meet the specifications of the majority of pulps, it is necessary to remove at least 50% of the lignin. This means that at least 50% of the hemicelluloses and 10–15% of the cellulose is removed from the wood.

In practical application, the degree of delignification is determined and controlled by the residual lignin in the pulp. There are several chemical tests for the determination of lignin (5). Determination of Kappa number is probably the best of the presently applied methods. The lignin content of the pulp can be calculated from the Kappa number by using a conversion factor of 0.15 (31, 32).

Yield vs. Kappa Number

In evaluating literature on conventional kraft pulping, it was observed that the pulp yield from softwood generally increased by 1.4% (on o.d. wood) in the Kappa No. range of 30–90 and by 1.8% in the Kappa No. range of 90–140, for every 10-unit increase in Kappa number. This is, however, only valid at constant sulfidity and constant effective alkali charge. The observed Kappa number – yield relationship has been confirmed by pulping experiments on southern pine (32). The pulp yield at a given Kappa number can therefore be predicted from the following equations if the yield constant, A, is known:

In the Kappa No. range of 30–90:

Total pulp yield (% based on o.d. wood) =
$$A + 0.14 \text{ Kappa No.}$$

In the Kappa No. range 90–140:

Total pulp yield (% based on o.d. wood) =
$$A - 3.5 + 0.18 \text{ Kappa No.}$$

The constant A can also be used for characterizing the pulp yield from a given chip source. The yield constant is mainly dependent on the quality of the wood. However, effective alkali charge, sulfidity of the cooking liquor, and chip size have a partial influence.

In hardwoods, a similar yield equation was established (32) in the Kappa No. range of 10–90:

Total pulp yield (% based on o.d. wood) =
$$A + 0.16 \text{ Kappa No.}$$

The influence of Kappa number on yield appears to be the same for hardwood as for pine in the Kappa No. range of about 90–140 (32).

Yield vs. Alkali Charge

It has been shown (26, 33) that in pulping of softwood an increase in the effective alkali charge of 1% NaOH, based on wood, will decrease the total yield about 0.15%. The small drops in total pulp yield caused by increasing the alkali charge is explained by the fact that the retention of glucomannan increases and retention of xylan decreases (26). This is not the case for hardwoods, which have very small amounts of glucomannans compared with xylans. The influence of effective alkali charge is therefore much greater. An increase by 1% NaOH (based on wood) will decrease the total yield about 0.4% (34).

Figure 3 shows the total yield for southern pine at different practical effective alkali charges as a function of
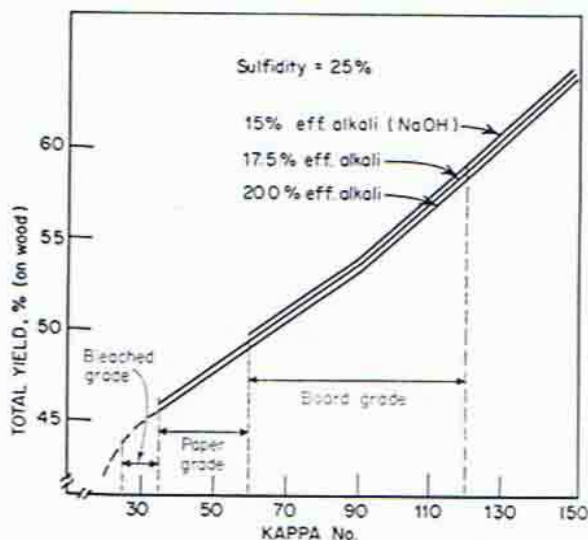
the Kappa number. The approximate Kappa number ranges for different types of industrial pulps are given. Kappa numbers below about 28 should be avoided, as indicated in Fig. 3, because the yield loss would be considerably more than 0.14% per Kappa No. unit.

Figure 4 shows total yield as a function of Kappa number within the practical range of alkali charges for mixed hardwoods from the southern United States.

Yield vs. Sulfidity

The influence of the sulfidity on pulp yield for hardwood (birch) and softwood (pine) is illustrated in Fig. 5 (35). The effect on yield is most pronounced at sulfidity values below about 15%. Increasing the latter from 15% to 40% means a yield increase of about 1% for pine and only about 0.2% for birch. The influence of sulfidity on yield seems to be somewhat higher at low effective alkali charges (33) and is obviously dependent on the type and amount of lignin in the wood.

Yield vs. Chip Size

Reduction in chip size improves the uniformity of pulping and increases the screened pulp yield at a given Kappa number (24, 36). There are also strong indications that reduction in chip size by "shredding" (36) can lead to 0.5–1% higher total yield for pine (32, 37) and 1–1.5% for oak (32) at a constant Kappa number. A substantial part of the yield increase for oak was, however, due to the fact that it was possible to reduce the effective alkali charge by 2% NaOH and still maintain the same or shorter cooking time (32).

Yield vs. Maximum Pulping Temperature

The total pulp yield from softwood (pine) is not significantly influenced by the maximum pulping tempera-

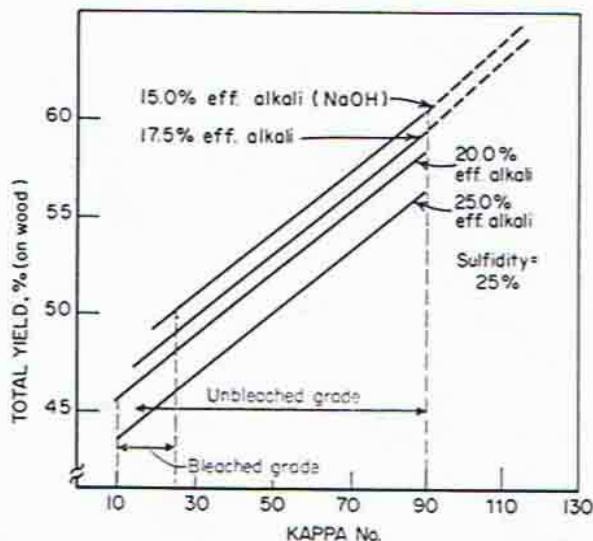Fig. 3. Total pulp yield in kraft pulping of southern pine as a function of Kappa No. (Kleppe).

