AN ABSTRACT OF THE THESIS OF

MONTREE PROMACHOTIKOOL for the degree of MASTER OF SCIENCE

in FOREST PRODUCTS presented on May 5, 1978

Title: THE EFFECT OF WOOD DENSITY ON THE KRAFT PULPING PROPERTIES OF DOUGLAS-FIR (PSEUDOTSUGA MENZIESII (MIRB.) FRANCO)

Abstract approved: Redacted for privacy

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Three samples of different wood densities of Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) were cooked by the kraft process. The yields and the Kappa numbers were studied to establish the rates and the energies of activation of the pulping and delignification reactions respectively. Wood properties did not show significant effects on the pulping reactions compared to the effects of time and temperature. However, their influences on delignification was greater than on pulping reactions.

The intermediate density wood sample which had the lowest amount of lignin and the highest amount of sapwood underwent the most delignification and showed the highest yields. Heartwood penetrability affected the pulping reactions in the beginning stages and became less effective at higher temperatures and longer cooking times. Fluoro-

metric analysis was used to measure the lignin in the waste liquors and linear relationships between fluorescent intensities and cooking times were found at 165^{o} and 175^{o}C. These results agreed with the relationships of Kappa numbers to cooking times for each wood sample. A non-linear relationship between fluorescent intensities of waste liquors to cooking times were found at 185^{o}C which may be due to lignin condensation reactions.

Wood density influenced the physical strength properties of handsheets. Paper made from low density wood pulp had higher tensile strength, bursting strength and folding endurance, but the paper from high density wood pulp showed higher tearing resistance.

The Effect of Wood Density on the Kraft Pulping Properties of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco)

by

Montree Promachotikool

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Commencement June 1979

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ACKNOWLEDGMENT

I would like to express my sincere gratitude and deep appreciation to Dr. Walter J. Bublitz, my major professor, for his kindly assistance, encouragement, guidance and valuable suggestions during the courses and the work of this study.

I am grateful to Dr. Milford D. McKimmy and Dr. Richard W. Thies, my member committees, for their reading the thesis critically and offering advice for revisions.

My gratitude would also extend to Dr. Paul N. Hinz for his assistance in statistical analysis and to Dr. Helmuth Resch who gave me a chance for working on this study.

Special thanks and gratitude extends to Mr. Jerry L. Hull for his help and suggestions in experimental procedure.

The deepest gratitude is expressed to the people of Thailand and the Royal Thai Government Civil Service Commission for their financial support until the end of the study.

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INTRODUCTION

Although many studies of the mechanism of pulping processes have been performed in the past, these mechanisms are not completely understood today. Part of our lack of understanding is due to inadequacy of the correct chemical structure of the lignin molecule and the delignification reactions that occur during the pulping process. Additionally, variations in wood quality occur naturally, and the effect of these variations on pulping response is not completely understood.

Wood density has been used for many years as perhaps the single most important parameter of wood quality. It is a property that is relatively easy to measure, and it has been shown to be very significant to the lumber industry and other consumers of wood in terms of its effect on wood behavior. As a consequence, foresters and genetecists tend to consider the growing and breeding of trees primarily in terms of this one wood parameter, and high density wood is normally preferred to low density wood. This concept holds true in the paper industry also; one example is that since a digester has a limited volume, filling a digester with high density chips means that more dry weight of wood can be charged per batch than if filled with low density wood chips. In turn, this means more pulp production

per batch if high density wood is used, if the assumption is made that the gravimetric pulp yield, calculated as a percent of the wood input, is the same for all chips regardless of wood density. Little information exists in the literature to verify this assumption.

The purpose of this research project was to investigate the role that wood density plays in pulp production. While there is no argument that high density wood chips increase the volumetric yield of a digester if gravimetric yields are constant, other aspects of pulping high density wood are less well understood. Little is known about pulping (delignification) rates of wood as they may be affected by density, or about the yield - residual lignin relationship as a function of wood density. It has been shown that differences in pulp strength properties can be attributed to differences in the parent wood density, although this relationship has not been thoroughly investigated. If it were shown that wood density did not greatly influence the pulping responses, other wood parameters would be examined, such as Klason lignin content or permeability, in order to establish which factors most significantly affect the response of wood to pulping conditions. In the most fundamental terms, the response can be expressed in terms of the relative rates of delignification as they are affected by variations in the process parameters of time and temperature.

The goals of this thesis were:

1) To study (by pulping at different times and temperatures) the various facets of pulping response of Douglas-fir chips, such as rate of delignification and pulping reaction, activation energy of delignification and pulping reaction, yield-lignin relationships and chemical makeups of the pulps, as they might be affected by variations in wood quality.
2) To study the kraft pulping response of Douglas-fir chips using the flurometric analysis of the waste liquor as an analytical tool for detecting dissolved lignin.
3) To compare strength properties of the pulps from the different wood samples under comparable conditions of pulp preparation.

