STRENGTH AND DRAINAGE PROPERTIES OF LINERBOARD FROM HIGH-YIELD PULPS

PART I. LITERATURE SURVEY

Project 3133

Report One

A Progress Report to

FOURDRINIER KRAFT BOARD INSTITUTE, INC.

November 30, 1972
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The literature references as a whole speak forcefully of the need to conserve raw material by increasing pulp yield at every level of utilization. They also point out the limitations of both the raw material (wood) and the pulping process (kraft). It is in the already high-yield area of wood utilization that the limitations intrude most forcefully. An already high lignin/carbohydrate ratio will be further dislocated by increasing yield since it is in the early part of every cook that the polysaccharides are removed to a greater extent than is lignin. When lignin content reaches a certain level it shields the cellulose from the bond-developing action provided by mechanical refining and quality suffers. The major thrust in research seems to be in the direction of methods for stabilizing the polysaccharide fraction of wood against alkaline degradation long enough to permit relatively greater selectivity of lignin removal. Some of the methods have been known for many years but commercial utilization has lagged because of cost limitations. The concept itself is sound and new research investment would seem best directed toward developing means of making presently known methods more economical and an accelerated search for new means of attaining old goals.

The paucity of references to pulping unbarked wood would seem to indicate that this could be an area ripe for investigation. Although "bark" is a general term, bark itself is made up of several quite different components and it is well known that the bark of trees of the same species can vary in appearance and composition in a marked manner depending on the age of the individual specimen. Even
the season of the year can make a great deal of difference in any general set of statements defining "bark." It could well be that a significant fraction of this waste material could ultimately find utilization in certain grades of linerboard.
INTRODUCTION

The Institute has proposed the establishment of a project to investigate the strength and drainage properties of linerboard from high-yield pulps. The phase of the work having to do with a literature survey of the field was authorized in a letter from Gross to McKee, dated Sept. 29, 1972. Preparation of the survey is covered by Project 3133.

"High yield" is a relative term and its interpretation depends on one's understanding of what constitutes "normal yield." In the field of linerboard manufacture, the move toward the use of higher lignin content wood pulp has been a gradual one, covering many years. As a result, an author publishing in the early years of the past decade could justifiably term a pulp "high yield" which today would not necessarily bear that title. The 1950 edition of the series "Pulp and Paper Manufacture," (1) says that "the coarsest product being made by alkaline pulping is a softened, partially delignified product which has to be further milled or treated in a refiner to reduce it to pulp. This is used in the manufacture of board liner, corrugating medium, and fiber insulation." However, it is doubtful if much or any of the "60% yield from softwood" pulps further cited by the author actually found its way into kraft linerboard at that time. Today it not only occurs but it is common practice to use pulps in the 60% yield range for linerboard. In this discussion, particular attention is paid to the actual yield levels cited to keep all of the references in the same framework.

To make the survey more readable and easier to scan for particular references, it is presented in sections. The various headings are meant to be self-explanatory.
GENERAL DISCUSSION OF HIGH-YIELD PULPING

The October, 1972 issue of *Tappi* magazine contains a review article on high-yield chemical pulping by McGovern (2). Only a part of it deals with the kraft process but it provides a current source of references against which this bibliography could be checked. Dr. W. Jensen (3) has pointed out, in a review article published in Europe, that the kraft process has maintained a steady increase in the number of new plants and in the productivity of existing installations over the past decade. He called attention to continuing efforts to increase pulp yields in the face of the knowledge that the process itself is notorious for its indiscriminate attack on plant constituents. He made reference to the various means available for stabilizing cellulose end groups to enhance resistance to hydrolytic attack, and predicted further advances in commercial application of those processes which have not as yet gone beyond the experimental stage. He cited changes in economic considerations which would bring this about. Sjostrom's (4) findings are much the same as those of Jensen, i.e., methods for producing high-yield pulps will be sought with increasing vigor as economic factors make it mandatory to conserve a shrinking source of raw material. Marshall (5) predicted that an increasing shortage of wood will require a more efficient utilization and noted the availability of such technically feasible methods as stabilization of polysaccharide end groups and redeposition of hemicellulose. Hartler (6) provides a good coverage of the options available for increasing yield in sulfate pulping.