Fig. 4. Total pulp yield in pulping of southern mixed hardwoods as a function of Kappa No. (Kleppe).

ture in the range of about 150–175° (*38*). This is demonstrated in Fig. 6. In the range of 175–185°C, there is a small reduction in yield which is more pronounced at lower sulfidities (*38*). At pulping temperatures above 190°C, the yield loss is substantial (*39*). Maximum pulping temperatures of about 170–175°C are most common. Higher pulping temperatures, 180°C or higher, require good impregnation and thin chips for liquid-phase cooking.

Yield vs. Wood Quality

It is obvious that the varying content of extractives, lignin, and hemicellulose in wood will influence the pulp yield considerably. Much variation in wood composition exists between, as well as within, the different species of pulp wood (*5*). The relative ratio of summerwood to springwood seems to be important for coniferous wood. It is reported that a 2–8 % higher total pulp yield is obtained (*40, 41*) from summerwood compared to that obtained from springwood.

The extractives are removed from the wood residue without interfering with the removal of the other wood components. Pulp yield should, therefore, preferably be calculated on an extractive free wood basis.

Increased Retention of Carbohydrates by Stabilization to Prevent Peeling

The peeling reactions, which are responsible for a major decrease in pulp yield, can be stopped if the reducing end groups of the molecules are transferred into alkali stable groups. This can be done in three basic ways:

1. Reduction of the end groups to primary alcohol groups.
2. Specific oxidation of the end groups to carboxylic acid groups.
3. Blocking of the end groups with agents reacting with aldehydes.

A variety of methods for stabilizing the carbohydrates in wood according to the given principles can be found in the literature (*2, 5, 42–48*). There are, however, only two publicly known methods which at present seem economically feasible for use by industry. These are the polysulfide (*49–51*) and hydrogen sulfide (*52*) methods:

Polysulfide Pulping. By impregnation of wood with polysulfide liquor, the accessible reducing carbohydrate end units are oxidized to carboxyl groups (*53*) if the hydroxyl ion concentration and temperature are high enough (*54*). The ability of a polysulfide solution to stabilize carbohydrates increases with the concentration of elementary sulfur and with the ratio of elementary sulfur to sulfide sulfur (*54, 55*).

Pulping can be carried out by impregnation of wood chips with a pure polysulfide liquor (Na_2S_4) at elevated temperature, 100–130°C (*56*), withdrawing the excess liquor for reuse, and finally performing a normal kraft cook. Polysulfide pulping can be also successfully carried out by impregnating the chips with a liquor made by dissolving elementary sulfur in white liquor. Impregnation should then be performed below about 110°C because the polysulfide solution will decompose to thiosulfate and sulfide at high temperature (*49, 57*).

When white liquor is used for making the polysulfide solution, the ratio of added sulfur to sulfide sulfur should preferably be kept below 2.5 to 1 (*58*), because of the instability of the polysulfide liquor at high pH (*57*). For obtaining a large yield increase with respect to elementary sulfur added, it is very important to keep the polysulfide concentration as high as possible in the chips. Competition apparently exists between the stabilizing reactions, the peeling reactions, and the decomposition of polysulfides.

The yield increase is generally dependent on the amount of elementary sulfur added, impregnation and pulping conditions, and wood species. Reduction in chip size, improved impregnation by steaming of the chips, and reduction in the maximum cooking temperature increases the yield effect (*51*). The yield increase is greater at higher Kappa numbers (*49, 61*). The effect of the added sulfur on pulp yield, utilizing three different cooking techniques, is shown in Fig. 7. The smallest effect of the sulfur is found when the added or consumed sulfur is dissolved in this whole cooking liquor. The maximum yield increase obtained with this cooking technique is in the range of about 2–4% sulfur. At a Kappa No. of 35 yield increases about 1.5% for every percent of elementary sulfur added in pulping of pine and spruce. The effect can be raised to about 2% if the sulfur is introduced only in that part of the white liquor which is adsorbed by the wood during proper impregnation. The rest of the cooking liquid is then added at higher temperatures (90–140°C). The greatest effect was found for spruce (*32*), by dissolving the sulfur in a pure Na_2S liquor to form Na_2S_4. After impregnation of the wood with this liquor at 110–130°C, the excess liquor was withdrawn for reuse and the delignification performed with regular white liquor. It was found that by using this method a yield increase of about 4% per percent added sulfur was obtained. This diminished to about 3 when the sulfur addition was raised from 0.5% to 1.5%. Hardwoods give lower yield increases than softwoods (*51, 59*).

Carbohydrate analyses of the polysulfide pulps have shown that the yield increases are caused to a large extent by improved retention of glucomannan for softwood (*49, 60*) and xylan for hardwood (*51, 59*), as expected. The loss of cellulose during pulping is also reduced somewhat, especially at higher yield increases (*49, 51, 59*).

The reaction of the polysulfides required an amount of effective alkali which is about equivalent to the amount of the added elementary sulfur. The consumption of effective alkali, as NaOH, increases in one-stage polysulfide cooking by approximately two-thirds of the weight of the added elementary sulfur (*58*). By increasing the effective alkali by this amount, the delignification

proceeds somewhat faster than by conventional kraft cooks, as a result of the increased sulfidity of the liquor (62). No change in cooking time occurs if the increase in effective alkali, as NaOH, is approximately one-third of the elementary sulfur added (58).

Hydrogen Sulfide–Kraft Pulping. A yield increase of about 2–3% on wood has been achieved by pretreating wet wood chips with H_2S before conventional kraft pulping (63, 64). By applying slightly alkaline conditions during the pretreatment through addition of such alkaline buffers as sodium carbonate and optimizing the time, temperature, and H_2S pressure, yield increases of about 5–6% have been reported for both softwoods and hardwoods (52). Favorable pretreatment conditions are as follows: liquor-to-wood ratio about 4:1, retention for about 40 min at a maximum temperature of about 127°C (260°F) and a total pressure of 130–140 psig (52). The excess H_2S is vented at the end of the treatment and can be reused. The chips are pulped by the conventional kraft process after the unabsorbed impregnation liquor has been withdrawn. The total H_2S consumption by the treatment is claimed to be only about 1% based on wood (52). This makes the process very attractive from the point of view of industrial application. The effective alkali consumption during the subsequent kraft pulping stage is also reduced by about 3% (as NaOH) based on wood weight (52).

