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How Lignin, Hemicellulose, and Cellulose Affect the Properties of Oxygen Versus Kraft Pulps

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HOW LIGNIN, HEMICELLULOSE, AND CELLULOSE AFFECT THE PROPERTIES OF OXYGEN VERSUS KRAFT PULPS

by

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ABSTRACT

A batch of chips was subjected to an oxygen pulping and a kraft pulping system. The resulting pulp was tested in its unbleached condition. It was then bleached, tested again. Handsheets were tested using the Pulmac zero span tensile tester and other standard physical tests. The pulps were tested using the Pulmac permeability tester. This procedure gave the opportunity to look at how the differences between the individual fibers and their components affect the differences in the strength between oxygen and kraft pulp handsheets.

The oxygen pulp was severely degraded than was the kraft pulp. This led to shorter, weaker individual fibers, but fibers. with better bondability. The increased bondability gave oxygen pulp handsheets with superior strength in every test except tear. The increased bondability was caused by the higher hemicellulose content in the oxygen pulp. Bleaching increased the strength of both pulps, but oxygen pulp strength was increased to a higher degree. The oxygen pulp also had a larger specific surface area than did the kraft pulp. This increased the number of sites availible for bonding which helped to increase the sheet strength. For these handsheets, the bondability played a more important role in the final strength than did the strength of the individual fibers.

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INTRODUCTION

Because of the many advantages of oxygen pulping, it appears to be developing into the pulping process of the future. One of the gains of oxygen pulping is less environment pollution. This process will reduce the amount of atmospheric pullutants as well as eliminate the kraft odor. Oxygen pulping will also improve the pulp mill effluent quality. One source(6) reports Worster and Pudek have found through simulating the waste waters expected from oxygen-alkali pulping of softwoods that the waters will have a lower foaming tendency. Along with this they found the waste waters to have a lower toxicity and about a twenty percent lower BOD requirement. Hata and Sogo(11) have found the BOD/COD ratio of an oxygen-alkali soda pulp to be forty to fifty percent higher then the ratio for NSSC or kraft waste liquors. This means more of the oxygen pulp wastes can be removed through a biological treatment system. Environmental considerations are becoming emphasized more and more each year.

There are also many economical advantages of oxygen pulping. Oxygen pulps will give yields greater than or at least equivalent to those achieved when pulping the same chips using the kraft process. This same oxygen pulp has been shown to beat faster than the kraft pulp(4,22). This

would save on refiner power reqirements. In comparing the two pulps, two sources(2, 12) have found the oxygen pulp to be brighter (one source recorded a 17-20 point difference) and to have a lower kappa number (7-12 points different). These two observations point toward lower bleaching costs due to the apparent reduction in liquin content. This is supported by the observations of Saukkonen and Patenius(22). They found their oxygen pulp to consume less chlorine chemicals than the kraft and still end up with higher brightness. In addition to this, bleaching will increase the density, burst and tear properties of oxygen pulp while it has little effect on the kraft pulp.

Oxygen pulping is not without its drawbacks. It has been shown again and again that the strength properties of oxygen pulps are lower than those of the kraft pulps. Also, while bleaching oxygen pulps, many fiber fragments resulting from mechanical fiberization and oxygen delignification are lost while bleaching(4). This reduces the higher yield advantage of the oxygen pulp. Despite these disadvantages, oxygen pulping still seems to be the pulping process of the future.

HISTORICAL BACKGROUND

Experiments designed to study the use of oxygen for pulping began in the late sixties. The idea of using oxygen for pulping was brought over from the success of using it for bleaching. Since that time, there is yet to be an oxygen pulping process developed to industrial scale.

Studies on oxygen pulping have been limtied to investigating how different pulping conditions perform and how degradation inhibitors effect the strength properties. These investigations have found quality pulps could be prepared with oxygen-alkali pulping processes. Hata and Sago(23) found liquor pH to effect the lignin removal. A lower pH (8-9) is desirable for cooking. They also found the addition of alkali in increments as the cook procedes gives better results than starting with a high initial alkali content. Another development in this area is the use of a two stage process. In the first stage, a soda cook is used to give a high yield. Then the remaining fibers are subjected to oxygen-alkali delignification during the second stage. This reduces some of the problems encountered with a single stage cook.

Different investigators used different oxygen pressures. Most of them seem to feel high pressures are better. Abrahamsson and Samuelson(1) have done investigations

observing the effect of the concentration of carbon dioxide during pulping. They have found carbon dioxide has a retarding effect in the dissolution of hemicellulose. Also, they found decreasing the concentration of carbon dioxide would give an increase in the depolymerization of carbohydrates. Experiments looking at the optimum chip size were also conducted. Hata and Sogo have gotten the best results with chips less than three millimeters thick(11). Shavings also gave desirable results. At the present time, smaller chips work best in order to achieve a homogenous cook. There are problems of getting complete oxygen diffusion of the chips in the time required. If the cooks are held at oxygen-alkali conditions for a long period of time, the oxygen will penetrate through the chips, but oxidative depolymerization will occur and reduce the pulp strength.

Other recent investigations have been those using inhibitors as carbohydrate stabilizers. Minor and Sanyer(17,18) used iodide as a carbohydrate stabilizer. By using iodide, they were able to improve both the screened and total yield, increase the viscosity, achieve a higher handsheet strength, and increase the hemicellulose retention. They also found this effect would increase as the pH decreased with an optimum pH between 7 and 9. The other inhibitor used was magnesium(22). This also increased the strength properties and the pulp yield.

THEORETICAL BACKGROUND

Phillips and McIntosh(20) seem to have a good interpretation of what is occuring during the oxygen pulping process. They describe four physicochemical steps necessary for osygen in order to for degradation of the lignin to occur. First of all, the oxygen must change from a gaseous phase to a liquid phase. Then it must diffuse through the liquid and reach the fiber surface. Once at the surface, it must penetrate the fiber wall. Then it continues through the cell wall until it encounters a reactive lignin structure in an alkaline environment. They pointed out the reaction with lignin requires the presence of a free phenolic hydroxyl group. Therefore the rate at which this reaction occurs will depend on the porosity of the cell wall.

During the oxygen-alkali cook, weak acidic groups are introduced in the lignin and thus it dissolves in the cooking liquor. This phenomenon is better explained by Chang et al.(5) They feel the oxidation of lignin occurs by an electrophilic attack by the oxygen on the ionized phenolic structures. This causes the breakdown of the lignin structures by forming soluble acidic degradation products. As the cook proceeds, the lignin continues to degrade into lower molecular weight compounds. This changes the lignin into a form that can't be precipitated on the fiber, even after acidification of the

cooking liquor.

Kleinert(14) has found that delignification in a isothermal oxygen-alkali system takes place in two stages. For a very short time at the beginning, rapid delignification occurs. He found the second stage to be slow and to exhibit a pseudo-first order reaction mechanism. He also found the total alkali consumption for oxygen pulp was three times that of kraft or caustic soda pulping.

Oxygen pulps have been found to have a high hemicellulose content. Conners and Sanyer(7) feel this is due to the high alkali content of the cooking liquor. The alkalinity would prevent solubilization of the hemicelluloses and, at the same time, their redeposition on the surface of the fiber during digestion.

OXYGEN PULP VS. KRAFT PULP

Because of the different types of pulping processes used, the oxygen pulp will have different properties than the kraft pulp. There are five main areas with an existing difference between the two pulps. They are the differences between the overall sheet strength values, the lignin, the hemicellulose, the cellulose, and the individual fibers.

STRENGTH DIFFERENCES

As a whole, the soda oxygen pulp strength properties are uniformily lower than kraft pulp. This lower strength is probably due to the more severe degradation to the cellulose. It could also be due to the difference between the amount and distribution of the hemicellulose. Several sources found the burst factor and the burst-tensile relationship of oxygen pulp equivalent to a similar kraft pulp(10, 20, 4). The tearing resistance was much lower, thereby giving a lower overall strength value(4, 10). Two sources have found the bonding strength of the oxygen pulps to be greater than kraft pulps at a constant bursting strength(4, 22). They have also found this difference to vanish as the two pulps become refined more.

The type of alkali charge will effect the strength properties. It has been shown that a high alkali concentration will decrease the pulp strength(6, 17, 22). To minimize the

effect, the pulp should be pulped in a pH range of 8 to 9.5. One source(6) observed an increase in the tear factor with an increase in the alkali charge. Chang et al(4) have observed bleaching will increase the burst and tear strength of the oxygen pulps while here is little effect on the kraft pulps. Another way in which oxygen pulp differs from kraft pulp is increasing the wet pressing pressure will not increase the burst strength and the apparent density uniformity(4). This is apparently due to the difference in flexibility or in surface area. There is a definite uniform relationship for kraft pulps. Another factor which influences strength properties is the temperature at which the pulp is cooked. The higher the temperature is, the more the strength of the pulp is decreased. This effect begins at some temperature above 120°C(22).

The yield achieved depended on what type of oxygen pulping process was used. In general a one stage oxygen pulp gives a much higher yield than a kraft pulp(17). Soda oxygen pulps (two stage) gave a yield which was greater than or equivalent to kraft(4). Oxygen-alkali pulps gave yields lower than kraft(10). At equivalent yields, kraft pulp is stronger than oxygen pulp. Decreasing the yield of the oxygen pulp will only reduce the potential strength of the pulp. The addition of a carbohydrate degradation inhibitor such as potassium iodide will increase the yield(17). Chang et al(4) points out that the oxygen pulps have a

higher ash content due to the oxidation of acidic groups. This will increase the yield value, but only to a magnitude of less than one percent.

It is commonly known that oxygen pulps have a higher apparent density than kraft pulps. This has been found to be true at any level of refining or freeness. One source(16) attributes this difference to the thinner walls of the oxygen fibers. He found the oxygen fibers to be fifteen percent thinner than kraft at a forty-seven percent yield. This causes the cell wall to be more flexible and gives flatter fibers, thereby giving a more dense sheet. It was shown(6) that as the alkali charge is increased, the difference in the densities between the two pulps becomes greater.

This difference in sheet density introduces more problems in evaluating the differences between the two pulps. Normally when comparing the densities of two handsheets of the same species, it is assumed that the denser sheet has a higher degree of fiber to fiber bonding. This assumption must be overlooked when comparing the oxygen pulps to the kraft pulps. Also the effects of wet pressing on the density of oxygen pulp are not normal. Normally there is a uniform relationship between density and tensile strength as the wet pressing pressure is changed. This is not true for the oxygen pulps. Apparently the degree of fiber packing and conformability in an oxygen pulp sheet

unlike that of a kraft pulp.

LIGNIN DIFFERENCE

Another difference between oxygen and kraft pulp lies in the lignin. The amount and position of lignin in a fiber can determine how that fiber behaves. Kellogg and Wangaard(13) show there is a significant increase in fiber strength and stiffness with an increase in its permangamte number.

Phillips and McIntosh(20) explain the topochemical distribution of lignin within the fiber will even effect how the fiber delignifies. They believe if the bulk of the lignin lies on the outer layer of the fiber, initially the delignification will take place there and not affect the inner layers. They have shown this with some work performed using southern pine. They felt there was initial preferential delignification in the secondary wall and the lignin in the middle lamella was less affected for the oxygen pulp than it was for the kraft. Other data showed a high lignin content in both the middle lamella and the secondary wall for their highest yield pulp. At the same time, the lignin content was high for the middle lamella and low for the secondary wall in the lowest yield soda-oxygen cook. Phillips and McIntosh(20) also believe the distribution of the lignin across the fiber explains the failure for the soda oxygen pulps to collapse.

Oxygen pulp lignin is also different from the kraft lignin in that the oxidized lignin is more soluble in acid..

Hata and Soyo(23) found the amount of lignin precipitated from a soda oxygen black liquor was even less than that of soda black liquor. The presence of oxygen promotes delignification in the oxygen pulping process, while it is the presence of sulfur in the kraft process.

The presence of lignin in the two pulps seems to effect them differently. One source(16) has found the oxygen pulp to be 17-20 points brighter and to have a kappa number of 7-12 points lower. Chang et al(4) have found the removal of lignin to affect the cellulose structure more using a soda oxygen cook. They suggest the removal of lignin probably disrupts the existing hydrogen bonding pattern of the fibrils more than a kraft pulp does. They show if the kappa number is greater than thirty-five, the burst factor seems to be independent of the number. For a kraft pulp, the burst factor will generally increase with an increase in lignin removed. Soda oxygen pulps seem to be unaffected by the lignin levels in a kappa number range of 120 to 35(4). They also show the kappa number below which the amount of delignification is lower than the amount of cellulose degradation to be lower for a kraft pulp than for an oxygen pulp.