Farkas (7) called increasing pulp yields one of the most important problems of the pulp and paper industry and acknowledges that weaknesses inherent in the kraft process seriously impede progress toward the solution. He drew
attention to the fact that a large fraction of wood polysaccharides are soluble in strong alkali at temperatures well below those necessary for solubilizing lignin. As a result, high-yield kraft pulps usually have abnormally high lignin contents. He suggests that the use of small, uniform chips, combined with deaeration and preimpregnation would prove helpful in high-yield pulping.
It is usually acknowledged that simple adjustment of such process variables as time, temperature, chemical dosage, etc., has limited utility in efforts to improve pulp yield without sacrificing quality. However, a general understanding of the contribution of the various parameters to the efficiency of the pulping process could lead to adjustments in cooking conditions to find those best suited for high-yield pulping. As noted earlier, Farkas (7) thought attention to quick, early penetration of cooking liquor into the wood chips would be advantageous. He explored this thesis in the laboratory (8) and made commercial scale runs based on his findings. He preimpregnated softwood chips, preferably with black liquor, to produce kraft pulps with improved yield at savings in chemicals and without sacrificing quality. He also made detailed studies (9) of the efficiency of alkali utilization by isolating the effects of total alkali, liquor-to-wood ratio (alkali concentration) and sulfidity with special attention to maximum yield at a given level of pulp quality. He concluded that a low initial concentration of alkali (high liquor ratio) was important to achieve this end. He also found that pulping efficiency increased with increasing sulfidity rapidly up to 15% and more slowly from there to 40%, at which point the trend was reversed. In later work (10) he devised an equation which expressed the relationship between yield and various combinations of alkali dosage and liquor ratio. Luzina (11), using pinewood as a raw material, also produced an empirical equation from his data on kraft pulping in the yield range of 49-60%. Nepenin and Pazuhkina (12) studied the effects of liquor concentration and sulfidity and concluded that, at a given level of active alkali, increasing the sulfidity shortened the cook and permitted better carbohydrate preservation.
Chomin (13) cooked pinewood using a constant sulfidity and varying time and maximum temperature to produce kraft pulps in the yield range of 50-58%. He found that variations in maximum temperature did not affect quality at a given yield level until the temperature reached 170°C. Above that point, the mechanical strength was reduced. Calorific value of the black liquor did not vary appreciably between 50 and 58% yield. Malakhova, et al. (14) made high-yield digestions of pinewood and two hardwood species simulating both batch and continuous kraft cooking. They found that the quick rise to maximum temperature of the continuous system was more conducive to preservation of the wood polysaccharides than was the case in conventional cooking. Hardwoods, in spite of their lower lignin content, used up more chemical than softwoods. When a mixture of softwoods and hardwoods was pulped, the lignin content of the softwood fraction was higher than it was when softwoods alone were cooked under identical conditions. Bristow, et al. (15) published results of a transition from batch to continuous kraft pulping of pinewood to high-yield levels which verified the observations of Malakhova, et al. (14). That is, the quick, uniform rise to maximum temperature achieved in a continuous digester made yields in the 60% range feasible where the maximum achieved with batch pulping was 55%. The authors developed a quick (5 min.) Kappa number test to monitor the product.

Crane and Rothrock (16) considered that the amount of increased yield, chip shredding, and hardwood addition were variables which could be expected to influence the quality of high-yield pulp. Their investigation indicated that a 15-20% decrease in tensile and bursting strength occurred when the yield of softwood kraft was raised from 47 to 54%. Shredding the chips reduced cooking time and rejects but changes in pulp quality were minor. At the 54% yield level a 10/90 hardwood/softwood mixture improved tensile and tear at the expense of a
small drop in Mullen as compared with a 100% softwood cook. Hardwood additions of up to 30% were investigated. Hatton (17) studied the differences in lignin content of accepts and rejects in the high-yield kraft pulping of western hemlock over the screened pulp Kappa number range of 45-95. A rapid method was devised for determining maximum pulp yield and Kappa number of pulps with zero rejects. Poppel, et al. (18-19) measured total energy consumption (thermal and mechanical) for high-yield pulps. They reported no marked changes in the 60-65% yield range and advised that within this range cooking conditions can be adjusted to give the best pulp quality.
STABILIZATION OF WOOD POLYSACCHARIDES