The yield increase is mainly a result of stabilization of glucomannan in softwood and xylan in hardwood (52). Higher retention of cellulose is also obtained (52). The stabilization reaction appears to be a reductive thiolation of the reducing end units of the carbohydrates (65).

Sorption and Increased Retention of Xylan

A certain portion of the hemicelluloses which are removed from the wood residue during kraft pulping are still dissolved as polysaccharides in the liquid phase (66). In pulping of hardwood (birch), up to about 8% xylan, based on wood, can be present in the pulping liquor (2). The amount increases as the effective alkali charge is increased. For softwood the maximum amount of hemicellulose in the liquor is about 1.5–2% based on wood (2). The highest concentrations of hemicelluloses are found at 150–160°C or just as the cooking temperature is reached (66). As the cook proceeds further, the dissolved hemicelluloses are fragmented by alkaline hydrolysis and peeling reactions.

Part of the dissolved xylan can be readsorbed by the wood fibers if the pH (20°C) is below about 12 (67). Some of the dissolved xylans are therefore likely to be adsorbed during normal kraft pulping of hardwood (68). A 1–2% yield increase has been found in pulping of birch if the unabsorbed cooking liquor is withdrawn at maximum xylan concentration, the liquor neutralized to a pH of about 11.5, and returned at the end of the cooking period (67). A yield increase of the same magnitude has been found in pulping of birch (69), if the excess
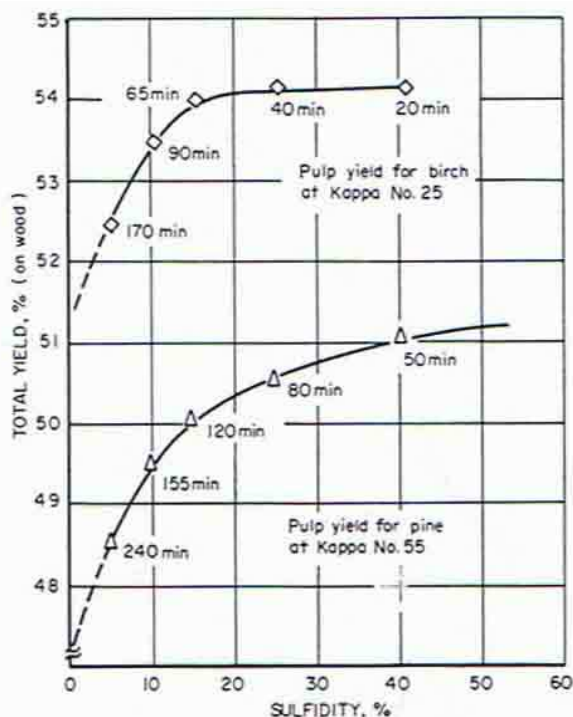
Fig. 5. The effect of sulfidity on total pulp yield in pulping of pine and birch (based on the data from Aurell, 35). (The cooking times at constant pulping temperature and effective alkali charge are indicated.)
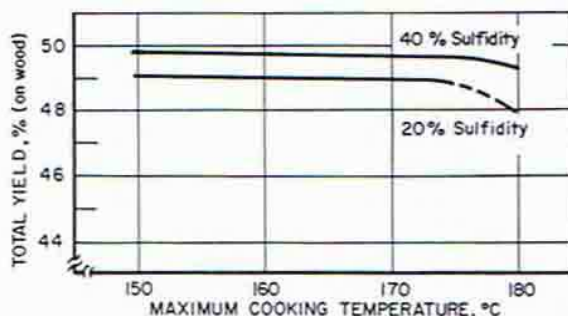
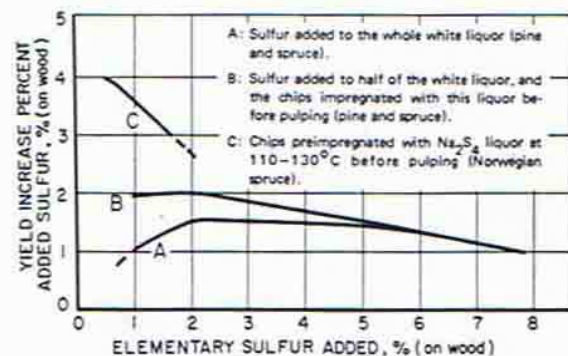Fig. 6. The influence of maximum pulping temperature on pulp yield (Hägglund, 38).

Fig. 7. Yield increase by applying different amount of elementary sulfur in polysulfide pulping of softwood according to three different cooking techniques [based on literature (50, 51, 58), and unpublished data (32)].

cooking liquor withdrawn from a previous cook at 140–160°C is added to the white liquor, and the cook finished at a low liquor-to-wood ratio. The effect is reported to be about half for softwood (pine) as compared with birch. The reason for the yield increase has not been established. It can be assumed, however, that both the dissolution and sorption of xylan is dependent on the xylan concentration in the cooking liquor. A saving of 2–4% of effective alkali as NaOH, based on wood, is claimed for this cooking technique (69).

Pulp Properties

The properties of the pulps are to a high degree dominated by the fiber morphology (70–72), the lignin content, and the carbohydrate retention. The sulfidity of the cooking liquor and the effective alkali charge are other factors which are of practical importance.

The influence of yield on the strength properties of the pulp are demonstrated for conventional kraft and polysulfide pulps in Figs. 8–10.

Increasing the lignin content of the pulp, in general, decreases its strength properties. Breaking load and bursting strength of paper made from the pulp has, however, a maximum in the yield range of 45–55%. Elongation at break is relatively unchanged in the yield range of 45–60%, but decreases at higher yields. Bulk increases with lignin content when compared at constant pulp freeness. Tearing strength decreases as the yield increases from 50% to 65%. Improving the carbohydrate retention by, for example, adding elementary sulfur to the cooking liquor, increases the bonding strength of the paper and gives higher breaking load and bursting strength (49). Tearing strength is, however, more than commensurately reduced. The beating energy required to give a desired breaking length, or burst factors, decreases with higher hemicellulose content in the pulp. Beating energy increases semilogarithmically with the lignin content of pulps.