HEMICELLULOSE DIFFERENCE

The total amount and the distribution of hemicellulose on the fibers will effect their overall properties. Connors and Sanyer(7) have found the presence of insufficient

hemicellulose within the surface of the fiber could give poor fiber adhesion and decrease the bonding strength. This means an increase in hemicellulose content would decrease the tear value due to increased bonding and would increase mullen, tensile, and fold. Also Abrahamsson and Samuelson(1) found a similarity between the dissolution of hemicellulose and a drop in viscosity, thus showing a decrease in fiber adhesion.

Oxygen pulps have a higher retention of hemicellulose. Abrahamsson and Samuelson(1) believe almost all hemicelluloses except for the xylan type are removed during the early or precooking period of oxygen pulping. Only a small fraction of the low molecular weight xylan is removed. During an oxygen cook, the hemicellulose seems to have a tendency to remain in the fiber. Connor and Sanyer(7) feel it is the high alkali content of the cooking liquor which prevents the hemicellulose from solublizing. They also note this prevents the redeposition of the hemicellulose on the fiber surface which normally occurs during digestion in a kraft cook. The absence of hemicellulose from the surface of the fiber would decrease its bond strength. Chang et al.(4) suggest the hemicellulose which is removed from the cellulose structure seems to have more effect in a soda oxygen pulp than it does a kraft pulp. They suggest the removal causes less cohesion within the cell wall and probable changes the bonding pattern in the fibrils more in a soda oxygen

pulp than it does in a kraft pulp.

Oxygen and kraft pulps vary with respect to hemicellulose. The position of hemicellulose seems to differ between the two pulps. Since the oxygen pulp contains more hemicellulose within the single fiber, It will beat faster than kraft pulp. The kraft pulp has more hemicellulose precipitated at the surface of the fiber. This gives it stronger fiber to fiber bonding. Differences even occur in the bleaching of the two pulps. Saukkonen and Palenius(22) have found the yield loss in kraft pulps during bleaching is due to the loss of hemicellulose. The yield loss achieved during soda oxygen pulp bleaching is basically due to cellulose loss. Nakamura and Matsuura(19) found bleached oxygen pulp to have higher bonding ability and a lower scattering coefficient than kraft pulp. This is evidently due to the higher content of hemicellulose in oxygen pylps.

CELLULOSE DIFFERENCE

Another part of the fiber which influences its final properties is the cellulose. Cellulose is the backbone of the fiber and gives it most of the strength. Severe degradation of the cellulose will give the fiber poor strength properties and lower the stiffness. A high alkali content will give more severe degradation. Also, as the time for the cook increases, the purer the fiber becomes, but also the cellulose becomes more degraded.

The carbonyl content can be used as a measure of the

degradation of the cellulose. As the cellulose becomes more degraded, the viscosity of the cellulose decreases and the carbonyl content increases. Minor and Sanyer(17) found the carbonyl content of oxygen pulp to be twice as high as that in kraft pulp. Chang et al(4) feel oxygen pulping varies cellulose more than a kraft cook does. They feel there is less cohesion within the cell wall after on oxygen cook. They also postulate that in the cell walls, the fibrils are not bonded as well as in a kraft cook since the soda oxygen pulp fibers have a greater pore volume.

Even though oxygen pulps give a high cellulose yield, much of this is lost through either washing or bleaching. Connors and Sanyer(7) explain how this can happen. A high alkali cooking liquor can cause stripping from the fiber surfaces. This creates fiber fragments which are easily lost during washing or bleaching. The use of a carbohydrate degradation inhibitor such as potassium iodide may eliminate some degradation(17).

INDIVIDUAL FIBER DIFFERENCES

Individual fibers are the building blocks of a paper sheet. One should be able to monitor how a certain sheet is going to perform by monitoring the properties of the individual fibers. The properties of a single fiber will reflect the amount, condition, and position of the lignin, hemicellulose, and cellulose within it. Even though the handsheet tensile is only ten to twenty percent of the

individual fiber tensile, the influence of the fiber strength increases as the sheet density increases(13). Kellogg and Wangaard(13) found that fiber strength is more influential in handsheets up to a density of 0.6 gm/cm^3 when measuring tear strength. Chang et al(4) looked at the effect of individual fibers using the Caulfield technique for measuring the fiber saturation point. It measures the amount of water within a cell wall. They found soda oxygen pulps to have a higher pore volume. They feel a fiber with a higher pore volume would reduce its perimeter more when dried. They speculate this would cause the fiber to have a more circular cross section which would give less intense bonding and cause the fiber to be stiffer.

There appears to be a difference between oxygen pulp and kraft pulp fibers. Saukkonen and Palenius(22) found the oxygen pulp fibers to be softer, more flexible, faster beaten, and higher in bonding ability than the kraft pulp fibers at an equivalent yield. When Phillips and McIntosh(20) compared the two fibers, they found the soda oxygen-alkali to remain round and rigid as compared to the flat kraft fibers. Another source(22) while looking at the fibers as a group found the soda oxygen pulps to have a lower proportion of short fibers.

The sheet strength is dependent on both the strength of the bond between the fiber and the strength of the fiber itself. One way to measure the strength of the fiber is the

zero span tensile test. Kellogg and Wangaard(13) have found their experience supports the use of the zero span tensile as a means of measuring individual fiber strength. They have selected sheet density as means of measuring fiber to fiber bonding. Because of the difference in densities between the oxygen and the kraft pulps, this method will not work for comparing the two pulping methods. Several sources feel the oxygen pulps have a better bonding ability than do the kraft pulps. One source(4) has found the oxygen pulp to have equivalent ring crush values and burst-tensile relationships as kraft. Two sources(4, 22) have shown at the same burst factor, the bond strength of soda oxygen pulps is greater than a kraft pulp of equivalent yield and kappa number. This elevated bond strength decreases as the two pulps become more refined.

The oxygen pulps have shorter fibers than kraft pulps. This is evident in the lower tear strength values and the higher ring crush values(4, 10, 22). Bleaching of the oxygen pulp reduces the amount of short fibers at a higher rate than it does for kraft. This gives the two types of pulps an equivalent fiber length after bleaching(22).

Another difference between the two types of fibers is their specific surface and specific volume. Specific surface is a measure of the amount of surface area for a certain unit weight of wet pulp. Cowan(8) has found this area to be a measure of how much the drainage will be hindered and

of the area which is available for bonding. He also points out there is a strong relationship between the specific surface area and the strength properties. It is believed the soda oxygen pulp cell walls fibrilate more than kraft(4). This would give them a higher specific surface. The specific volume is a measure of the volume of the fibers and the water retained by them based on a certain unit weight. Again Cowan(8) points out the specific volume will effect the drainage resistance and the sheet strength. He also says there is a strong relationship between specific volume and the strength properties. Robertson(21) show increasing the beating will increase the amount of water held by the fibers. This occurance is supported by Chang et al(4) when they state soda oxygen pulps, which beat easier than kraft pulps, are easier to create new pore volumes in and have a greater pore volume. A fiber with a higher pore volume will retain more water. Overall, the soda oxygen alkali pulps appeared to be rounder and more rigid than the kraft fibers(20).

Compressibility is another area in which different types of fibers may vary. Compressibility is a measure of the manner in which pulp particles can be compressed together to form a sheet(8). Cowan(8) states compressibility indicates how easily a dense mat of pulp will inhibit the drainage and increase the amount of bonding. One source(22) found the oxygen fibers to be softer and more flexible than kraft fiber while another(17) found them to be stiff fibers

The amount of degradation which occurs on the two types of fibers appears to be different. The degree of polymerization of oxygen pulp was shown to be lower than that of a kraft pulp(2). Viscosity is another means for looking at degradation. Hata and Sogo(10) found the oxygen-alkali pulps to have a lower intrinsic viscosity than kraft. Another source(15) found there was still a high viscosity after the first stage cook. Apparently it is the oxygen-alkali stage which does the majority of the degradation of the fibers. Several conditions affected oxygen pulp viscosity. A high alkali concentration decreased pulp viscosity, while the addition of potassium iodide increased viscosity(17).

STATEMENT OF PROBLEMS AND GOALS

Since oxygen pulping is a relatively new process, many basic areas still need to be looked at in more detail. One of these is the strength properties of the pulp. It is commonly known that oxygen pulp is weaker than kraft pulp. This difference may be due to cellulose degradation and/or the amount and distribution of both lignin and hemicellulose within the fiber. Therefore, the effect of these three components on the pulp strength should be investigated. The following hypotheses will be proved or disproved:

Lignin will not effect the strength properties of oxygen pulp as much as it does for kraft pulp. The removal of lignin in oxygen pulps will not change the handsheet properties as drastically as for kraft pulps.

Oxygen pulps will have a higher hemicellulose content at an equivalent yield. This will give the oxygen pulp a greater bonding ability than kraft pulp.

Oxygen pulp cellulose will be more degraded. The oxygen pulp will have shorter, weaker fibers.

Due to more severe cooking conditions, oxygen pulp will have more surface area. This surface area will give it better bondability than for kraft pulp.

EXPERIMENTAL APPROACH

Before it was possible to begin a investigation, it was necessary to decide which method would be used for the oxygen cook. Even though it produced a lower yield than the one stage cook, a two stage process was used because of shorter time required for cooking. It seemed to be more applicable to industrial scale pulping process than a one stage process. The two stage method used to pulp the wood was practically indentical to the method used by North Carolina State University (3-6). Their method was chosen because of the extensive amount of work they performed with the process.

Chang, McKean, and Seay give a description of their procedure in a recent article (6). Their procedure was followed as closely as possible. Jack pine (Pinus banksiana) chips were used for this experiment. For the first stage soda cook a 2 cubic foot stationary batch digester was used. A batch size of 2500 grams (calculated oven dry) of chips were used with specified circulation rate. The liquor was then added to the digester with a liquor-to-wood ratio of 4:1 with 17% soduim hydroxide on o.d. wood. The liquor was initiall heated with steam and brought up to temperature with an electrical heating unit. The liquor was heated to 170°C. The heating up time was 125

minutes. The cook was held at this temperature for 200 minutes. The chips were washed and the yield was determined. Because of the high yield, the chips remained whole. In order to turn the chips into a useable form, it was necessary to refine them before subjecting them to the second stage. This was done by passing through the disc refiner three times at plate distances of 0.100", 0.055", and then at 0.033" at low consistencies. The fibers still remained in rather large bundles and the shive content was very high. This step was necessary in order to insure good surface contact.

For the second stage cook, the N+K digestor was used. One hundred grams of soda pulp (based on oven dry) was added to the digester. The fiber was cooked at a five percent consistency in an eight percent NaOH (based on wood) liquor. The digester was brought to 150 psig at room temperature with oxygen and then heated to 120°C. The cook continued at this temperature for one hour. The pulp was then washed and screened. The yield and the kappa number of the pulp were determined.

The draft cook was vonducted similarily to the cook for the first stage of the oxygen pulp with the following exceptions. The liquor composition was changed to 18.5% effective alkali (NaOH) with a sulfidity of 25%. The cook was held at temperature for 2 hours. The yield and kappa number were determined. The pulp was then refined by passing it through the Bauer disc refiner one

time at a plate separation of 0.033".

A portion of the pulp (approximately one fourth) was used to make handsheets for both types of cooks. Then these handsheets were compared. The remainder of the pulp was subjected to very mild delignification. The acid chlorite holocellulose method was used under extremely mild conditions in order to minimize the amount of degradation. Most of the lignin was removed and mostly holocellulose remained. The yield after delignification was calculated. Approximately forty percent of the holocellulose was used to make handsheets for testing. Again the oxygen pulp handsheets were compared to the kraft pulp after undergoing identical treatment. The remainder of the holocellulose underwent treatment with dilute alkaline solutions (18% NaOH). Again extremely mild conditions were used to reduce oxidation and degradation. The resulting pulp was mainly "alpha" cellulose with the hemicellulose remaining in solution. The yields of each were then measured. The "alpha" cellulose was used to make handsheets for testing. The oxygen process "alpha" cellulose was compared with that from the draft process.