LITERATURE REVIEW

Mechanism of Alkaline and Kraft Delignification

Basic studies of the mechanism of kraft pulping have been continuing since the early 1910's, including research in the mechanism of delignification. Sutermeister (62) first studied the mechanism of pulping and found a linear relationship between the removal of wood and sodium hydroxide consumption. Later in 1926, Arrhenius (2) proposed a first order reaction for the alkaline and kraft pulping processes. However, Bray (17), Lewis and Laughlin (67) indicated that the first order law has certain limits when applied to the pulping process. Although some investigators (67, 77) have observed that deviations from this principle are particularly serious during the end of cooking stages, alkaline and kraft delignification is generally believed to follow first order reaction principles (22, 30, 56, 62, 64). Kleinert (56, 57) proposed that free radical mechanisms may be involved in the alkaline delignification of wood.

Studies of the physical mechanism of pulping suggest that it is controlled by penetration and diffusion theories (53, 63, 72, 82). Stamm (87) in 1953 also stated that the rate of absorption of cooking liquors by wood chips is controlled by the rate of diffusion of water vapor into the capillary structure through the cell walls. However, Kulkarni and Nolan (62) in 1955, suggested that delignifi-

cation takes place at a moving interface as the cooking liquor penetrates into the wood. Several investigators, however, believe in penetration and diffusion theories (87, 92, 93). Moreover in 1962, Hartler and Onisko (44, 45) studied sulfate pulping and concluded that the data supported the diffusion theory as opposed to the moving interface theory. In another study, Wilder and Daleski, Jr. (102) reviewed five steps of the overall reaction process that should be considered: (1) penetration of the liquid into the void spaces of the chip, (2) molecular diffusion of the reactant chemicals that are consumed by the chips, (3) the actual chemical reactions with the wood components, (4) desorption of the reaction products and (5) diffusion of the desorbed reaction products out of the chips. Recently, Kleinert and Marraccini (55) confirmed that diffusion phenomena, as well as pressure, temperature, and liquor-to wood ratio, are the major factors in penetration of alkali into the wood.

Chip Thickness

According to the penetration and diffusion theory, chip thickness is one of the important factors controlling the degree of penetration of cooking liquor into chips (45). As a result of his experiments, Richardson (82) found that alkaline solutions had almost equal diffusion rates in the longitudinal and perpendicular directions to the axis of wood. From this information, the optimum size

of chip dimensions has been studied. Larocque and Maass (63, 64) studied the rate of delignification of different chip sizes (2, 10, 15 and 20 mm. thick) and concluded that, up to 10 mm., chip thickness had no influence on delignification rates. Backman in 1946 (3, 14) suggested that chips of 3 mm. (1/8 inch) thickness are the optimum size for efficient delignification. His studies show that chemical concentration in the liquor has to be increased with increasing chip thickness to assure a constant rate of delignification.

Later, Bland and Batterham (13) concluded that if any of the chip dimensions were less than 3.1 mm. (1/8 inch), variations of the other two dimensions would have negligible influence on delignification. Moreover, the importance of chip thickness has been emphasized by Kulkarni and Nolan (62) who stated that both the overall reaction and delignification rates are increased as chip thickness decreases.

Density

Lusby and Maass (72) stated that variations of wood density had no influence on the rate of diffusion of sodium hydroxide into chips. Moreover, Larocque and Maass (63, 64) observed that the variations in the density of wood had no effect on delignification rates. They anticipated that high density wood contained a high lignin content based on their observations that higher lignin content pulp was

obtained from high density wood. Worster and Sugiyama (107), comparing pulp mill and saw mill Douglas-fir chips, suggested that longer cooking times may be necessary with higher density wood and also with higher lignin content wood. However, delignification rates can be influenced by wide variations of wood density (105, 63). Stone and Green (93), and Clayton (24) indicated that penetration rates are not affected by wood density, but ionic diffusion of chamical movement into wood varies somewhat with wood density. Thus, wood density has almost no effect on the rates of delignification compared to the penetration rate, chemical concentration in the liquor, and the temperature of pulping.

Permeability

According to Stone (92), penetration of cooking liquor is not only controlled by the operating conditions such as the pressure applied, temperature, and viscosity of the liquor, but also is dependent on the permeability of wood which is affected by wood structure. He also stated that there was still no method for the determination and expressing penetrabilities on a quantitative basis. As a result, liquid and air permeabilities should be the simple methods for evaluation of penetrabilities of cooking liquor. Moreover, Bublitz and Blackman (20) in 1971, proposed that decreasing permeability of wood reduces penetration and

delignification of Douglas-fir chips by the kraft process.