The influence of sulfidity on strength is demonstrated in Fig. 11 for pine pulps of Kappa No. about 21–52 (38). A considerable increase in the tearing strength is obtained by increasing the sulfidity. Other strength properties such as tensile and bursting strength follow the same trend as the tearing strength (38). The improvement in strength is most pronounced at lower sulfidity, but is noticeable up to and even above 50% sulfidity (73).

Increasing the effective alkali charge gives pulps a slightly higher tearing strength, whereas the tensile and bursting strengths are somewhat reduced (73, 74), though higher beating energy is required. If the effective alkali concentration is kept at an even, relatively low level during the whole cooking period by injection of white liquor, somewhat stronger pulps are obtained (75).

Changes in maximum cooking temperatures in the range of 160–180°C do not have any practical influence on pulp strength, whereas cooking at 190°C or higher reduces strength considerably (39).

It has been demonstrated by kraft pulping of spring-

wood and summerwood from loblolly pine that the strength of individual fibers and fiber bond strength decreases continuously during the delignification (76, 77). The effect is much more pronounced for summerwood than for springwood.

Extreme damage of wood chips by longitudinal compression can make the wood structure more susceptible to hydrolytic attack during kraft pulping (78). This can result in a moderate reduction in the strength properties of the pulp (79). However, shredding of chips with modern equipment probably does not have any practical influence on strength (80, 81).

Brightness of pulps is mainly influenced by the lignin content and the effective alkali concentration or pH at the end of the cook. The brightness seems to be a minimum in the yield range of 65–75% from where it increases almost linearly with increasing or decreasing yield (5). At a given lignin content of the pulp, the brightness is directly proportional to the final pH in the cook-
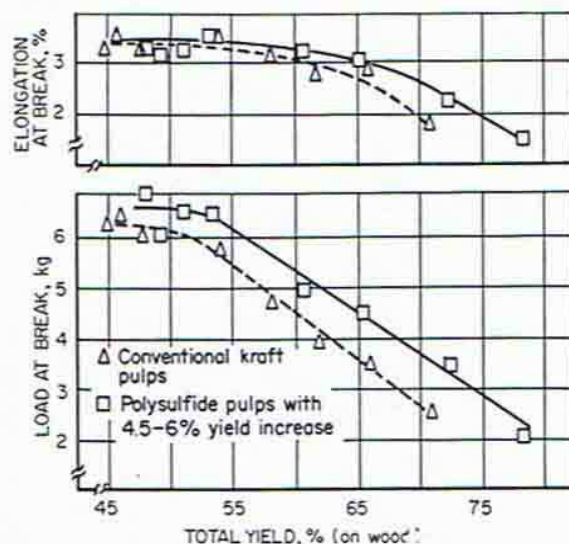

Fig. 8. Stress–strain properties of handsheets made from pine kraft pulps at 600 ml CSf, as a function of total pulp yield (Kleppe).
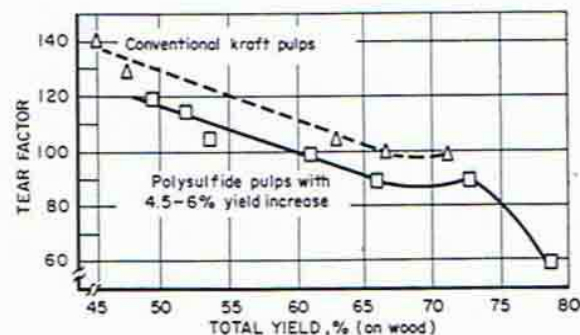

Fig. 9. Tearing strength of handsheets made from pine kraft pulps at 600 ml CSf, as a function of total pulp yield (Kleppe).

42

ing liquor within the range of about 10.5–13 pH units (82, 83). It has been demonstrated that the brightness can be increased by about 10 SCAN units by increasing the alkali charge (82). Additions of black liquor to kraft cooks reduces the brightness (83).

The color of pulps also depends to a high extent on the lignin content of the pulp (84). Effective alkali charge, sulfidity, and maximum pulping temperature have a partial influence on the color characteristics (83, 84).

The strength properties and brightness of the pulps are usually the yield-limiting factors in the production of unbleached kraft pulps utilizing today's technology. For high brightness paper and board products, the pulp should be cooked to the lignin content which gives the lowest total bleaching and pulping cost. Modern bleaching gives a more selective lignin removal than does kraft pulping (85, 86). Bleaching pulp of relatively high Kappa number (35–40) can therefore be of advantage if the price of wood is high compared with the price of the

bleaching agents. Bleaching of high Kappa number pulp should also lead to improvement in the strengths of the bleached products.

POLLUTION ASPECTS

The sources of pollution in kraft pulping are dissolved organics from various wood constituents, hydrosulfide ions in the pulping liquor, and products from the reaction between the methoxyl groups in lignin and the hydrosulfide ions. About 96–98% of the spent cooking liquor is removed from the pulp, evaporated, and burned. The prime origin of the pollution would, therefore, be the remaining spent liquor in the washed pulp, liquor spillage, and the volatile components in the spent cooking liquor such as H_2S, CH_3SH, CH_3—S—CH_3, and CH_3OH.

The degradation products of the carbohydrates as well as the wood extractives are easily biodegradable and create a water pollution problem by depletion of dissolved oxygen, if discharged into rivers or lakes. Some of the substances, such as resin acids from the extractives, are also directly toxic to aquatic life.

The degradation products from lignin are slowly biodegradable in water, but only to a limited degree. Degraded lignin will, therefore, cause only insignificant water pollution by depletion of the dissolved oxygen. However, the products from kraft lignin are strongly chromophoric in nature and will lead to a brown coloration of the water. This could cause an esthetic problem.