Each type of pulp had a series of tests run on it. Yields were calculated after each treatment. The yield after each type of cook was calculated first. Then yields were calculated after the removal of lignin and after the removal of the hemicellulose. Then Canadian standard freeness was run for each of the pulps. Viscosities were

run after each treatment following the pulping on each pulp. This was used to show if one type was more degraded than the other was. Then the fiber lengths of the pulps were determined.

The handsheets were used for physical testing. First of all the basic tests of tensile, tear, mullen, and fold were run. These values were used to see how these pulps compared with other pulps. Handsheet density was also calculated. Then two other types of apparatus were used: the Pulmac zero span tester and the Pulmac permeability tester. The Pulmac zero span tester was used to calculate individual fiber strength, fiber length, and bonding ability. The Pulmac permeability tester was used to characterize the specific surface and specific volume of the fibers.

PROCEDURES

The kappa number was determined according to TAPPI Standard Methods.

All handsheets were made using the Noble and Wood handsheet mold. Basis weight was approximately 60 g/m^2.

The tensile, tear, mullen, fold, and Canadian standard freeness were determined according to TAPPI standard methods.

The Pulmac zero span tensile tester and the Pulmac permeability tester were run according to the procedures in their operating manuals. Interpretations of the results from these two instruments were discussed in articles by Cowan (8,9).

The holocellose was made using the acid chlorite holocellulose method. It was the same procedure as described on page 395 of B. L. Browning's "Methods of Wood Chemistry":

1. Add 40 g (based on air dry) of pulp into a 2 liter Erlenmeyer flask.
2. Add enough distilled water to bring to 1240 ml of distilled water.
3. Add 4 ml of glacial acetic acid.
4. Add 12.0 g of reagent grade sodium chlorite (Carry out under well-ventilated hood).
5. Invert another Erlenmeyer flask in the neck of the reaction flask and bring to a tempera-

ture of about 65°C with a steam bath.

6. Heat contents for 1 hr. with occasional swirling.
7. Then add 4 ml of glacial acetic acid.
8. Follow with 12 grams of sodium chlorite.
9. Continue heating for another hour.
10. Repeat steps 7-9 for at least 2 more times.
11. Remove after 3½ hours and place in ice bath and cool to a temperature less than 10°C.
12. Filter on a buchner funnel with a minimum amount on ice water to remove color and odor of chlorine dioxide.
13. Calculate the yield of hohocellulose.

"Alpha" cellulose** was produced by reacting 18 grams (based on oven dry pulp) of the holocellulose with 1200 ml of 18% NaOH. This was done for one hour at room temperature. After one hour, the cellulose was first washed with 9% NaOH and them with distilled water. The yield was determined and the pulp was used to make handsheets.

Viscosities were run using a no. 200 Ostwald capillary viscometer. Cupriethylenediamine was used as the solvent.

**The author realizes the "alpha" cellulose referred to in this report was not true alpha cellulose. The term "alpha" cellulose was used to name the pulp made using the following procedure.

The procedure was as follows:

1. Add 15 ml of 0.1667 M solvent to 0.125 grams (based on oven dry) fiber.
2. After about 15 minutes add 10 ml of 1.0 M solvent. This brings the total concentration of solvent to 0.5 M.
3. When all of the fiber is dissolved, place 20 ml of the solution in the viscometer.
4. Place the viscometer in a temperature bath of 25°C and record the time it takes for the solution to pass between the two lines.
5. Use this time, the density of the solution, and the viscometer constant to determ ne the relative viscosity. The relative viscosity value was calculated by dividing the time necessary for a solution of 0.125 grams of fiber dissolved in 25 ml of solvent by the time necessary for the solvent to pass through the capillary tube.

The fiber lengths were measured b placing pulp samples on lides and projecting the fiber images. The lengths of the images were measured. The resulting magnification was 23.4 times. Over 300 fiber lengths were measured for each sample. From these lengths it was possible to calculate the average fiber length and to draw a fiber length distribution curve.

RESULTS

The yield for each pulp was calculated after each physical change occured to the fiber. The results of these calculations are summarized in Table I. All yield

Table I

YIELD AFTER EACH PROCESS

Process	Percent Yield Kraft Pulp	Soda-Oxygen Pulp
Initial cook (based on o.d. chips)	53.1	54.1 77.6 after soda cook
Acid Chlorite Bleaching (based on o.d. chips)	48.5	47.2
(based on u.bl. pulp)	91.3	87.2
Subjection to 18% NaOH (based on o.d. chips)	40.2	37.1
(based on bl. pulp)	83.0	78.6

values were calculated immediately after the pulp was washed. The yield after the initial cook was calculated before the pulp was refined.

The above pulps were then made into handsheets. The handsheets made from the pulp immediately after the initial cook were called unbleached kraft or oxygen handsheets. The ones made from the pulp after it had been subjected to the acid chlorite treatment were called oxygen or kraft holocellulose handsheets. Last of all, the pulp which had been subjected to 18% NaOH was made into handsheets named

kraft or oxygen "alpha" pulp. Table II shows the dimensions of the resulting handsheets. Each of the values used in

Table II

DIMENSIONS

Type of Handsheet	Basis Weight (g/m^2)	Caliper (X.001")	Density (g/cm^3)
Unbleached Kraft	56.0	9.2	0.24
Unbleached Oxygen	55.5	8.3	0.26
Kraft Holocellulose	58.3	7.7	0.30
Oxygen Holocellulose	58.6	6.9	0.33
Kraft "Alpha" Pulp	57.6	10.4	0.22
Oxygen "Alpha" Pulp	59.6	10.5	0.22

Table II were averages taken from ten handsheets. The basis weights for each type of handsheet were approximately the same. The calipers for the oxygen pulp were consistently lower than those of the kraft pulp except for the "alpha" cellulose. This also meant that the densities for the oxygen pulp handsheets were higher than those for the kraft pulp. The kraft pulp made a more bulky sheet than did the oxygen pulp. The densities for both types of pulps were low. This was probably due to the low level of refining and the low wet pressure used.

Next the optical properties were observed. The results are summarized in Table III. The kraft pulp had a higher brightness value for the holocellulose and "alpha" handsheets. The kraft handsheets also had a higher opacity value for unbleached and holocellulose pulps. The opacity values

for all of the handsheets were high. This was apparently due to the high bulk of the handsheets. A high bulk handsheet has a larger number of air voids and a low degree of babonding air voids there are, the higher is the opacity value. The brightness and opacity values were calculated from ten different handsheets for each condition.

Table III

OPTICAL PROPERTIES

Type of Handsheet	Brightness	Opacity
Unbleached Kraft	35.1	98.6
Unbleached Oxygen	33.0	96.3
Kraft Holocellulose	74.9	84.3
Oxygen Holocellulose	75.3	82.6
Kraft "Alpha" Pulp	78.0	73.7
Oxygen "Alpha" Pulp	77.0	77.3

The physical properties of each type of handsheet were then evaluated. A summary of these properties can be found in Table IV. The tensile strength of the oxygen pulp

Table IV

PHYSICAL PROPERTIES

Type of Handsheet	Instrom Tensile Breaking Length(m)	Fold	Tear Factor (g/gsm)	Burst Factor ($g/cm^2/gsm$)
Unbleached Kraft	1046	18	4.68	36.9
Unbleached Oxygen	1195	71	3.33	41.4
Kraft Holocellulose	1043	24	4.70	35.7
Oxygen Holocellulose	1283	74	4.51	45.7
Kraft "Alpha" pulp	62.5	0	.43	0.0
Oxygen "Alpha" pulp	80.8	0	.35	0.0

was consistently higher than that of the kraft. In both cases the fold strength increased through bleaching. The same result was found for the tensile and burst factor values for the oxygen pulp, but not for the kraft pulp. These two values decreased for the kraft pulp. The tear values gave different results. The tear values for the kraft were higher than those for the oxygen pulp. Bleaching the samples increased the tear strength for the oxygen pulp but not for the kraft. The "alpha" cellulose handsheets gave very low strength values in each category. The burst factor, fold, and tensile values were calculated by using the average value of ten repetitions for each condition. The tear values were the average of five runs, using four sheets per run.

Kappa number and viscosity were run on the handsheets. These results are in Table V. The kappa number for the

TABLE V

DEGREE OF PULPING AND DEGRADATION

Type of Handsheet	Kappa Number	Viscosity(cp)
Unbleached Kraft	40.5	-
Unbleached Oxygen	47.7	-
Kraft Holocellulose	-	35.1
Oxygen Holocellulose	-	12.5
Kraft "Alpha" Pulp	-	37.9
Oxygen "Alpha" Pulp	-	17.7

oxygen pulp was significantly higher than that for the kraft pulp. The viscosities for the holocellulose and "alpha" kraft pulps were much higher than those for oxygen pulps.

The viscosity values for the "alpha" pulps are not totally correct. These fractions could not be completely dissolved in the solvent. After several hours, viscosities were run on the solutions as they were. The values are believed to be representative although not entirely accurate.

The Pulmac permeability tester was used to determine the specific surface and the specific volume of fibers in a pad. The results of this test are found in Table VI.

Table VI

FIBER DIMENSIONS

Type of Handsheet	C. S. Freeness(ml)	Specific Surface(cm^2/g)	Specific Volume(cm^3/g)
Unbleached Kraft	695	11,400	2.46
Unbleached Oxygen	691	15,600	2.76
Kraft Holocellulose	680	13,00	2.38
Oxygen Holocellulose	650	18,900	2.86
Kraft "Alpha" Pulp	737	9,600	1.31(1 run)
Oxygen "Alpha" Pulp	723	10,200	0.98

This data shows that the specific surface of the oxygen pulp was consistently higher than that of the kraft pulp. The specific surface of both pulps increased after acid chlorite bleaching. Treatment with 18% NaOH reduced the specific surface to its lowest value. The specific volume for the oxygen pulp was higher for the unbleached samples, but lower for the "alpha" pulp. The specific volume increased with bleaching for the oxygen pulp, while it decreased for

the kraft pulp. The results for specific surface and volume are the average of two values. Each of the values were computed from the slope and intercept of a graph. Each graph consisted of six data points. The freeness values were all high. Again, this was due to the very low level of beating. The freeness of the two pulps decreased after the holocellulose treatment and increased after subjection to 18 percent NaOH. For all pulps, the freeness value of the oxygen pulps was consistently lower than that of the kraft pulps.

Next the Pulmac zero span tensile tester was used to evaluate the properties of the individual fibers. By measuring the breaking length of the samples at various spans fo both a wet and a dry sample, a plot of breaking length versus span could be drawn. From this plot, the fiber strength index, the fiber length index, and the bonding index were calculated. The plots of the data for each condition are contained in Figures 1 through 6. A summary of the results can be found in Table VII. Table VII shows the oxygen pulp fibers were consistently weaker than the kraft ones. This was true for both the wet and dry conditions. For both conditions, the strength of the oxygen fibers increased as a result of bleaching. This was true for the kraft pulp only in the dry condition. Calculation of the bonding index for each condition showed

Figure 1

A Plot of Breaking Length us,
Span of Both Wet and Dry Samples
For Unbleached Kraft