Jensen (3) and others previously cited called attention to the improvement in alkaline pulping yields possible when wood polysaccharides are stabilized to resist the so-called "peeling reaction" usually involved. The literature of the past decade contains several review articles covering the advances in this area. Worster (20) performed the service in 1965 and Teder (21) in 1969 found 88 references on the polysulfide process alone. Jensen (3), while mentioning borohydride and polysulfide as proven oxidants of the polysaccharide end groups, gave special emphasis to a more recent suggestion—a gaseous pretreatment with hydrogen sulfide. This is the subject of an article by Vinje and Worster (22) and a Canadian patent issued to Vinje and Thomson (23). The claims of Vinje are very attractive. In one instance cited by him, softwood pulped to the same lignin content (ca. 18%) had 70.4% yield with pretreatment and 55.2% without. This would indicate a very favorable 16+/13+ ratio of carbohydrate/lignin removal due to $H_2S$ treatment as compared with 29+/15+ without. In addition, the alkaline pulping could be modified in the direction of milder conditions or shorter times because of the claimed reduction in resistance to delignification provided by the pretreatment. Sodium borohydride has been shown to be an effective agent for stabilizing polysaccharide end groups and, as such, has been studied quite extensively. Hartler (24) obtained a Canadian patent on its use in pulping and Gugnin (25) describes the effects of changing the process variables involved in kraft pulping in the presence of borohydride. It has not, however, proven to be economically feasible to capitalize on this knowledge because of the cost factor. Venemark (26) calls the use of borohydride, dithionite, and hydrazine only of academic interest because of production costs. A patent for the use of hydroxylamine was issued to Paterson (27). He claimed improvement in pulp yield and viscosity, but made no representations concerning yields in excess of 55%.
Interest in polysulfide kraft pulping has been active since the work of Berthier with maritime pine was published in 1953. Scopp obtained an early patent on the process but the main deterrent to its commercial application has been the problem of chemical recovery. Landmark, et al. (28) spoke to this point and showed that practical means existed for circumventing it. Landmark and Kлепpe (29) patented a process for producing a 60% yield pulp with a polysulfide liquor and Kлепpe and Vethe (30) described the properties of high-yield polysulfide kraft pulps, although Sanyer (31) called attention to the lack of an effective recovery system. At least two references, Hilmo and Johnsen (32) and Kinzner (33) report commercial applications of the process. Neither, however, indicate the production of pulps in the 60-70% yield range. Because the simple addition of polysulfide sulfur to a cooking liquor was found to be susceptible to reduction of the polysulfide sulfur to the monosulfide and thiosulfate at relatively low temperatures, variations in the process have been suggested. Work in Japan resulted in a two-stage cooking procedure suggested by Taga, et al. (34). Miyao, et al. (35) further found Na$_2$S$_4$ to be the most useful of the polysulfides in this application. Nakano, et al. (36) combined the polysulfide pretreatment with a short cycle cook in the vapor phase (only about 15 min. at maximum temperature). Clayton and Sakai (37, 38) discussed the process further and were allowed a Canadian patent on it (39).

Barker (40) sought a method by which the advantages of polysulfide pulping could be realized without affecting the normal kraft recovery cycle and soda sulfur balance. His patent (41) calls for the use of manganese dioxide to oxidize the existing sulfides to polysulfides. Recovery of the precipitated MnO is a relatively simple matter. He pointed out that small additions of polysulfide sulfur to kraft white liquor result in only small increases in yield, while large
increases in S adversely affect the mills sulfur balance. Morud and Rolland (42) suggest using Ca polysulfide or ammonium polysulfide. The latter alternative is the subject of a patent by Borregaard (43). The use of NH₄Sn was considered preferable because it would not increase the ash content of the pulp or contaminate the black liquor with calcium. The authors (42) also mention generation of polysulfides in kraft cooking liquor by treatment with cupric oxide. The reaction between the sulfide and the CuO forms cuprous oxide (Cu₂O) which is insoluble and, therefore, easily removed.