The noncondensible gases CH_3–SH, CH–S–CH_3, CH_3—S—S—CH_3, and H_2S are responsible for the characteristic odor in kraft pulping. The most obnoxious odor comes from methyl mercaptan and dimethyl sulfide which are formed from the methoxyl groups in lignin and hydrosulfide or mercaptide ions in the pulping liquor (87). The rate of formation of these organic sulfur components is directly proportional to the hydrosulfide ion concentration in the cooking liquor above about 150°C. Increasing the cooking temperature at a given degree of delignification would increase the amount of CH_3—S—CH_3 compared with the amount of CH_3—SH (87). The total amount of organic sulfur compounds formed would decrease slightly (87). A reduction in sulfidity and an increase in effective alkali charge, combined with high pulping temperature, reduces the amount of odor produced.

The total amount of organic sulfur compounds usually formed during pulping is very small, being only a few pounds per ton of pulp (88). However, they create an air pollution problem because they can be detected by the human nose in concentrations as low as a few parts per billion. The main portion of CH_3SH and CH_3—S—CH_3, and some H_2S, is vented with the water vapor during venting or "blowing" of the digester. Some of the organic sulfur components are also vented together with a major amount of H_2S and CH_3OH during the evaporation of the spent liquor. The loss of H_2S from the black liquor is very dependent on the pH and sulfide
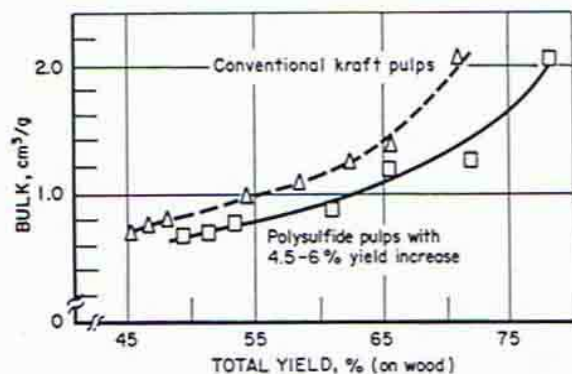

Fig. 10. Bulk of handsheets made from pine kraft pulps at 600 ml CSf, as a function of total pulp yield (Kleppe).
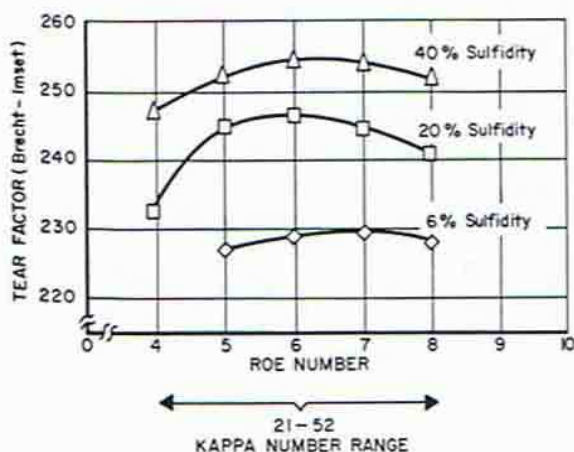

Fig. 11. The influence of sulfidity on tearing strength of hand sheets made from pine pulp of different lignin content (Häglund, 38).

concentration of the liquor. A decrease in pH of 1 unit will increase the H_2S vapor pressure by a factor of 10 (89).

The trend in prevention of air pollution by the kraft process is toward collection of the noncondensible odorous gases and burning them in the recovery unit or the lime kiln. This has been practiced in a few North American mills for several decades (90). The malodorous components in the blow gas and evaporator condensate can by removed by steam stripping and collected for burning. It is reported in the literature that most of the odor can be dealt with at a reasonable cost in this way (91). The compounds CH_3SH and H_2S can also be removed by scrubbing with an alkaline or oxidizing solution. Loss of H_2S and some organic sulfur in the recovery cycle can be considerably reduced by air (oxygen) oxidation of weak or strong black liquor. The sulfide is thereby converted to its respective oxidation products which are not volatile.

Water pollution is being increasingly abated by direct reuse of contaminated condensates for making new cooking liquor or for washing of the pulps. Purification of condensate by stream-stripping (91) or with activated carbon is also possible (92). Good housekeeping is probably the most important factor for abatement of water pollution in the pulp mill.

The waste liquor from bleaching of kraft pulps is at the present time a major source of water pollution. It contributes to more than half of the total BOD load in an integrated pulp and paper mill (93). It is also the major source of color in water discharge. Evaporation of effluents from the bleach plant and the burning of the residual organics have, until now, not been done because of high evaporation costs and the fear of interference of chloride ions in the pulping and recovery system. Proposed modifications of the bleaching process may, however, make evaporation and burning possible (94, 95).

Removal of color from kraft mill and/or from bleach plant effluents may be necessary for esthetic reasons, especiall: in areas where the water is not naturally colored. This can be done by the massive lime precipitation process (96, 97), with activated carbon treatment, or a combination of the two (96).

The hope exists that some day it will be possible to purify and recirculate most of the waste water in a kraft mill. A prerequisite for this goal is probably an economical breakthrough in the technology of removing inorganic substances.

PULPING SYSTEMS

Continuous Pulping

The introduction of the continuous digester in kraft pulping has to be characterized as the major development in pulping technology during the last 30 years. Continuous pulping with high-heat diffusion washing and cold blow have several advantages over conventional batch pulping (98, 99). For moderate to high capacity continuous production units, the installation and operational costs are lower. The steam consumption is reduced to at least two-thirds of what is used in batch processing. The brightness of continuous digester pulps is higher at comparable cooking conditions (100). Because of the cold blow, the pulps are usually found to be about 10–20% stronger than conventional batch pulps (2, 32). Higher Kappa numbers and thus higher yields can be obtained. Digester corrosion is also claimed to be reduced.

A continuous digester is more adaptable to computer process control. The H factor can be determined from a heat and material balance for the digester. Techniques are also available for monitoring the amount of dry wood and water entering the digester (101). Development is under way to obtain a continuous and rapid lignin determination of the pulp (102). Effective alkali can also be measured continuously in the various zones of the digester (103, 104). Pulping in continuous digesters makes air pollution abatement easier as the sudden blow from the batch digester can be avoided. Disadvantages with continuous pulping are as follows (99):

1. The maintenance cost is usually higher.
2. There could be increasing problems with scaling.
3. Downtime is more critical.
4. The yield of turpentine may be lower.