FSI = 15.26 km
FLI = 0.66 mm
BI = 38.7 %

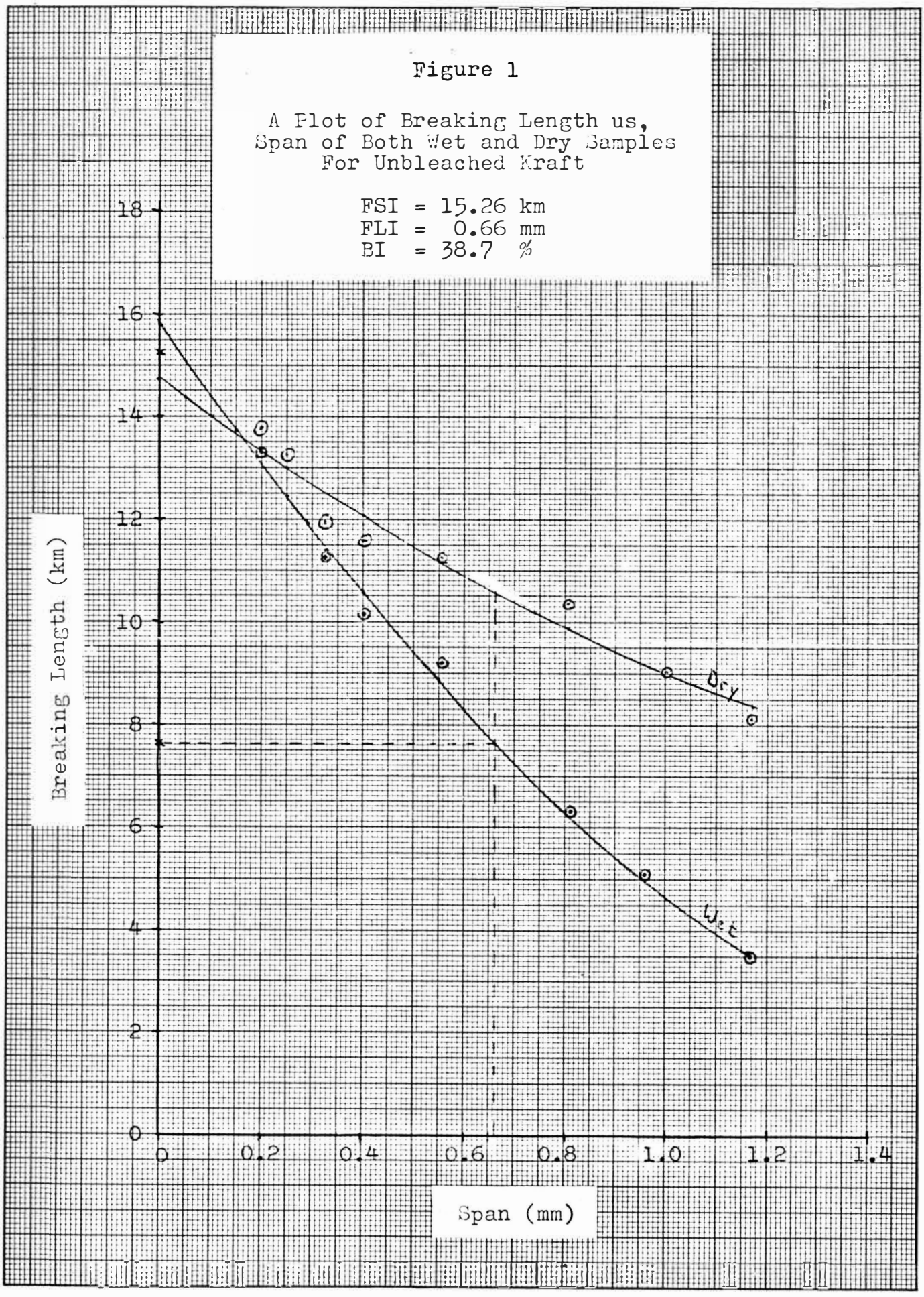


Figure 2

A Plot of Breaking Length vs. Span of Both Wet and Dry Samples For Unbleached Oxygen

FSI = 12.32 km
FLI = 0.56 mm
BI = 49.7 %

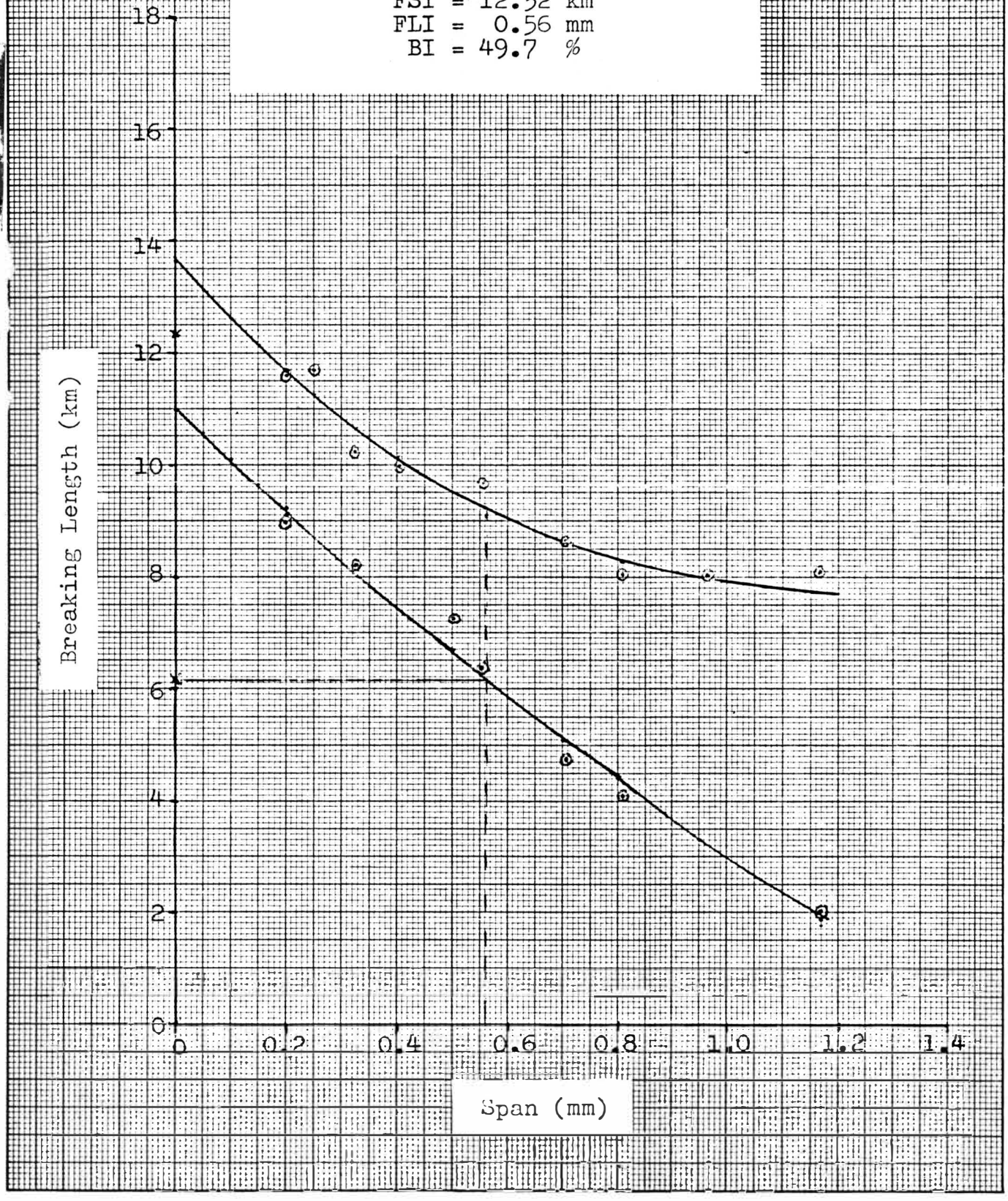


Figure 3

A Plot of Breaking Length vs. Span of Both Wet and Dry Samples For Bleached Kraft

FSI = 14.02 km
FLI = 0.475 mm
BI = 58.5 %

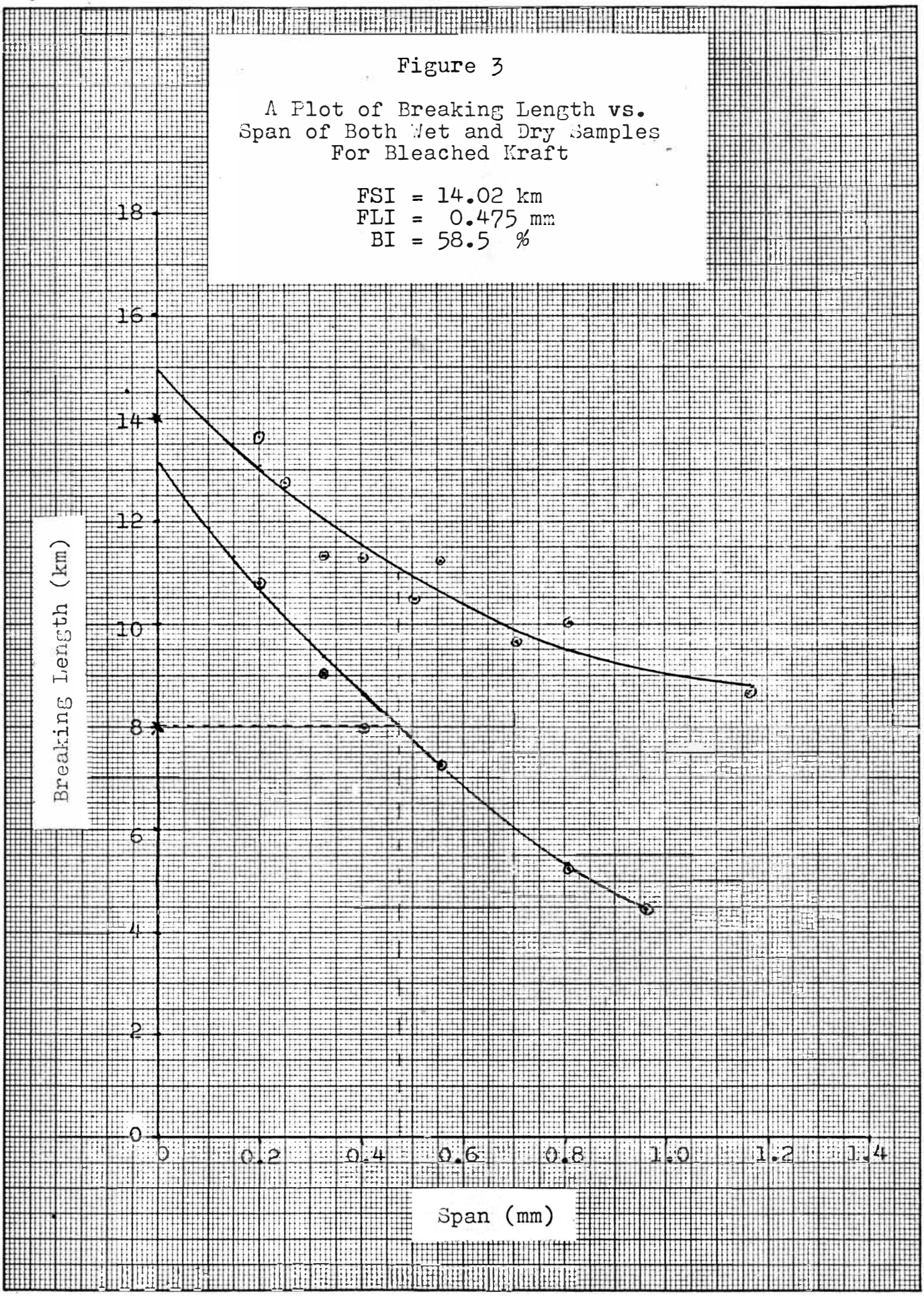


Figure 4

A Plot of Breaking Length vs. Span of Both Wet and Dry Samples For Bleached Oxygen