Numerous studies of permeability of wood have been reported over many years. Bell and Cameron (10) applied Poiseuille's equation to study the movement of water and solutions through porous materials. Stamm (80, 88-91), assuming that the flow of liquid through capillary structure of wood is laminar, proposed that Poiseuille's equation be used to calculate the rate of fluid flow. This equation was applied to study the penetration of cooking liquor to wood for pulping by several investigators (53, 87, 92). However, Poiseuille's equation cannot be applied accurately with gas flow. This is due to the fact that molecular slip of gas flow through pit pores occurs when the mean free path of gas molecules becomes larger than the diameter of a capillary through which flow occurs (80, 81, 91). In addition, Darcy's law was used on an expression of the permeability of gas and liquids to wood (15, 26, 71). However, it was found that contrary to Darcy's law, liquid flow rate through heartwood decreases with time (16, 53). Gramhall (16) in 1971, proposed the correction factor to the Darcy's equation with reducing exponential with depth of penetration. Miller (76) developed a method of visual estimation to measure the penetrability of Douglas-fir. This method was applied to measure the permeabilities of refractory and permeable Douglas-fir heartwoods as they related to the pulping rate of wood by Bublitz and Blackman

(20). Moreover, Graham (40) also developed a sink-float test for estimating the permeability of Douglas-fir.

As was true for pulping liquors (24, 93), several investigators found that liquid permeability had no relationship to wood density (15, 37, 58, 76). Blackman (12) in 1970 showed that refractory Douglas-fir heartwood undergoes less delignification than permeable Douglas-fir heartwood, and that refractory Douglas-fir heartwood is significantly denser than permeable Douglas-fir heartwood.

Influence of Wood Structure on Delignification and Permeability

Wood structure is generally accepted as being one of the most important factors on pulping delignification rates. The factors that should be considered are the bordered pits, sapwood and heartwood, resin canals, earlywood and latewood, tracheid dimensions, and ray cells.

A. Bordered Pit Structure

In 1913, Bailey (29) showed that carbon black suspensions moved through wood by transfer from one fiber to another through the adjacent pits. As a result, it is generally accepted that one of the important factors influencing wood permeability is the pit structure. Cote' and Krahmer also confirmed this theory by electron microscope examination (29). Wardrop and Davies (100) proposed that the penetration of pulping liquors proceeds through

the ends of opening fibers and from cell to cell with lateral movement through the rays. However, Griffin (60) in 1919 established the concept of pit aspiration controlling the degree of penetration of liquid into conifers. Later it has been generally accepted that the torus can, under certain conditions, seal the pit aperture and form aspirated pits. This situation is believed to decrease the flow of liquids and gas through wood (5, 69, 70, 75). Phillips in 1933 (5, 43), found that the degree of pit aspiration was related to moisture content, position in the growth ring, and distance from the pith. He also observed that the unaspirated pit increases with increasing wall thickness. Moreover, Erickson and Crawford (35), and Krahmer and Cote' (60) found that pit aspirations of sapwood can occur during drying of wood. It was observed that pit aspiration does not occur in coniferous sapwood when the water is replaced by alcohol prior to drying (35, 68). They concluded that pit aspiration during drying of wood may be due to the surface tension of the capillary fluid. Hart and Thomas (43) in 1967 discussed the mechanism of aspiration that occurs due to liquid tension. Comstock and Cote' (28) proposed three factors that may control pit aspiration, (1) surface tension forces due to liquid evaporation, (2) stiffness of the pit membrane that opposes the surface tension forces, (3) adhesion of the torus to the pit border that occurs when they are brought into contact

with each other by surface tension. In contrast, Estep (37) found little or no additional pit aspiration occurring during seasoning of Douglas-fir heartwood.

B. Sapwood and Heartwood

According to Wellwood (102), pulping qualities of sapwood and heartwood are different because of the presence or absence of extraneous materials. As revealed by Wardrop and Davies (100), the pit structure is the path by which pulping media can can come into contact with the middle lamella. Stemsrud (101) in 1956, found that the penetrability of liquids in heartwood is decreased as a result of aspiration of the pits and the incrustation of the torus and membrane. From the study of air permeability and creosote retention of sapwood and heartwood of Douglas-fir, Koran (58) proposed that the presence of extraneous materials in the capillary structure of included sapwood and true heartwood in the opening of the pit membrane causes the reduction of penetration.