The success of continuous pulping is clearly demonstrated by the fact that of the pulp capacity expansion in the southern United States during the period 1962–1968, at least 87% was in 31 continuous digesters (105). The average daily capacity of these digesters is about 560 tons.

A modification of continuous pulping is countercurrent pulping (106). Hot white liquor is introduced directly above the washing zone of the digester, and flows countercurrently to the downflowing chips. The spent liquor is discharged at the top of the digester. The advantage of this type of cooking is that a high pH can be obtained at the end of the cook, thereby producing high pulp brightness. A brightness gain of about 10 SCAN units has been reported (100) with this method. A very low effective alkali concentration also can be tolerated in the spent liquor, so that the effective alkali charge can be better utilized (106). A somewhat lower pulp yield caused by lower retention of xylan (100) is, however, reported, the yield loss consequently being most pronounced for hardwoods.

A variety of different cooking techniques are possible in the development of continuous digesters, such as prolonged presteaming or hydraulic impregnation of the chips in a separate vessel, impregnation and separation of excess liquor in another vessel (Mumin), combined with vapor or liquid phase pulping in the continuous digester (100). Main advantages of using these techniques are more uniform pulping and higher brightness (100) of the pulps. Continuous digesters with a Mumin unit are also used for production of prehydrolyzed kraft pulps (6) and can be advantageously used in polysulfide pulping (6).

Rapid Vapor Phase Pulping (107, 108)

The chips are presteamed for removal of air and dropped into an impregnation vessel, where they remain for about 20 min. All white liquor needed is charged to the impregnation vessel, and the temperature is kept at about 150°C. The chips are then separated from the unabsorbed cooking liquor and passed through a second vessel where the temperature is kept at about 185°C by direct steam heating. A retention of about 15 min is sufficient to produce bleachable pulps. The impregnation liquor is heated indirectly, and excess water is flashed off.

The main advantages of this cooking technique over conventional continuous pulping are shorter retention times and better utilization of charged alkali. Somewhat higher retention of xylan can also be expected. The effective alkali charge can be reduced because of the high pulping temperature, low liquid-to-wood ratio, and probably a higher xylan retention, but control of pulping may be a problem.

Alkafide Process (108, 109)

This process applies rapid vapor phase pulping using a pulping liquor originally containing pure Na_2S. The effective alkali charge can thereby be reduced by approximately 20%. The pulp strength is also somewhat higher than that obtained by pulping with conventional kraft liquors of about 30% sulfidity. Another advantage of the process is that the green liquor need not be causticized (109). However, the recovery of the Na_2S and corrosion in the different process steps could give serious problems. The amount of odorous organic sulfur compounds is bound to be higher than by the conventional kraft process as a result of the high concentration of hydrosulfide ions in the pulping liquor.

Polysulfide Pulping

Moderate yield increases of about 2–4% can be realized by the consumption of about 0.5–2% of elementary sulfur. The highest yield effect of the sulfur is found by complete impregnation of the chips with a Na_2S_4-liquor at 110–130°C, withdrawing the excess liquor for reuse, and performing a conventional kraft cook after rapid heating to maximum temperature. This is especially the case when only 0.5 to 1% elementary sulfur is added. Practical application of the above pulping technique can only be realized in a modified continuous digester.

Pulping in batch digesters can give 3–3.5% yield increase for 2% elementary sulfur added, if the appropriate cooking technique is used. This has been demonstrated in industrial pulping in Norway (110). All the yield increases here referred to are for bleachable grades and are based on wood.

The proposed methods for converting the hydrosulfide in the spent liquor to polysulfides are economically questionable (111). Therefore, the amount of sulfur which can be added is only the sulfur lost in the process. The loss of sulfur is to a high degree dependent on the sulfidity ($[S]/2[Na]$) of the cooking liquor (112) and the efficiency of the recovery. Usually the sulfur loss varies between 1 and 2% calculated as elementary sulfur based on wood. This amount of sulfur can give an appreciable economic gain if applied at maximum efficiency (110). The influence of a moderate yield increase on the strength properties of the products made from the pulp is too small to be of practical importance (110). Industrial polysulfide pulps require, as expected, less beating energy (110).

A polysulfide liquor of sufficiently high concentration (about 4 g of sulfur per liter) (113) will passivate the digester at the very moment the liquor is charged (114). Corrosion of the digester can thus be prevented or considerably reduced (113, 114).

Polysulfide pulping will generally generate more air-polluting substances than conventional cooking at lower sulfidity. However, if the elementary sulfur added is kept below about 2%, based on wood, and enough effective alkali charged to give an unchanged final pH, the cooking time can be reduced. The reduction in time will compensate for the higher sulfidity. The amount of odorous organic sulfur compounds would therefore be about the same as for the conventional kraft process.

Hydrogen Sulfide – Kraft Pulping (52)

By stabilizing the carbohydrates in wood with hydrogen sulfide at relatively high pressure and temperature under slightly alkaline conditions, about 6% higher pulp yield (based on wood) can be obtained in the subsequent conventional kraft cook. This method is very attractive as only about 1% sulfur (based on wood) is consumed. The strength properties of the pulps are comparable to polysulfide pulp at the same yield increase. Reduced tearing strength may be a problem for certain paper or board products. Recovery of the added H_2S should not be necessary, as at least 1% sulfur (based on wood) is usually lost in the present kraft process. Hydrogen sulfide can probably also be stripped economically from black or green liquor. The H_2S process should preferably be applied in a continuous closed system. The use of batch digesters could be hazardous due to the risk of H_2S poisoning and explosion. Corrosion is another factor which can limit the use of batch digester.

FUTURE TRENDS AND RESEARCH NEEDS

Present indications are that the kraft process will be the dominating pulping process for at least the next 20 years. The most important goal for the industry will be to keep the environment surrounding the mills free of water and air pollutants.

The development in process technology is clearly in the direction of more continuous processes with better control, higher efficiency and yields, and also more "closed" systems (115). This will make pollution abatement both easier and cheaper.

Making the kraft mills odorless will probably be the most difficult goal to meet. Collection and burning of

the odorous sulfur compounds is economically feasible, but small and accidental leaks will likely make a kraft mill always detectable. The possibility of destroying the odorous compounds in the digester before blowing should be investigated.