FSI = 12.89 km
FLI = 0.52 mm
BI = 61.5 %

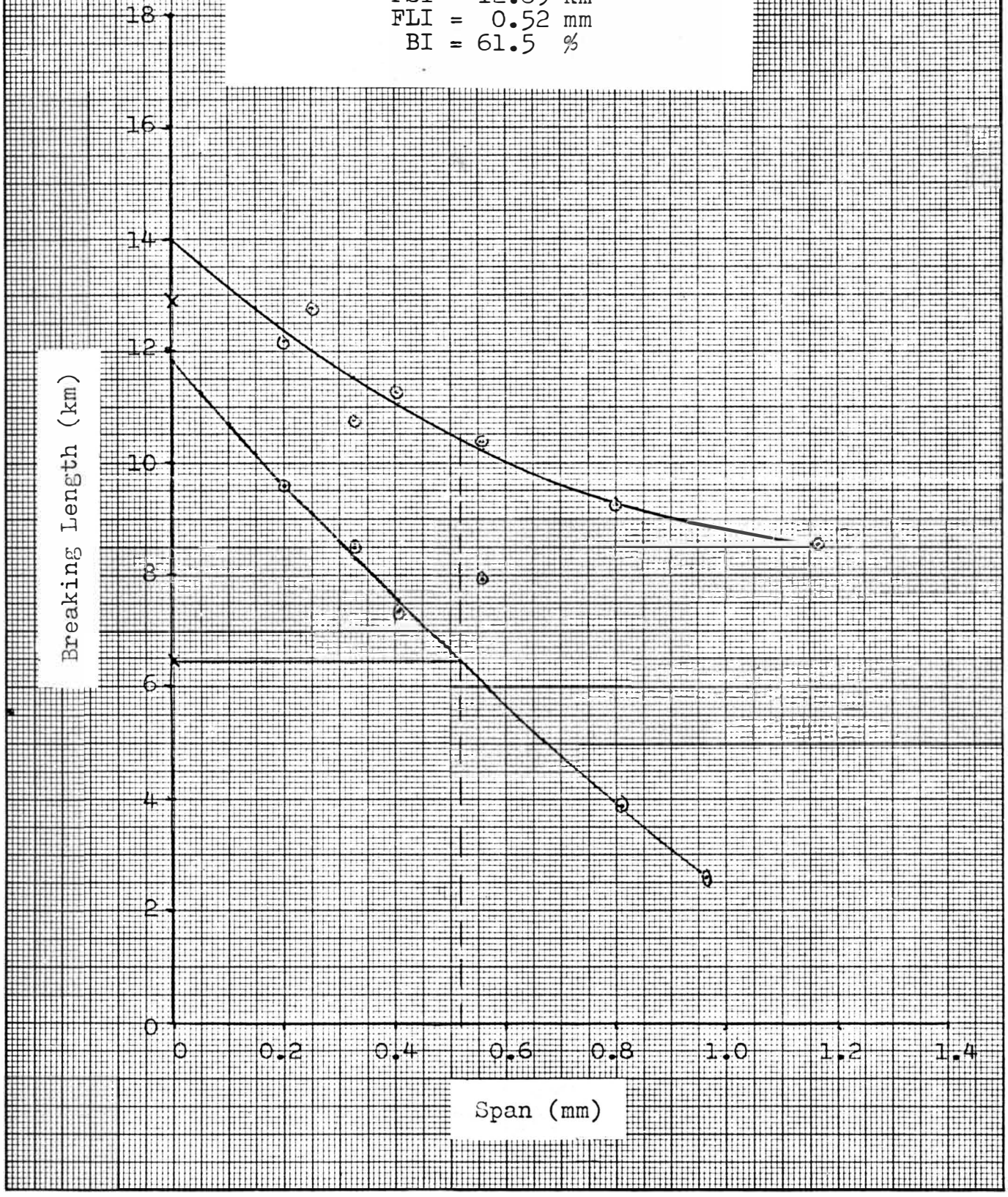


Figure 5

A Plot of Breaking Length vs. Span of Both Wet and Dry Samples For Insoluble Kraft

FSI = 11.56 km
FLI = 0.355 mm
BI = 22.8 %

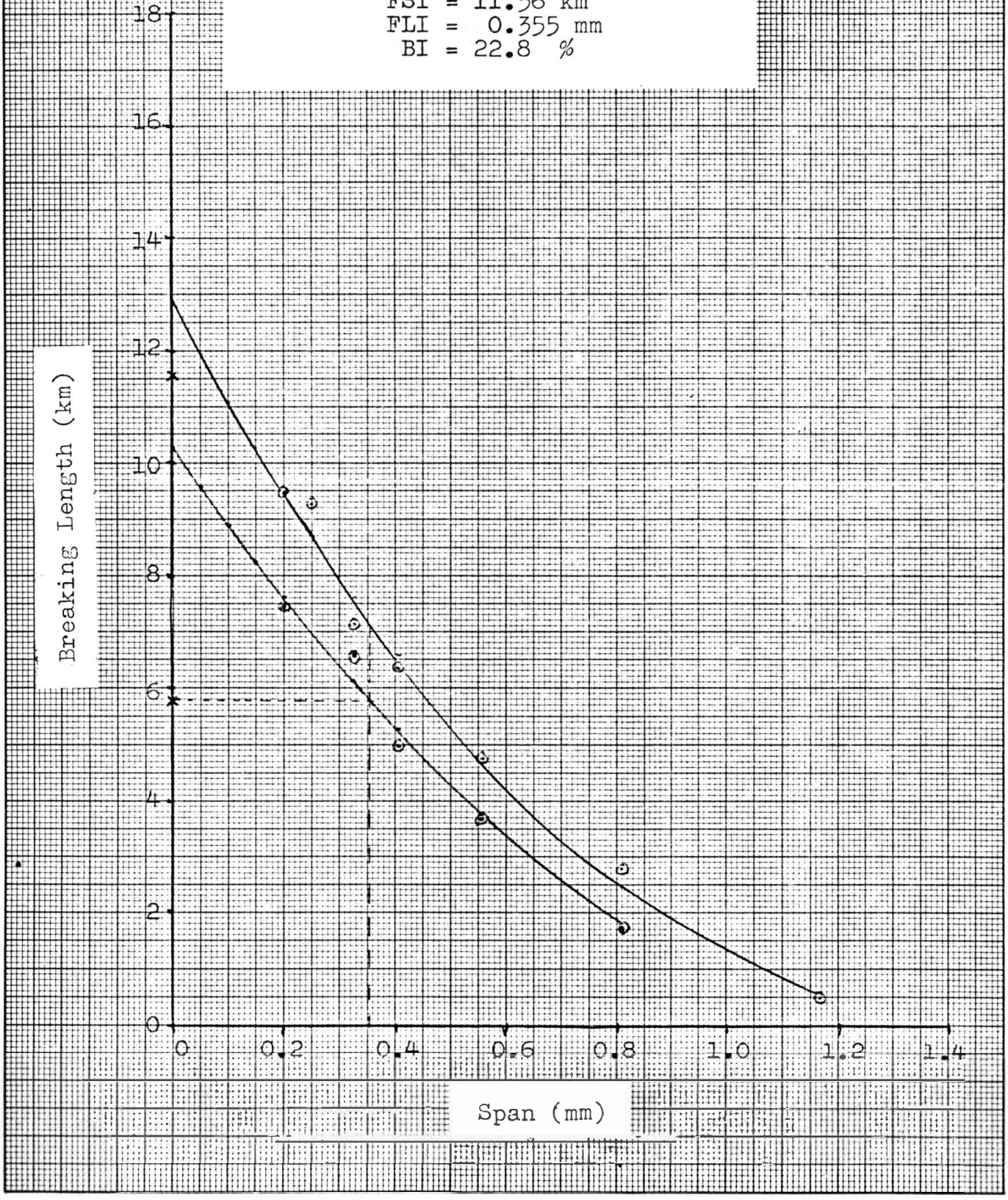


Figure 6

A Plot of Breaking Length vs. Span of Both Wet and Dry Samples For Insoluble Oxygen

FSI = 10.86 km
FLI = 0.26 mm
BI = 30.8 %

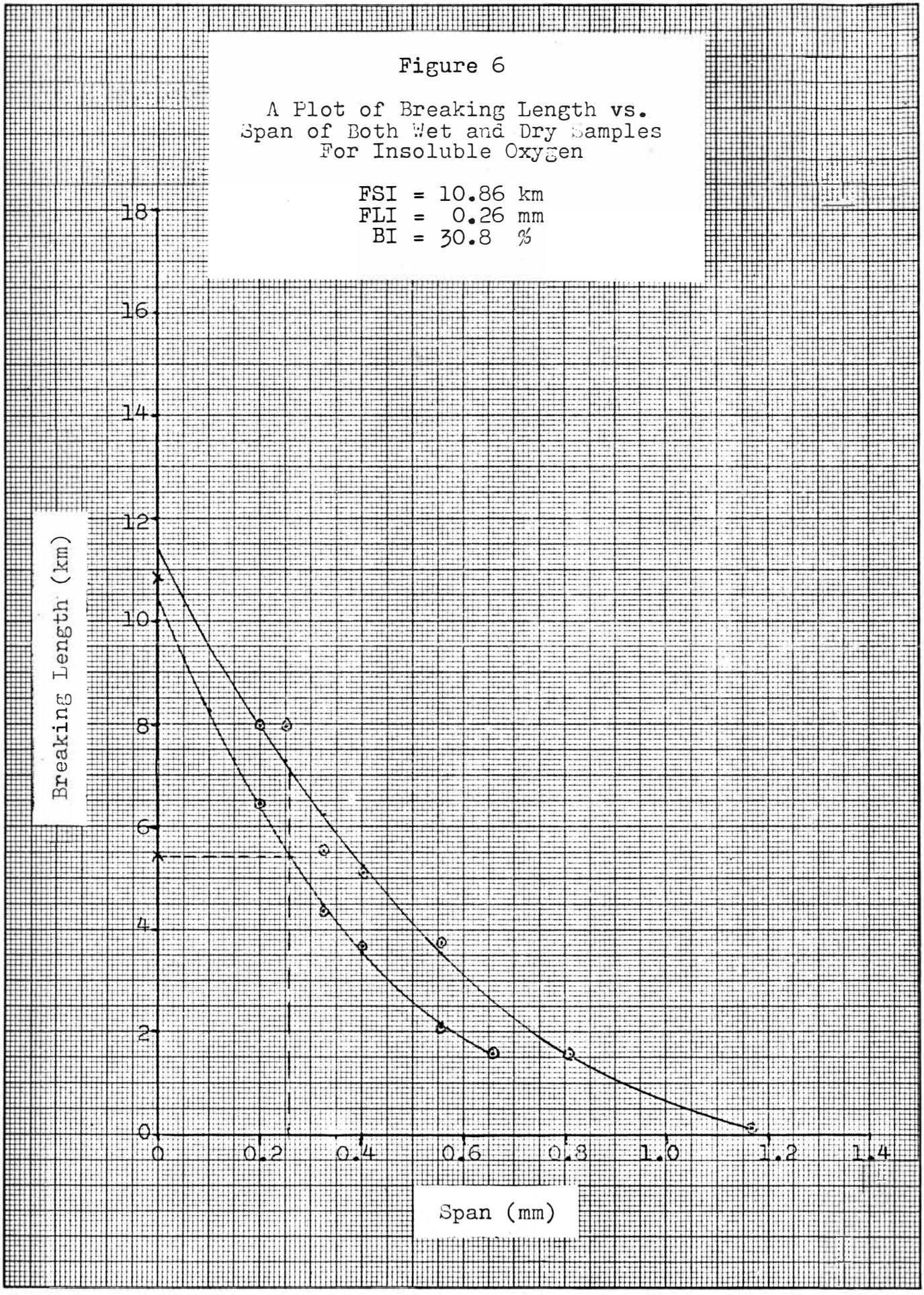


Table VII

INDIVIDUAL FIBER PROPERTIES

Type of Handsheet	Fiber Strength Index Dry(km)	Wet(km)	Average(km)	Bonding Index(%)
Unbleached Kraft	14.71	15.81	15.26	38.7
Unbleached Oxygen	13.64	11.00	12.32	49.7
Kraft Holocellulose	14.92	13.12	14.02	58.5
Oxygen Holocellulose	13.97	11.81	12.89	61.5
Kraft "Alpha" Pulp	12.84	10.27	11.56	22.8
Oxygen "Alpha" Pulp	11.37	10.35	10.86	30.8

Calculation of a bonding index for each condition showed the oxygen pulp to have a consistently higher ability to bond than did the kraft pulp. Bleaching the pulp increased the bondability for both pulps. Each point on the graph of breaking length vs. span represents the average of six measurements.