Aurell and Hartler (44) published results of experiments which led to the establishment of empirical parameters useful in predicting the Kappa number of a pulp made with a given polysulfide kraft cooking schedule.
MISCELLANEOUS SUGGESTIONS FOR YIELD ENHANCEMENT

Several suggestions for the use of additives or manipulation of pulping methods to enhance pulp yield have emerged during the past decade. Swakon (45) obtained a patent calling for the addition of carbonyl sulfide (and optionally Na₂S) to aqueous solutions of NaOH. His patent disclosures do not permit a judgment of the degree to which his claims of yield improvement are involved with simple undercooking because of a tie-up of available chemical. Tirado, et al. (46) have patented their suggestion that condensable gases from a kraft cook, circulated back into the cooking liquor tend to raise both yield and pulp quality. Their claim that solutions of sodium sulfate (possible misspelling of sodium sulfite?) or sodium carbonate can be substituted for kraft or soda liquor are not supported by data. Dillen and Noreus (47) developed a cooking schedule in which all free kraft cooking liquor is drained from one batch digester while the dissolved hemicelluloses are still relatively undegraded and introduced to another batch of chips in lieu of black liquor or water. Yield increases are said to be modest unless polysulfides or borohydride are also added. A patent (48) was granted on such a process in 1965. Borisek, et al. (49) reported an increase in yield in a bleachable, viscose grade kraft pulp simply by impregnating chips with black liquor at 50-120°C. for 0.5 to 2 hr. and exchanging the black liquor for a white liquor containing quite high levels of Na₂CO₃. Temperatures and times of pulping were normal.

Ritman (50) pulped Pinus radiata in two stages, obtaining an easy beating pulp at 60% yield. His first stage employed sodium sulfide (Na₂S) as the cooking chemical, the final treatment was with a solution of sodium sulfite (Na₂SO₃). He claimed "kraft quality" pulp, potential application in continuous pulping systems and an established (Billerud) recovery.
Bender, et al. (51) described a novel way of delignifying wood at or near room temperature. They claim very good carbohydrate/lignin ratios for pulps made by reacting wet wood chips with 2-3% solutions of nitrogen dioxide in organic solvents followed by an extraction with 1-2% NaOH at 85-90°C. Unbleached pulp strengths in the 60-83% yield range were described as somewhat low.

Lescot (52) worked with hardwoods and softwood Asplund fiber and his suggestion that the oxygen-caustic bleaching system be applied to pulping was a novel approach. Unfortunately, his experiments were not successful. He concluded that lignin in the native state would not react with oxygen.

Nedelcheva and Ivanova (53) attempted to relate pulp physical properties and lignin contents by starting with a semichemical type pulp and delignifying in stages with sodium chlorite. Pinewood pulp properties improved steadily as lignin content decreased. Nikalova, et al. (54) warn that inclusion of branchwood chips along with conventional chips in an effort to increase forest land productivity may give pulps with reduced carbohydrate-to-lignin balance because of the higher lignin content of the branchwood. Matyushkina, et al. (55) report that high-yield kraft pulps with satisfactory mechanical properties can be obtained by pulping pine root- and stumpwood.
PULPING UNBARKED WOOD

A few references were discovered covering kraft pulping of unbarked pinewood. Modrzejewski and Surewicz (56) carried out laboratory scale cooks on whole bark, bark fractions, and wood-bark mixtures. They reported that the presence of bark results in higher than normal chemical consumption and that difficulties in washing and screening were encountered. They could not find economical or technical justification for pulping unbarked pinewood. Horn and Auchter (57) conducted experiments with west coast softwoods kraft pulped with and without bark to a bleachable grade. They concluded that it was technically feasible to produce an acceptable bleached kraft pulp from unbarked wood when the chips have an average bark content of 10%.
LITERATURE CITED


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