Moreover, Krahmer and Cote' (60) found that the change of pit structure associated with heartwood formation and with the resultant decreased permeability is due to pit aspiration, pit occlusion with extractives, and pit incrustation with ligninlike substances. They also stated that aspirated pits of sapwood may occur during drying, but that the permeability of sapwood was still higher than

that of heatwood. The approximate ratio of air permeability of early sapwood to late heartwood for Douglas-fir was 34 to one. Graham in 1964 (39), studied air permeability and also observed the same result for sapwood and heartwood of Douglas-fir. Recently, Bailey and Preston (6) confirmed that the low permeability of Douglas-fir heartwood, both longitudinally and laterally, is caused by the presence of extractives.

C. Resin Canals

The main channels for the longitudinal movement of liquids and air through wood are the tracheids and resin ducts in Douglas-fir. However, it was stated that resin ducts are not effective for the movement of material over the complete penetration. This is because they are occluded with resin (59, 87, 91). Erickson and Crawford (35) in 1959, indicated that resin canals cannot contribute significantly to liquid penetration. Moreover, Koran (58) in 1964, found that neither creosote nor air permeability was influenced by the amount of longitudinal resin canals in refractory Douglas-fir. Erickson and Balatinecz (36) found that resin canals have a monor effect on the longitudinal permeability of Douglas-fir.

However, it has been reported that woods with longitudinal resin canals such as Japanese red pine (Pinus densifolia Sieb. et Zucc.) and Monterey pine (Pinus radiata

D. Don) had higher permeability than those without resin canals (86).

D. Earlywood and Latewood

In general, earlywood tracheids have larger and greater amounts of pits than latewood tracheids (86). However, Phillips (5) in 1933, found that the percentage of unaspirated pits increased with wall thickness across the ring from springwood to summerwood. He discussed that the resistance to unaspirated pits of summerwood is due to the greater rigidity of the summerwood pit membrane. Erickson and Crawford (35) also showed that dye solutions passed through springwood and summerwood at the same speed in green wood, but after seasoning, the dye moved more rapidly through summerwood than through springwood. In contrast to Koran (58), he stated that the percent summerwood did not have an influence on creosote retention or air permeability. Liese and Bauch (68) in 1967, studied the adhesion forces of pit membranes and they found that aspirated pits occur in springwood of Pinaceae when the surface tension of water is about 26 dynes/cm. They also stated that the adhesion force for closing the pit in summerwood is higher and the surface tension of water is not high enough to produce aspirated pits in summerwood tracheids. They indicated the other reason is the stiffness of latewood pit tracheids.

Bramhall (15) found higher permeability in latewood than in earlywood Douglas-fir; also the permeability of latewood was not influenced by the drying method, but the permeability of earlywood was considerably increased by low-surface-tension drying. Recently, Meyer (75) also confirmed that sapwood earlywood longitudinal gas permeability increases during seasoning of wood because more pit aspiration takes place.

E. Tracheid Dimensions

Although the permeable and refractory Douglas-fir were found to have the same diameters of bordered pits, Krahmer (59) showed that the average fiber length of the permeable wood is significantly longer than that of the refractory wood. Liese and Bauch (69) stated that the differences of permeability in Douglas-fir are related to the length and cross-sectional area of the tracheids as well as the condition of the bordered pits. Moreover, Meyer (75) indicated that, considering only tracheid length, longer tracheids have higher permeabilities than shorter tracheids, because longer tracheids have more pits to permit fluids to pass through more rapidly. On the other hand, Koran (58) found that fiber length was not a major factor in determining the air permeability or creosote retention of mountain form Douglas-fir.

F. Ray Cells

According to Wardrop and Davies (100), lateral penetration takes place through the rays, and the ray parenchyma were apparently more easily penetrated than the ray tracheids. Bailey (100) in 1913 and later Schulze and Theden (101) stated that ray cells may play a significant factor in the lateral movement of liquids in conifers. Sargent (84) studied the movement of creosote into coniferous heartwood and also found that the rays were good passageways for penetration. In an anatomical view, Krahmer (60) pointed out that since every longitudinal element is in contact with one or more rays, the influence of rays could be considerable. Moreover, Jensen et. al. (52) showed that radial penetration was greater than tangential penetration because of the lateral penetration through the rays. Behr et. al. (9) showed that oil flows through ray parenchyma cells to longitudinal tracheid via simple pit pairs and half bordered pit pairs. In Douglas-fir, however, the radial penetrability is reduced by heavily incrusted ray tracheids in sapwood (69). In addition, Bailey and Preston (6) studied permeability of Douglas-fir and found no movement of silver nitrate and hydrazine hydrochloride solution taking place through the pits between longitudinal and ray cells. They also indicated that the rays are of little significance in the penetration in the radial direction.