Table VIII

FIBER LENGTH

Type of Handsheet	Pulmac Fiber Length Index(mm)	Average Fiber Length(mm)
Unbleached Kraft	0.66	1.34
Unbleached Oxygen	0.56	1.65
Kraft Holocellulose	0.475	1.41
Oxygen Holocellulose	0.52	1.35
Kraft "Alpha" Pulp	0.355	0.70
Oxygen "Alpha" Pulp	0.26	0.74

Table VIII shows the fiber length values from both the Pulmac zero span tensile tester and from individual fiber length measurements. Figures 7 through 12 show the

Figure 7
Unbleached Kraft

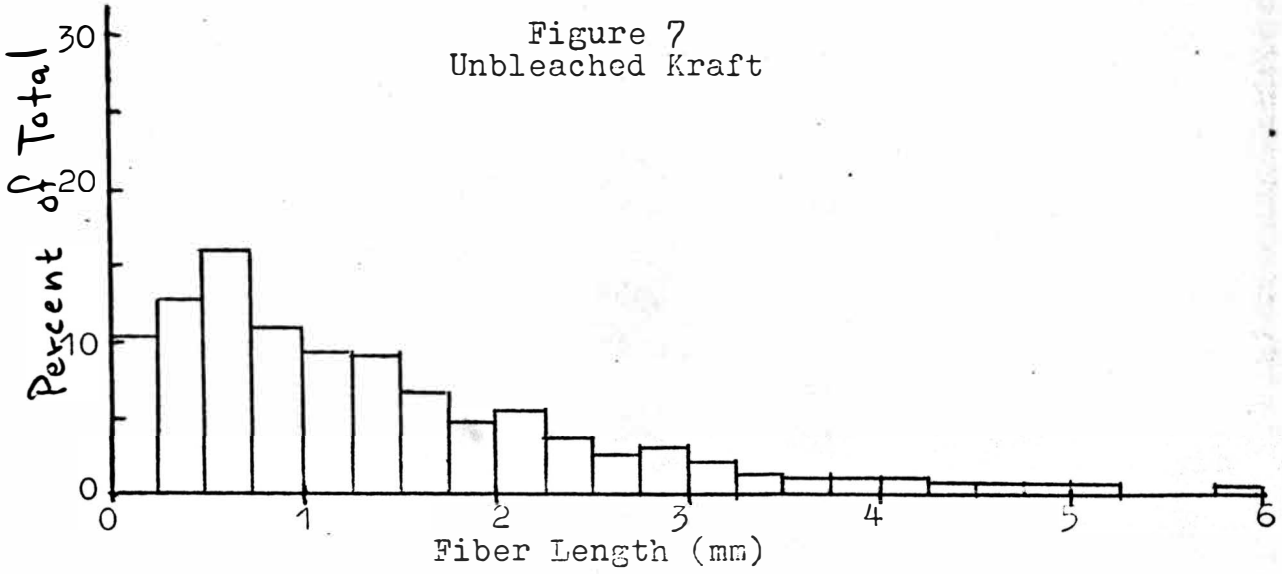


Figure 8
Unbleached Oxygen

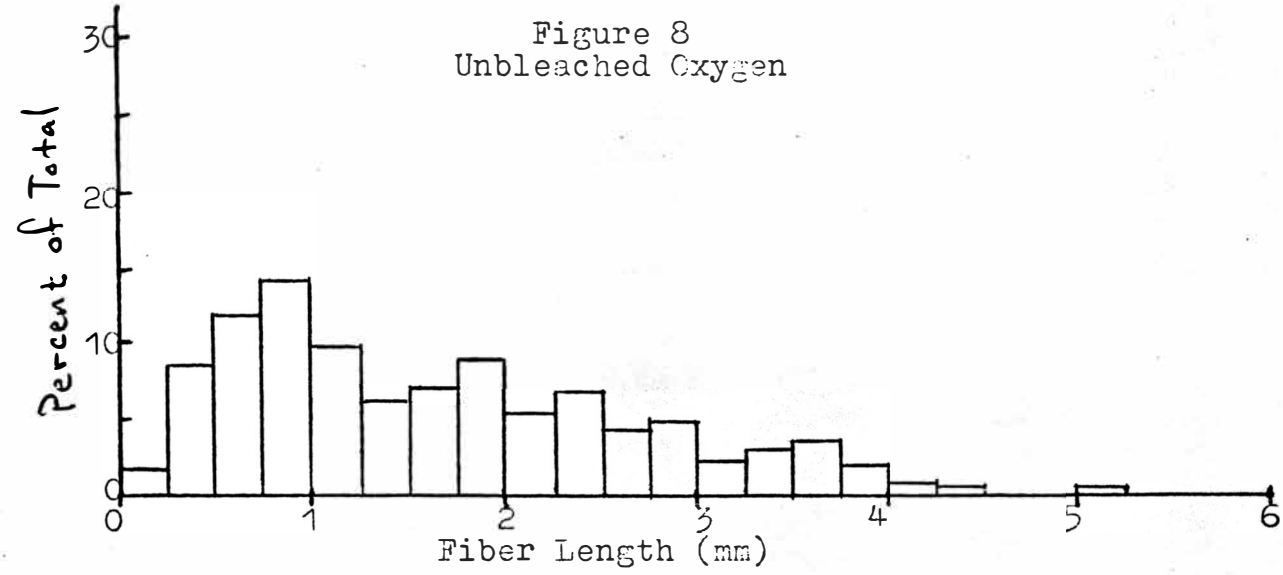


Figure 9
Kraft Holocellulose

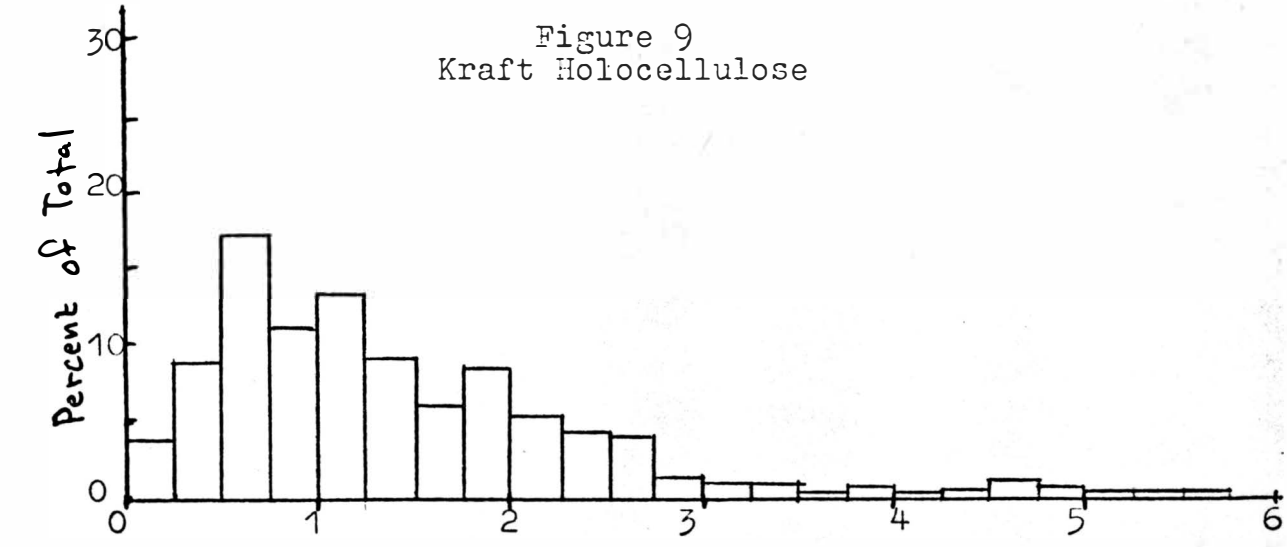


Figure 10
Oxygen Holocellulose

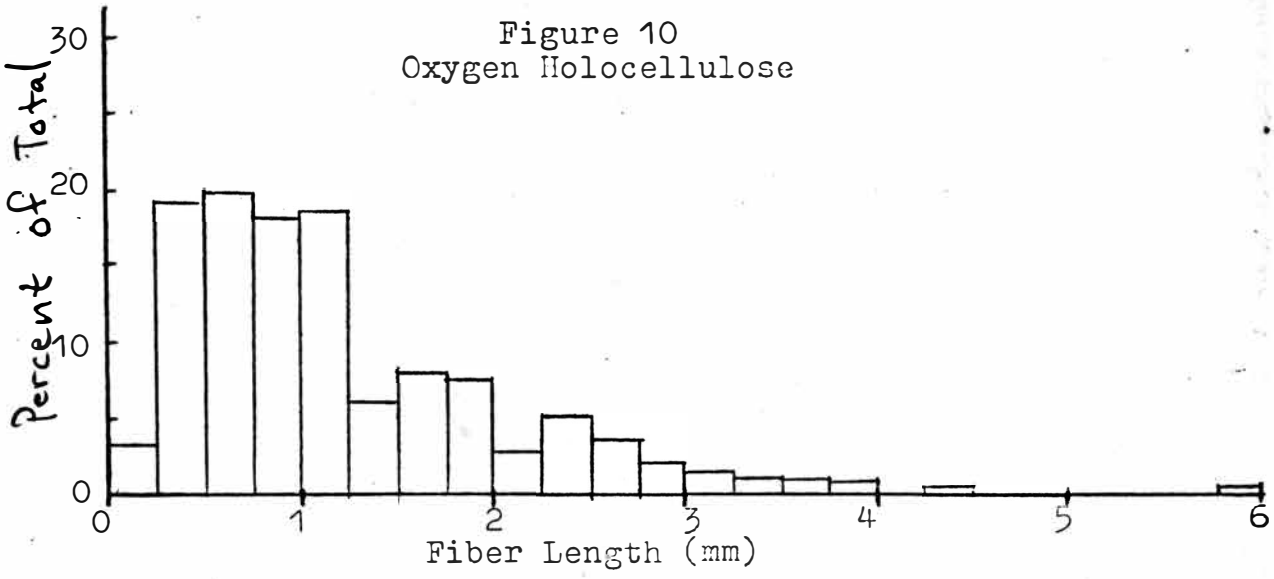


Figure 11
Kraft "Alpha" Pulp

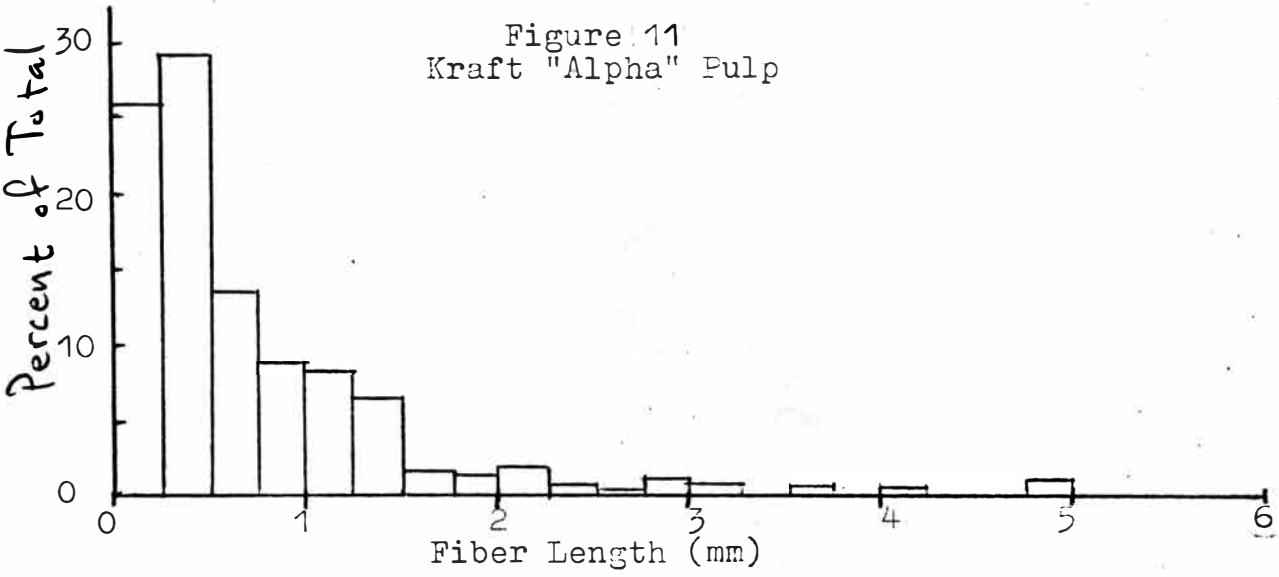
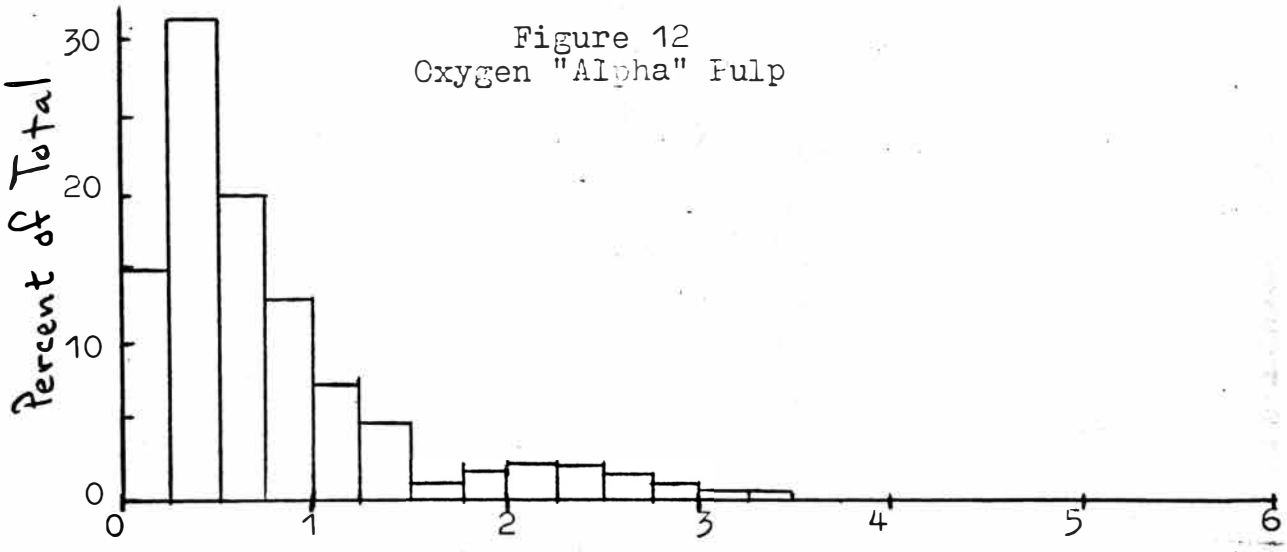


Figure 12
Oxygen "Alpha" Pulp



actual fiber length distribution for both pulps after each treatment. The results apperared to be contradictory. The fiber length index showed the kraft effective fiber length to have been longer than the oxygen except in the holocellulose. The actual fiber length results were exactly the opposite. Both methods gave values which were much lower after the final caustic treatment.