Alkaline pulping without sulfur is another possibility if nonpollutant additives which promote delignification or increase pulp yield by carbohydrate stabilization can be found. The low yield and poor strength properties of soda pulp compared with kraft pulp are the reasons why today's production of soda pulp is almost insignificant. If these obstacles can be removed economically, non-sulfurous alkali pulping could be adopted by the industry in a short period of time. This is because the existing expensive recovery systems can be used without modifications.

The possibility exists that effluent from a bleach plant can be practically eliminated if the chlorination stage and first alkali extraction stage can be replaced by an oxygen/alkali stage (95) and the effluent from this stage evaporated and burned economically. High-yield soda pulping combined with lignin removal by oxygen/alkali bleaching is a worthwhile research project.

Neutral sulfite semichemical pulping combined with kraft pulping can be used for removing most of the SO₂ from the kraft recovery furnace by absorbing the SO₂ in the NSSC liquor (112). High-yield NSSC pulps from softwood (pine) can probably be used as a cheap mixing component with kraft pulps for production of liner board. The trend toward higher lignin content and thereby higher yield for unbleached pulp grades will continue as the technique of fiberizing, beating, and pulping control improves.

Carbohydrate stabilization with polysulfide and H$_2$S is expected to be adopted by the industry. This is especially true in mills where the wood is relatively expensive and the "know-how" is available.

LITERATURE CITED

1. Eaton, A. K., U. S. pats. 106,143 (1870), 119,224 (1871).
2. Clayton, D. W., in "The Pulping of Wood," Joint Textbook Committee of the Paper Ind., McGraw-Hill, 1969.
3. Dahl, C. F., U. S. pat. 296,935 (1884).
4. Stockman, L., IUPAC-EUCEPA Symposium on Reco very of Pulping Chemicals, 1968, Helsinki, Finland.
5. Rydholm, S. A., "Pulping Processes," Interscience Publishers, 1955.
6. Rydholm, S. A., Pulp Paper Mag. Can. 68 (1): T2 (1967).
7. Enkvist, T., Holm, B., Kourula, A., and Martelin, J. E., Paperi Puu 39: 297 (1957).
8. Gierer, J., Lenz, B., and Wallin, N. H., Acta Chem. Scand. 18 (6): 1469 (1964).
9. Marton, J., in "Lignins, Chemistry and Utilization," (Sarkanen, K. W. and Ludwig, Eds.), to be published by J. Wiley and Sons, New York.
10. Kleinert, T. N., Tappi 49 (3): 126 (1966).
11. Kulkarni, G. R. and Nolan, W. J., Paper Ind. 37 (2): 142 (1955).
12. Kleinert, T. N., Tappi 49 (2): 53 (1969).
13. Hägglund, E., Tappi 32 (6): 241 (1949).
14. Vroom, K. E., Pulp Paper Mag. Can. 58 (3): 228 (1957).
15. Wilder, H. D. and Daleski, E. J., Tappi 47 (5): 270 (1963).
16. Larocque, G. L. and Haas, O., Can. J. Res. 19: 1 (1941).
17. Stillman, R. E., presented at the 21st TAPPI Alkaline Conference, Mobile, Ala., 1967.
18. Teder, A., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
19. Caroll, C. W., Tappi 43 (6): 573 (1960).
20. Dickersheid, J. L., Tappi 41 (9): 526 (1958).
21. Rahkonen, V., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
22. Lusby, G. R. and Maas, O., Can. J. Res. 10-B: 180 (1934).
23. Hartler, N. and Onisko, W., Svensk Papperstid. 65 (22): 905 (1962).
24. Hartler, N., Paperi Puu 44 (7): 365.
25. Sarkanen, K. V. and Chang, H.-M., presented at TAPPI 22nd Alkaline Pulping Conference, 1968, San Francisco, Calif.
26. Aurell, R. and Hartler, N., Svensk Papperstid. 68 (3): 59; (4): 97 (1965).
27. Meller, A., Holzforschung 14 (3): 78; (5): 129 (1965).
28. Franzon, O. and Samuelson, O., Svensk Papperstid. 60 (23): 872 (1957).
29. Whistler, R. L. and Be Miller, J. N., in "Advances in Carbohydrate Chemistry", New York, Academic Press Inc., 1959.
30. Mutton, D. B., Pulp Paper Mag. Can. 65 (2): T44 (1964).
31. Tasman, J. E. and Berzins, V., Tappi 40 (9): 699 (1957).
32. Kleppe, P. J., unpublished work.
33. Legg, G. W. and Hart, J. C., Pulp Paper Mag. Can. 61 (5): 299 (1960).
34. Aurell, R., Svensk Papperstid. 67: 89 (1964).
35. Aurell, R., Svensk Papperstid. 66: 978 (1963).
36. Nolan, W. J., Tappi 40 (3): 170 (1957).
37. Vethe, A., Norsk Skogind. 21 (5): 180 (1967).
38. Hägglund, E., Svensk Papperstid. 48: 195 (1945).
39. Stockman, L. and Sundkvist, E., Svensk Papperstid. 61: 746 (1958).
40. Watson, A. J. and Dadswell, H. E., Appita 15 (6): 116 (1962).
41. Gladstone, W. T., personal communication.
42. Meller, A., Tappi 36 (8): 366 (1963).
43. Hartler, N., Svensk Papperstid. 62 (13): 467 (1959).
44. Samuelson, O. and Hartler, N., Svensk Kem. Tidskr. 62 (10): 197 (1950).
45. Reeves, R. E., Schwartz, W. M., and Giddens, J. E., J. Am. Chem. Soc. 68 (7): 1383 (1946).
46. Jayme, G. and Worner, G., Papier 6: 80, 220, 381 (1952).
47. Clayton, D. W. and Marraccini, L. M., Svensk Papperstid. 69 (9): 311 (1966).
48. Procter, A. R. and Apelt, A. M., Tappi 52 (8): 1518 (1969).
49. Kleppe, P. J. and Kringstad, K., Norsk Skogind. 17 (11): 428 (1963).
50. Venemark, E., Svensk Papperstid. 67 (5): 157 (1964).
51. Sanyer, N. and Laundrie, J. F., Tappi 47 (10): 640 (1964).
52. Vinje, M. G. and Wörster, H. E., Tappi 52 (7): 1341 (1969).
53. Alfredsson, B., Samuelson, O., and Sandstig, B., Svensk Papperstid. 66: 703 (1963).
54. Teder, A., Svensk Papperstid. 71: 149 (1968).
55. Teder, A., Svensk Papperstid. 72 (9): 294 (1969).
56. Taga, G., Nishi, T., and Miyao, S., J. Japan. TAPPI 18 (1): (1964).
57. Gustafson, L. and Teder, A., Svensk Papperstid. 72: 249 (1969).
58. Landmark, P., Kleppe, P. J. and Johnsen, K., Tappi 48 (5): 56A (1965).
59. Kleppe, P. J. and Kringstad, K., Norsk Skogind. 18 (1): 113 (1964).
60. Virkola, N. E., First Nordic Sulfate Colloquium, 1961, Stockholm, Sweden.
61. Janson, J., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
62. Ahlgren, P. and Teder, A., Svensk Papperstid. 70: 135 (1967).
63. Day, G. P. and Haas, B. D., Swedish pat. 167,779 (1959).
64. Hartler, N., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
65. Procter, A. R. and Viekenkamp, R. H., J. Polymer Sci. C, in press.
66. Simmonson, R., Svensk Papperstid. 68 (8): 275 (1965); 67 (18): 721 (1964); 66 (20): 839 (1963).
67. Aurell, R., Tappi 48 (2): 80 (1965).
68. Clayton, D. W. and Stone, J. E., Pulp Paper Mag. Can. 64 (11): T459 (1963).
69. Dillen, S., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
70. Barefoot, A. C., Hitchings, R. G., and Ellwood, E. L., Tapp 49 (4): 137 (1966).
71. Wangaard, F. F., Kellogg, R. M., and Brinkley, A. W., Jr., Tappi 49 (6): 263 (1966).
72. Tamolang, F. N., Wangaard, F. F., and Kellogg, R. M., Tapp 50 (2): 68 (1967).
73. Hart, J. S. and Strapp, R. K., Pulp Paper Mag. Can. 49 (3): 151 (1948).
74. Curran, C. E. and Bray, M. W., Ind. Eng. Chem. 22: 830 (1930).
75. Wells, S. D., Martin, G. E., and Moltzan, D. R., Tech. Assoc. Papers 27: 167 (1944).
76. Ahlm, C. E. and Leopold, B. E., Tappi 46 (2): 102 (1963).
77. McIntosh, D. C., Tappi 45 (5): 273 (1963).
78. Lagergren, S. Et., Svensk Papperstid. 60: 632, 664 (1957).