Influence of Chemical Constituents on Delignification Rates

A. Lignin

According to Rydholm (83), rate of delignification also depends on variation of lignin content of wood. Erickson and Arima (85) found that the lignin content in Douglas-fir decreases radially from the pith to a constant level in the outer region of the trunk. In addition, Marton (74) stated that the distribution of the cell wall components has an important effect on the delignification rate. Earlier, Ritter (11) stated that 75% of the lignin is in the middle lamella and the other 25% is in the primary and secondary walls. In 1936, Bailey (4) showed that the middle lamella contained 71% lignin, 14% pentosan, and 4% cellulose. Szabo and Goring (94) applied the Flory theory of trifunctional polymerization in reverse to the problem of lignin degradation during pulping, and stated that lignins in the middle lamella and in the secondary wall have different rates of delignification. It was found that lignin is removed from the secondary wall first and then it was dissolved rapidly from the middle lamella at about the 50% point of delignification (78). However, this observation is in contrast to Bixler's findings (74), that lignin was removed first from the middle lamella during alkaline pulping.

B. Hemicellulose

Several investigators have found a large amount of carbohydrates, largely hemicellulose, removed at the start of the cook (103). Collier (25) in 1960, proposed the mechanism that hemicellulose is removed by the stepwise end-group degradation in alkaline pulping. Procter et. al. (78) suggested that the rate of lignin removal from the secondary wall may be related to the rate of hemicellulose removal. Moreover, several investigators proposed that the removal of hemicellulose may play an important role in the diffusion of lignin being removed from the cell wall. Recently, Kerr and Goring (54) stated that hemicellulose removal has a major effect on chemical pulping. They also showed that the removal of hemicelluloses increased both the pore size in the cell wall and the rate of delignification.

C. Extractives

Janes (51) stated that extractives may reduce the penetrability of pulping chemicals by plugging pit openings in fibers. Several investigators also indicated that water permeability of Douglas-fir increased following extraction with organic solvents or hot water (60, 76). Nevertheless, Koran (58) found that higher extractive content contributed to higher creosote retention. However, Rydholm (83) stated that the effect of extractives on

penetration in alkaline pulping is insignificant, since extractives can dissolve easily in alkaline pulping liquor.

Influence of Cooking Operation Upon Delignification Rates

A. Concentration of Cooking Chemicals

It is well known that the rate of delignification is dependent on the concentration of hydroxyl and hydrosulfide ions in the cooking liquor (24, 83). Larocque and Maass (64) found that the rate constants for delignification during soda pulping are directly proportional to alkali concentration. According to the diffusion mechanism of chemical transport within the chip, alkali solutions swell wood to the point where ions diffuse through the water and through the wood at almost the same rate in all three directions under the influence of a concentration gradient (24, 103). Bray (17), and Lewis and Laughlin (67) showed that alkali consumption has a linear relationship with the degree of carbohydrate removal during pulping. However, a rather complex relationship between free alkali consumption and degree of delignification was found in later studies (103).

B. Temperature and Time

According to Clayton (24), when pulping to constant pulp quality, temperature and time are interdependent

variables; the higher the cooking temperature the shorter the cooking time. Several investigators stated that increasing the temperature increases the rate of pulping reaction (30, 64, 72, 103). They also found that the removal rate of lignin is approximately doubled by a $10^{o}C$ increase in temperature (64, 103). Moreover, it was showed that the rate of diffusion of solutes into wood increases with increasing temperature (72, 87). Recently, Vroom (97), developed a numerical value called H factor to express cooking times and temperatures as a single variable. However, Enkvist (34) stated that delignification is much slower at low temperature ($140^{o}C$) and Kleinert (74) noted that bulk delignification is complete within ten minutes reaction time at high temperature ($185^{o}C$).

Kinetic Study of Alkaline and Kraft Pulping

Arrhenius (2) first observed that the amount of lignin dissolving in the cooking liquor at any time is proportional to the amount of residual lignin in the wood. He proposed that the delignification reaction is a first order reaction, that relates to temperature, and obtained the equation:

$$\ln k = B - E/RT$$

k = reaction rate

B = constant

E = energy of activation

T = absolute temperature

R = gas constant

Later, Larocque and Maass (64) calculated the activation energy of alkaline delignification. The value is found to be 32,000 cal./mole.