DISCUSSION OF RESULTS

After the two stage cooking process, the yield of the pulp was only one percent higher than that of the kraft pulp. This was not a significant increase, especially since the kappa number of the oxygen pulp was approximately seven points higher than that of the kraft. This means the increase in yield was probably due to the higher lignin content. The higher lignin content was desirable only if the final unbleached sheet properties of the oxygen pulp were equivalent to or better than those of the kraft pulp. The higher lignin content would also have a larger chemical consumption during bleaching.

The oxygen pulp demanded a much higher energy use than did the kraft pulp. The cooking times for the oxygen pulp were two hundred minutes at 170°C for the first stage and sixty minutes at 120°C for the second stage. The kraft pulp was at 170°C for only two hours. The oxygen pulp was refined more than the kraft pulp. For the oxygen pulp, it was necessary to make three passes through the refiner after the first stage and one pass after the final stage. The kraft cook required only one pass at the end of the cook. The oxygen pulping process consumed much more energy.

Bleaching the oxygen pulp gave a lower overall yield than did bleaching the kraft pulp. The total yield of fiber after beaching for the oxygen pulp was 47.2 percent based on the initial weight of oven dry chips. This was 1.3 percent lower than that of the kraft pulp. The initial advantage of a higher yield for oxygen pulp disappeared after bleaching. Bleaching the oxygen pulp removed 12.8 percent of the original material. Bleaching the kraft pulp under identical conditions removed only 8.7 percent of the original substance. This tends to support the previous statement that more lignin was present in the oxygen pulp. After bleaching both pulps, the lignin content for each pulp should be equal. Yet the total yield for the oxygen pulp was lower than that for the kraft pulp. This suggested a higher removal of other materials, such as hemicellulose or cellulose, during the pulping and bleaching of oxygen pulp.

The kraft and oxygen pulps reacted differently again when subjected to 18 percent NaOH. The amount of material that was present after bleaching was reduced by 21.4 percent after treatment with NaOH. This brought the final yield of oxygen material to 37.1 percent of the original weight of chips. When the kraft pulp was subjected to identical treatment, only 17 percent of the material was dissolved, and 40.2 percent of the original material remained. The 18 percent NaOH solution should have dissolved most of the hemicelluloses, having little effect on the cellulose. Assuming this to be true, a higher percent removal for the

oxygen pulp during this treatment means there originally was a higher percentage of hemicellulose in the oxygen pulp after bleaching than there was for the kraft.

The handsheets which were made from the pulps after each condition had high caliper and low density values. This was apparently due to the low level of refining and the low wet pressure used in forming the handsheets. Both types of handsheets were made under identical conditions. Nevertheless, the oxygen handsheets had a consistently lower caliper and higher density. This could have been explained if the oxygen pulp had better bondability than did the kraft pulp. The increase in density and decrease in caliper after the bleaching stage indicated a higher degree of bonding and perhaps some degradation of the fibers. The high calipers and low densities for the "alpha" cellulose portions indicated a very low level of bonding in these handsheets which is attributable to the very low hemicellulose content.

The brightness of the unbleached kraft pulp was higher than that of the oxygen pulp. Evidently the higher lignin content of the oxygen pulp lowered its brightness. After each pulp was bleached, both had approximately the same brightness. The opacity values seemed to correlate well with the other data. Opacity is directly related to the surface area of the fibers (or the number of air voids) present in the sheet. Since all of the handsheets had high bulk, all

of the opacity values were relatively high. The opacity values of the oxygen pulp before and after bleaching were lower than those of the kraft. This corresponded to the higher bondability of the oxygen pulp. This could be explained through the oxygen pulp having a higher hemicellulose content or because of a higher degree of degradation of the cellulose which would produce low molecular weight celluloses.

Physical testing of the handsheets showed the oxygen pulp to be stronger in most cases. The Instron tensile values showed the oxygen pulp handsheets to be stronger at every condition. Values from the tensile tester are dependent on the formation of the sheet, the individual fiber strengths, and the amount of bonding within the sheet. Since all handsheets were formed under identical conditions, formation should have caused little difference between the oxygen and kraft pulps. At this low degree of refining, the fiber strength probably had only a small effect on the tensile strength. As the fibers were refined or degraded more, the fibers became weaker and the amount of bonding increased. As this occurred, the strength of the fibers played an increasingly important role in tensile. For these samples, tensile was apparently dependent on the bonding. The oxygen pulp evidently made a sheet with a higher degree of bonding. Bleaching the pulps increased the tensile of each pulp. Bleaching apparently increased

the amount of bonding within the handsheet, as would be expected because the lignin has a lower degree of hydrogen bonding. The bleaching of the oxygen pulp had a much larger increase in tensile than did the bleaching of the kraft pulp. As expected, the tensile strength values of the "alpha" pulps were extremely low. The removal of most of the hemicellulose drastically reduced the bonding strengths of both pulps. The strength of the oxygen pulp remained a little higher, though.

The fold test again showed the oxygen pulp to be stronger than the kraft. Since the fold test is primarily a measure of fiber bonding, the osygen pulp apparently bonded better. The oxygen handsheets took at least three times as many folds before breaking as did the kraft. Both types of "alpha" handsheets were too weak to withstand any folds. The burst test is also dependent on bonding. Again the oxygen handsheets apparently had a strength superior to those of the kraft. Bleaching of both pulps increased their burst values. The oxygen pulp values increased much more than the kraft which indicated a larger increase in bondability due to bleaching, as would be expected due to the higher initial lignin content of the oxygen pulp.

The tear test showed the kraft handsheets to have superior strength in all cases. The tear value for the unbleached kraft handsheets was much higher than that of the oxygen. As the pulps were treated further, the tear

values became more comparable. The tear value is usually dependent on the number of fibers necessary to rupture, the number of bonds to break, and fiber length. Evidently, the higher tear value for the unbleached kraft indicated either stronger fibers, a different degree of bonding, or a difference in effective fiber length, or a combination of these three than that which occurred for the unbleached oxygen pulp. As the treatments continued, these properties for the two pulps apparently became similiar and the tear values became comparable.

The kappa numbers and the relative viscosity numbers for the two pulps at each condition gave a good indication of what types of components were in the fibers. The higher kappa number for the unnleached oxygen pulp implied a higher lignin content after pulping. The viscosities of the holocelluloses showed the oxygen value to be only about one-third as high as the kraft viscosity. This signified that the oxygen pulp had probably been degraded much more than the kraft pulp. It was very unlikely that degradation to this extent occured totally during the bleaching stage. this suggested the oxygen pulp was more severely degraded during pulping than was the kraft pulp. A difference in degradation was definitely true for the two pulps after the bleaching stage.

Measurement of the viscosity of the "alpha" pulp portion showed an increase in the relative viscosity for both pulps.

This increase suggested an increase in average molecular weight due to the removal of low molecular weight hemicellulose. This suggested that this fraction was now much lower in hemicellulose content. The treatment with 18 percent NaOH increased the relative viscosity of the kraft pulp by 2.8 cp, while it increased the oxygen pulps by 5.2 cp. The larger increase in viscosity for oxygen pulp insinuated there was probably more hemicellulose removed. This meant there had to have been a larger amount of hemicellulose present in the oxygen pulp after the bleaching stage than there was in the kraft pulp. The other possibility was that more of the kraft pulp was degraded during the caustic treatment. This would have decreased the amount of increase in viscosity. This should not have occurred to the extent necessary here since both pulps were subjected to identical treatments.

Viscosity values only give fair correlation with strength properties especially when comparing the viscosities of two different kinds of pulp. The use of these relative viscosity values along with the kappa numbers for the two pulps gave a good picture of their difference in composition. Initially both pulping systems used an identical fiber source. After pulping, the resulting kraft fibers were lower in lignin content, but the oxygen pulp was still more severely degraded. After bleaching both pulps, the kraft pulp showed a lower

amount of degradation and the oxygen pulp had a higher percentage of hemicellulose present. Removing the hemicellulose showed the oxygen "alpha" cellulose to have a higher degree of degradation.

With this type of chemical composition in mind, the physical dimensions of the fibers were observed. The oxygen pulp handsheets had a consistently hicher specific surface area. Bleaching the sample increased the specific surface of both oxygen and kraft pulps. Treatment of the bleached sample with HaOH reduced the specific surface area to its lowest value for both samples. For every sample, the specific surface area was lower than most literature values. This was because of the low level of refining applied to the pulp. A low specific surface was supposed to indicate a bulky sheet. This was certainly true for these samples. There was a documented, strong relationship between specific surface and the strength properties of paper. This was because specific surface was closely related to bonding potential. A linear regression analysis was run to look at the correlation between the values for specific surface and the results of the physical tests. This correlation was measured in terms of the regression coefficient (R^2). If the value of R was equal to one, the relationship was perfect. When R equalled zero, there was no correlation between the variables. A value greater than 0.9 was considered excellent,

while a value greater than 0.75 was believed to be a good correlation. Specific surface showed a correlation with tensile, fold, mullen and tear of 0.845, 0.817, 0.851, and 0.753 respectively. This showed good correlation with each test. Apparently, specific surface was a good indicator of bondability and strength.

Measurement of the specific volume for each type of pulp showed oxygen pulp with a higher value for the bleached and unbleached samples. Specific volume is the measure of the pulp swelling power. An increase in the amount of swelling will generally increase the strength properties. Swelling is normally increased by the removal of lignin or by increasing the hemicellulose content. The increase in specific volume after bleaching the oxygen pulp was explained by the removal of lignin. The volume decrease after bleaching the kraft pulp could possibly be explained by a removal of some hemicellulose. The higher swelling volume of the oxygen pulp over kraft pulp was probably due to its higher hemicellulose content or a more degraded cellulose. The low specific volume of the "alpha" pulps was expected because of their low hemicellulose content. A linear regression analysis of specific volume with the physical tests showed only fair to poor correlation. The specific volume was seemingly a poor indicator of the strength differences between the two pulps.

The freeness values of both pulps were high. This was

because the pulps were submitted to essentially no refining. The values for the oxygen pulp freeness were consistently lower than those for kraft. Since the actual values were so similar to each other, this only suggested the oxygen pulp was a little more refined.

By measuring the strength of the individual fibers, it was shown that the kraft fibers were stronger than the oxygen fibers. This was presumably due to the higher degradation of the oxygen pulp. As the kraft pulp was subjected to the other treatments, the fibers became increasingly weaker. For the oxygen pulp, bleaching the fibers seemed to make them a little stronger. The strength difference was minute. The "alpha" oxygen fibers were weaker than the other two stages. When a linear regression analysis was run to check correlation between the average fiber strength index and the physical handsheet strength tests, a poor correlation between the tests was found. This seemed to show that for these handsheets, the physical tests were not dependent on the strengths of the individual fibers. Correlations between the values for the fiber strength indes of the dry samples alone gave better, but not excellent, tesults. This was evidently due to the influence of bonding.