79. Cowan, W. F., *Tappi* 42 (2): 152 (1959).
80. Nolan, W. J., *Tappi* 51 (9): 378 (1968).
81. Scott, J. B., *Norsk Skogind.* 20 (9): 320 (1966).
82. Hartler, N., *Tappi* 50 (3): 156 (1967).
83. Norrstrom, H., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
84. Palinius, I., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
85. Valur, C., *Svensk Papperstid.* 54: 613 (1951).
86. Virkola, W. and Vartiainen, V., *Tappi* 47 (12): 765 (1964).
87. McKean, W. T., Hrutfiord, B. F., and Sarkanen, K. V., *Tappi* 48 (12): 699 (1965); 51 (12): 546 (1968).
88. Andersson, K. and Bergström, P., *Svensk Papperstid.* 72 (11): 375 (1969).
89. Shih, T. C., Hrutfiord, B. F., Sarkanen, K. V., and Johanson, L. N., *Tappi* 50 (12): 630 (1967).
90. DeHaas, G. G. and Hansen, G. A., *Tappi* 38 (12): 732 (1955).
91. Lindberg, S., *Pulp Paper Mag. Can.* 69 (7): T178 (1968).
92. Hansen, S. P. and Burgess, F. J., *Tappi* 51 (6): 241 (1968).
93. Rogers, C. N. and Kleppe, P. J., unpublished data from a Water Survey of the Southern Pulp Paper Board Industry.
94. Rapson, W. H., IUPAC-EUCEPA Symposium on Recovery of Pulping Chemicals, 1968, Helsinki, Finland.
95. Perotte, P., Myburgh, H. H., and Robert, A., *Pulp Paper Intern.* 11 (7): 29 (1966).
96. Smith, D. R. and Berger, H. F., *Tappi* 51 (10):37A (1968).
97. Davis, C. L., Jr., *Tappi* 52 (11): 2132 (1969).
98. Roberts, D., *Chemical Can.* 16 (5): 17 (1964).
99. Johnson, R., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
100. Annergren, G., Backlund, A., and Häglund, A., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
101. Brunton, D. C., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.
102. Henriksen, A. and Kessler, R. B., Paper presented at 23rd Alkaline Pulping Conference, Jacksonville, Fla.
103. Landmark, P., Paper presented at 20th Tappi Alkaline Pulping Conference, Richmond, Va., 1968.
104. Quesinberry, G. D., *Tappi* 51 (10): 40A (1968).
105. Kleppe, P. J., *Forest Prod. J.*, to be published.
106. Sloman, A. R., *Appita* 14 (2): 57 (1960).
107. Kleinert, T. N., *Pulp Paper Mag. Can.* 65 (7): T275 (1964).
108. Munk, L., Todorski, Z., Bryce, J. R. G., and Tomlinson II, G. H., *Pulp Paper Mag. Can.* 65 (10): T411 (1964).
109. Tomlinson II, G. H., Can. pats. 721,960 (1965), 725,072 (1966).
110. Hilmo, P. and Johnsen, K., *Pulp Paper Intern.* 11 (2): 39 (1969).
111. Sanyer, N., *Tappi* 51 (8): 48A (1968).
112. Bränland, R., IUPAC-EUCEPA, Symposium on Recovery of Pulping Chemicals, 1968, Helsinki, Finland.
113. Usitalo, E., *Paperi Puu* 40: 393, 443 (1958).
114. Landmark, P., personal communication.
115. Richter, J., Second Nordic Sulfate Colloquium, 1967, Stockholm, Sweden.