Determination of Degree of Delignification by the Kappa Number Test

Wiles (95) in 1934 first proposed that the oxidation of lignin in pulp by acid potassium permanganate could be used as a measurement of cooking delignification. However, it was observed by several investigators (95) that there is a downward curvature instead of linear relationship between permanganate number and lignin content in pulp. Hinrichs (48) found that the lignin content in kraft Douglas-fir pulps can be predicted by permanganate number up to a value of 40. Tasman and Berzins (95) proposed the correction factors of permanganate numbers and called the corrected ones KAPPA numbers. They stated that a straight line relationship occurs between the Kappa numbers and Klason lignin contents for both kraft and sulfite pulps up to approximately 22% lignin content for softwoods and 15%

lignin content for hardwoods. They also indicated that the lignin content can be predicted from the following relationship:

KAPPA number x 0.13 = Klason lignin content, %

Determination of Lignin Content by Fluorescence

According to Wade, Turner, and Ewing:

> "The phenomenon of fluorescence can be described as being the essentially instantaneous emission of light from a molecule which has absorbed light (96). A photon, which is a discrete packet of energy, is absorbed by a molecule, and the increased energy content of the molecule serves to excite certain electrons and shift them from the ground state (S_0) to higher energy levels (S_1, S_2,...S_N) (38). However, the energy which a molecule gains upon absorption of a photon does not remain in that molecule, but is lost through any of a number of mechanisms. Of particular importance to fluorescence is the loss of energy through heat. Excited molecules acquire extra vibrational energy as well as electronic energy, and these molecules will collide, generating heat through friction, and lower the energy of the molecule to the lowest vibrational state within the same electronic (singlet) level (38). This radiationless loss of energy leaves the molecule in an excited electronic state, and the molecule will then return to the ground state (S_0) by radiating the remainder of the energy through the emission of a photon. This photon contains less energy than that which initially excited the molecule, and the radiation is emitted at a longer wavelength (98)."

Therefore for dilute solutions, the fluorescent intensity is directly proportional to the chemical concentration (41). Several investigators have indicated that fluorometry may detect lignin sulfonate in pulping waste liquor (23, 106).

However, the fluorescent intensity of pulping waste liquors and the excitation wavelengths of maximum intensity are affected by pH, temperature, concentration of the sample, and pulping parameters (98). Recently, Bublitz and Meng (21) reported that the intensity of fluorescence of pulping waste liquor has a linear relationship with the lignin concentration in the sample. Also Wade (98) showed the same result and indicated that the fluorescence of kraft liquors occurs at an excitation wavelength at 280 nm. and an emission wavelength at 430 nm. Nevertheless, he stated that diluted kraft liquors were not stable for more than two days.

Influence of Fiber Morphology on Paper Strength

It was originally accepted that tensile strength and bursting strength of paper were directly influenced by fiber length (31). However, Annergren et al. (1) showed that thin walled fibers have a greater tendency to collapse and produce good fiber contact and higher paper bonding than thick wall fibers. They also indicated that wood density, the summerwood content, and the ratio of cell wall thickness to fiber width should be the deciding factors for paper strength. They stated that morphological effects caused the variations in pulp strengths of softwoods rather than chemical differences in the woods when pulped by the same process. Barefoot et al. (8)

found that the holocellulose content varied directly with cell wall thickness and they reported that the lignin content did vary slightly independently of its relationship with fiber morphology. Barefoot et al. (7) found that summerwood cell wall thickness (-) was the best single indicator of breaking length and bursting strength. They also found that it was positively correlated with tearing strength. They showed that fiber length (+) was the second most important factor as compared with cell wall thickness, and the effect was most significant at fiber lengths below 4 mm. Einspahr et al. (33) reported that the fiber length (+) had a significant effect on both breaking length and bursting strength for slash pine. Dinwoodie (32) showed that the cell wall thickness or the ratio of wall thickness to fiber diameter (-) has a major effect on breaking length. He stated that it (+) is the most important factor influencing on tearing strength within a species, and that fiber length is only somewhat less important. Moreover, Wangaard et al. (99) showed that fiber length has an influence only on the tear factor, but that wood specific gravity has an influence on burst factor, breaking length, and tear factor. Recently, Horn (50) confirmed that cell wall thickness had a major influence on tensile and bursting strength. He stated that fiber length was important only when a minimum length is required for bonding and stress distribution. He showed

that tearing strength of unbeaten pulp was influenced mainly by the fiber cross sectional area and cell wall thickness, and beaten pulp was affected primarily by fiber coarseness. He also suggested that wood density can be considered as a general predictor for estimating fiber strength of wood species.