The bonding index showed the oxygen handsheets to have a higher percentage of bonding than the kraft at each condition. For both pulps, bleaching them increased the

bonding indes. The insoluble fraction had the lowest bonding index. The linear regression analysis was run to compare the bonding index with the physical testing results. The bonding index a a 0.930. 0.779, 0.893, and 0.928 correlation with tensile, fold, tear, and mullen, respectively. These values correlated well. For these handsheets, the physical tests seemed to be very dependent on bondability and seemed to be fairly independent of the individual fiber strength.

A conparison of the unbleached oxygen and kraft pulps showed the kraft fibers had a larger fiber length index and a shorter average fiber length. Evidently, the lower degree of bonding for the kraft pulp caused it to have a higher effective fiber length index even though the average fiber length was shorter. This seemed to be true for each condition. The pulp with the shorter average fiber length consistently had the lower fiber length index. A linear correlation showed the fiber length index to have approximately a 0.84 correlation with tensile, tear, and burst. Therefore these physical tests were somewhat dependent on the fiber length index. The holocellulose average fiber length values showed a large decrease in fiber length for the oxygen pulp and a small increase in kraft fiber length as compared to the unbleached pulps. Apparently, the bleaching process seemed to have a more degrading affect on the oxygen pulp. Treatment

of the holocellulose with 18 percent HaOH gave a fiber length that was only half the size. This decrease was probably due to some mechanical action. The treatment with caustic left the fibers somewhat stuck together in a gel. These fibers were then diluted and dispersed with a high speed mixer for a short time. It was assumed that this mechanical action had little effect of actual fiber properties. This assumption was apparently wrong.

With the above results, it is now possible to prove or disprove the hypotheses. The first hypothesis was that lignin will not affect the strength properties of oxygen pulp as much as it does for kraft pulp. It also states that the removal of lignin in oxygen pulps will not change the handsheet properties as drastically as for kraft pulps. The oxygen pulp initially had a higher lignin content than the kraft. Even with the high lignin content, the oxygen pulp had stronger handsheet properties. This suggested a lesser effect by lignin. But when the lignin was removed from the two pulps by bleaching, the strength properties of the oxygen pulp appeared to have been retarded more by the lignin. For both pulps, the tensile, tear, fold, and burst values increases after bleaching, but the oxygen handsheet values increased to a greater extent. Along with the physical tests, the values for specific surface, bonding index, and density increased with bleaching. These results disproved

the hypothesis thatlignin will not affect the strength properties of oxygen pulp as much as it does for kraft pulp.

The second hypothesis was that oxygen pulps will have a higher hemicellulose content at an equivalent yield. This will give the oxygen pulp a greater bonding ability than kraft pulp. The results showed this typothesis to be true. Treatment of the bleached pulp with 18 percent NaOH resulted in a higher weight loss for the oxygen pulp than for the kraft pulp. This weight loss should have been related to the amount of hemicellulose or degraded cellulose present. Therefore, the oxygen pulp contained more hemicellulose than did the kraft pulp. Viscosity values for the bleached and insoluble fractions supported the higher removal of hemicellulose for the oxygen pulp. The oxygen pulp had a larger increase in relative viscosity after hemicellulose removal than did the kraft pulp. The higher hemicellulose content of oxygen pulp was also shown by its higher bonding ability. The higher values than kraft for bonding index, density, tensile, fold, burst, and specific volume indicated better bonding ability and therefore a higher hemicellulose content. The lower caliper and poacity values also showed this.

The third typothesis was that oxygen pulp cellulose will be more degraded. The oxygen pulp will have shorter, weaker fibers. The relative viscosity values showed the oxygen pulp to have a lower viscosity than kraft for both

the holocellulose and the "alpha" pulp. Since the "alpha" cellulose was basically cellulose, the viscosity values indicated the oxygen pulp to be much more degraded. The zero span tensile tester showed the oxygen pulp fibers to have a lower fiber strength index than the kraft pulp. The individual pulp fibers were weaker than the kraft fibers. This suggested higher degradation during the oxygen pulping process. The fiber length index defined the kraft fibers as having a higher effective length than the oxygen pulp after pulping. This meant the kraft fibers were degraded less during pulping. The osygen pulp fibers actually had a longer average length. The higher tear values for kraft pulp also imply that the fibers are stronger and less degraded. These results showed the third hypothesis bo basically true. The oxygen pulp did have weaker fibers than does kraft pulp, but the fibers were usually longer.

Finally, the last hypothesis was that due to the severe cooking conditions, the oxygen pulp will have more surface area. This surface area will give it better bondability than for kraft pulp. For this study, all specific surface area values were low. This was because of the low level of refining. The oxygen pulp still had a consistently higher specific surface value than kraft pulp. A linear regression analysis showed a 0.917 correlation between specific surface and the bonding index. Therefore, the increase in

specific surface increased the bondability of the pulp. The higher specific surface for the oxygen pulp gave it better bonding properties than for the kraft. This was verified by the results of the physical testing of the handsheets. All these results proved the final hypothesis to be true.

Most of the results from this study were consistent with what was found in literature. This oxygen pulp showed a small increase in yield over the kraft pulp and a lower overall yield after bleaching. The oxygen pulp fibers also had a higher hemicellulose content and a higher degree of degradation. The presence of lignin seemed to have more of a hinderin effect on the oxygen pulp than on the kraft. Therefore, bleaching the pulps increased the stength of the oxygen pulp handsheets more. The oxygen pulp handsheets had a higher density and a lower tear strength than did the kraft. All of the above results agreed with literature results The biggest contradiction occurred with the stronger oxygen pulp handsheets. his diffe ence was probabl due to the low degree of refining used in this study.

The oxygen pulp was shown to have more degradation than the kraft pulp. This higher degree of degradation gave the oxygen pulp the following properties: a higher specific surface area, a higher specific volume, lower viscosity values, a higher percentage of bonding, and weaker

individual fiber strength. The oxygen pulp also had a higher hemicellulose content. This caused the fibers to have a higher specific volume and better bondability.

CONCLUSIONS

Pulping identical chips using a kraft and an oxygen pulping system, and first removing the lignin and then the hemicellulose, provided a good means of looking at the strength differences between the two pulps in terms of their individual fibers. Analysis of the two pulps in this manner showed the unbleached oxygen pulp had a much higher degradation than the kraft pulp. This even ossured on an oxygen pulp with a lignin content higher than of the kraft pulp. The high degradation of the oxygen pulp was attributed to a longer cooking time and contact time with oxygen and alkali.

The unbleached kraft pulp had a longer fiber length index. The kraft fiber was significantly stronger than the oxygen fiber. This also indicated a lower amount of degradation for the kraft fiber. The oxygen fibers did have a higher ability to bond. The weakening of the fibers by oxidation resulted in a corresponding increase in ability to bond.

Bleaching the two pulps showed a large decrease in fiber length index for the kraft pulp and only a small dearease for the oxygen pulp. The average fiber length values showed just the opposite. This was accompanied by a large decrease

in individual fiber strength for the kraft fibers with no decrease at all for the strength of the oxygen fibers. The fiber strength still remained higher for the kraft fibers. Bleaching increased the bondability for both pulps with the oxygen pulp retaining its higher bondability value. The higher bondability increase along with the corresponding increase in specific surface area suggested that the removal of lignin left more areas available for bonding on the oxygen fibers than it did for the kraft fibers. This larger degree of bonding could also be due to the larger hemicellulose content of the bleached oxygen pulp. The larger hemicellulose content probably caused the oxygen pulp to have more swelling power. Also, the oxygen holocellulose was much more degraded than the kraft holocellulose.

Treatment of the two pulps with caustic showed the oxygen cellulose to be weaker than the kraft. This along with the shorter fiber length index implied that the oxygen cellulose was much more degraded. This was supported by lower relative viscosity values.

The physical tests showed the oxygen pulp handsheets to be stronger than the kraft except for tear strength. This indicated that the oxygen pulp had a much higher bondability and shorter fibers. This conclusion correlated well with what was found when looking at the fibers on more of an individual scale. The individual oxygen fibers were weaker, yet the handsheets were stronger. Apparently the oxygen

pulping caused more severe degradation of the fibers. The fibers were weaker, but the bondability of the fibers became greater. The higher bondability accounted for the increase in burst, tensile, and fold, while the weak, short fibers accounted for the decrease in tear.

This study showed that even in presence of lignin, the oxygen handshee s were stronger than the kraft. Removal of his lignin caused the oxygen handsheets to be even stronger. The oxygen pulps had a higher hemicellulose content. This accounted for its higher bondability and strength as compared to the kraft pulp. The oxygen pulping process caused more degradation than the kraft process. The resulting fiber index was lower and the fibers were weaker than those from the kraft process. The severe cooking condi ions increased the surface area of the fibers, possibly through degradation. This resulted in an oxygen pulp with better bondability than was found for the kraft pulp.

RECOMMENDATIONS

In this report, the values for lignin content, hemicellulose content, and cellulose content were all qualitative. It would be interesting to do the same type of study looking at the exact values for the quantities of components present.

Since the oxygen pulp had a much higher bonding ability than the kraft pulp, another recommendation would be to look at various combinations of kraft and oxygen pulp to observe their effects on strength. The conbination of high bonding ability with stronger fibers should give a strong paper.

Between the two stages of the oxygen pulping process, much che mical and energy is wasted. After the soda cook was finished the liquor was blown from the digester and the chips were washed. The chips were then refined, recharged with chemical, and brought to temperature again in the presence of oxygen. A process should be developed which could refine the chips between the two stages under high temperatures and pressures to eliminate the energy loss. This would also decrease the amount of chemical which would have to be added for the final stage.

LITERATURE CITED

1. Abrahamsson, K., and Samuelson, O., Svensk Papperstidning 78 (11): 417-21 Aug. 25, 1975

2. Carles, J. E., Angelier, R., and Monzre, P., ATIP Rev. 27 no. 5/6 385-97 1973 (Abstract)

3. Chang, H-M, Gratzl, J. S., McKean, W. T., Tappi 57 (5): 123-6 May, 1974

4. Chang, H-M, Gratzl, J. S., McKean, W. T., Reeves, R. H., and Stockman, V. E. Tappi 59 (8): 72-5 Aug., 1976

5. Chang, H-M, McKean, W. T., Gratzl, J. S., and Lin, C. K., Tappi 56 (9): 116-9 Sept. 1973

6. Chan, H-M, McKean, W. T., and Seay, S., Tappi 56 (5): 105-8 May, 1973

7. Connors, W. J., and Sanyer, N., Tappi 58 (2): 80-2 Feb., 1975

8. Cowan, W. F., Pulp and Paper Magazine of Canada 71 (9) 63-6 May 1, 1970

9. Cowan, W. F., and Cowdrey, J. K., Tappi 57 (2): 90-3 Feb., 1974

10. Hata, K., and Sogo, M., Japan Tappi 27 (5): 231-7 May, 1973 (Abstract)

11. Hata, K., and Sogo, M., Tappi 58 (2): 72-5 Feb., 1975

12. Jamieson, A. G., Samuelson, O., and Smedman, L. A., Tappi 58 (2): 68-71 Feb., 1975

13. Kellogg, R. M., and Wangaard, F. F., Tappi 47 (6): 36;-7 June 1964

14. Kleinert, T. N., Tappi 59 (9): 122-4 Sept., 1976

15. Lindstrom, L., and Samuelson, O., Tappi 58 (7): 146-9 July, 1975

16. Marton, R., Leopold, B., Kartovanra, K., and Koeppicus, R., "Canadian Wood Chemistry Symposium" 4: 45-7 July 4-6, 1973 (Abstract)

17. Minor, J., and Sanyer, N., Tappi 57 (5): 120-2 May, 1974

18. Minor, J. L., and Sanyer, N., Tappi 58 (3): 116-9 March, 197

19. Nakamura, M., and Matsuura, H., Tappi 58 (4): 98-102 April, 1975

20. Phillips, R. B., and McIntosh, D. C., Tappi 58 (2): 76-9 Feb., 1975

21. Robertson, A. A., Svensk Papperstidning 66 (12): 477-97 June 30, 1963

22. Saukkonen, M., and Palenius, I., Tappi 58 (7): 117-20 July, 1975

23. Sogo, M., and Hata, K., Japan Tappi 27 (4): 171-81 April, 1973 (Abstract)