Kraft Pulping of Douglas-fir

Numerous research papers on kraft pulping characteristics of Douglas-fir have been published in recent years (18, 42, 49, 65, 73). Hinrichs (48) in 1967, investigated kraft pulping variables on kraft delignification of second-growth Douglas-fir thinnings by computer regression analysis. He found that cooking rate could be increased by increasing the effective alkali charge, sulfidity, and temperature, and by decreasing the liquor to wood ratio. Bublitz (19) in 1971, studied the kraft pulping characteristics of thinnings from houng Douglas-fir trees. He revealed that they may be pulped to approximately the same yield and permanganate number as commercial pulp. In addition, Hatton and Keays (46) studied pulp yield and quality data from unbleached kraft pulp prepared from the components of unmerchantable tops, roots, stumps, branches and full bole of Douglas-fir. They recommended that unmerchantable tops could be cooked in combination with full boles in kraft pulping. Hatton and Keays (47), stated

that kraft pulping process variables did not influence the maximum total kraft pulp yield corresponding to a given permanganate number, and also reported the numerical relationships between total pulp yield and screened-pulp permanganate and Kappa numbers.

Recently, Bublitz and Blackman (20) studied the effect of permeable and refractory heartwood of Douglas-fir on the pulping and strength properties of the pulp. They found that pulp from refractory heartwood shows less delignification and is lower in tearing strength, but higher in tensile strength, stretch, and folding endurance at constant freeness than pulp from permeable heartwood. Wade (98) in 1977, applied the technique of fluorescent analysis to kraft black liquors from Douglas-fir. He found that the fluorescent intensities of the liquors could be correlated with various process parameters and pulps.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples of Douglas-fir Wood (Pseudotsuga menziesii (Mirb.) Franco) were obtained from trees at McDonald Forest near Corvallis, Oregon. Trees approximately 100-130 feet tall were sampled at breast height, half-way up, and at the crown (five inches minimum diameter).

The samples were cut into cross-sectional disks about two inches along the grain. Each disk was cut into four pie-shaped sections, each section extending into the juvenile wood, for determination of the wood density by the water immersion technique. The differences in wood density were sought both on inter-tree and intra-tree basis to choose three samples of low, intermediate, and high density. The ratio of heartwood to sapwood was determined for each wood sample of different density. The specimens selected were debarked by hand, chipped and screened on a Williamson chip screen (a round hole screen) for five minutes. The fractions retained on the 3/8" and 5/8" diameter hole screen were separated from the remainder for pulping. These fractions were then conditioned at room temperature for five days until the moisture contents of the samples reached equilibrium.

Liquid Penetrability of Heartwood

Heartwood samples from each wood sample were cut to six inches along the grain and one square inch in cross section using Miller's method (76). The blocks were impregnated with a 5% copper sulfate solution for 30 minutes at 80°F temperature and 110 psi pressure in the 12-liter laboratory digester. After treatment, the blocks were wiped clean, split radially and exposed to hydrogen sulfide gas to form a brown precipitate of copper sulfide to compare the degree of penetration by color.

Wood Analysis

The chip samples were ground in a Wiley mill and screened through a 50-mesh screen by TAPPI Standard T 11 os-74. Alcohol-Benzene Solubility and Klason lignin were determined on the wood meal sample by TAPPI Standards T 6 wd-73, T12 os-75 and T 222 os-74, respectively.

Pulping Procedure

A series of bomb cooks (50 grams o. d. wood) was performed at four different cooking times for each of three wood samples at each of three cooking temperatures. This made a total of 4 x 4 x 3 = 36 individual bomb cooks.

The active alkali and sulfidity were measured by TAPPI Standard T 624 os-68. The chemical charge and liquor to

wood ratio were constant for all cooks and the only variables were the maximum temperatures and cooking times as shown in Figure 1.

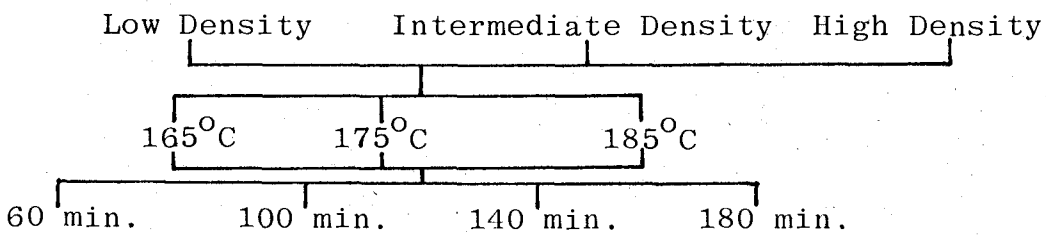

Figure 1. Pulping procedure

TABLE 1. PULPING CONDITIONS

Active Alkali, % Na_2O on O.D. Wood	18
Sulfidity, %	20
Liquor to Wood Ratio	8 : 1
Time to Temperature	60 min.
Time at Temperature	Variable
Maximum Temperature	Variable

Following each cook, the bombs were quickly cooled and opened. Samples of the pulping liquor were tested for fluorescence using a Turner Model 210 Spectrofluorometer. The pulps were analyzed for total yield, brightness, Kappa number, and Klason lignin content using TAPPI Standards T 452 m-58, T 236 m-60, and T 222 os-74 respectively. Kappa numbers were also estimated for high yield pulps from the intensity of fluorescence of the waste liquors using the techniques of Wade (98).

Pulp Testing

The remainder of the chips were pulped in a 12-liter capacity circulating digester to obtain sufficient pulp for determination of the strength properties of the pulps from different wood samples. One kg. of the chips (o. d. basis) from each wood sample was pulped to a target Kappa number of 30 ± 2 using the results of the bomb cooks to set pulping conditions. A constant temperature (175°C) was employed for all such cooks, and the only variable was the cooking time required to meet the target of 30 Kappa number. Repeat cooks were made until one pulp with Kappa number between 28 and 32 was obtained for each wood sample. Total and screened yields were determined for each accepted pulp sample. Each accepted sample was refined in the PFI mill for varying intervals by TAPPI Standard T 200 os-70 followed by forming and testing of handsheets for strength and optical properties using TAPPI Standards T 205 os-71, T 402 os-70, T 220 os-71, T 404 os-74, T 403 os-74, T 414 ts-65, and T 511 su-69, respectively. The pulp properties were compared on the basis of constant beating, constant freeness and constant bulk. Bauer-McNett screen classifications and weighted average fiber length determinations were made for each unbeaten pulp sample.

Dilution Procedure for Fluorometric Analysis

Pulping waste liquor samples were placed in the freezer to cool and were diluted immediately. 0.5 grams of each waste liquor was weighed into a 250 ml. beaker, and diluted to 250 grams with .01 N NaOH. Twenty grams of the diluted samples were diluted to 200 grams, a final dilution ratio of 1 : 5000 as suggested by Wade (98). This procedure required the least amount of dilution liquid and met the required UV transmission value of 95% or above. Then the samples were taken to the EPA Corvallis, Oregon for fluorometric analysis.

Spectral Conditions

A Turner model 210 absolute spectrofluorometer was used for fluorescent examination, due to its high sensitivity and versatility. Quartz cuvets (10 x 10 x 45 mm.) were filled with samples of the diluted liquor and placed in the sample compartment of the fluorometer for measurement.

TABLE 2. SPECTRAL CONDITIONS

Excitation wavelength	280 nm.
Emission wavelength	430 nm.
Fluorescent sensitivity	10 x, 30 x
Excitation bandwidths	15 nm.
Emission bandwidths	25 nm.
Dilution ratio	1 : 5000

Data Analysis

Assuming that the reaction is a first-order reaction, the rate of delignification was obtained from the following equation:

$$-\frac{dc}{dt} = kc$$

where c is the concentration of material

k is a proportionality factor

t is the time

-dc/dt is the rate at which the concentration decreases.

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k \int_{t_1}^{t_2} dt$$

$$-\ln c_2 - (-\ln c_1) = k(t_2 - t_1)$$

$$k = \frac{1}{t} \ln \frac{c_1}{c_2}$$

or $$k = \frac{1}{t} \ln \frac{a}{a-x}$$

where a is the initial concentration

x is the amount reacting in time t

a-x is the concentration remaining after time t

k is the specific reaction rate or rate constant

The activation energy was calculated from Arrhenius's equation and the constant B was obtained from Vroom (97) as a value of 43.20.

The analysis of variance was used to determine the relative significance of differences between the (wood) pulp properties. The levels of significance of the effect of pulping time, temperature and wood qualities on pulp yield, Kappa number, rates of pulping reaction and delignification, and energies of activation of pulping reaction and delignification were determined by analysis of variance. The paired "t" test analysis was used to compare the significance of the difference between the pulping responses of each wood sample. A linear regression was calculated for the relationship between Klason lignin contents of the pulps and the pulp Kappa numbers combining present data with Hinrichs' data (48). Linear regression analysis was also applied to the relationship of fluorescent intensity to cooking time, and to the relationships between the logarithms of the H factor with log yield, log Kappa number and fluorescent intensity. The F and t statistics were used to determine the level of statistical significance.

RESULTS AND DISCUSSION

Wood Parameters

The parameters of wood density, penetrability, heartwood to sapwood ratio, Klason lignin content, and extractive content, were measured and are shown in Table 3, and 4, respectively.

TABLE 3. WOOD PARAMETERS

Position in Tree	Density g/cc.	Penetrability[1]	Heartwood/ Sapwood
Top	0.405	4.0	0.898
Top	0.460	4.5	0.522
Base	0.563	6.0	2.704
F	134.198	No Statistical Test	45.764
Probability	***[2]		***

[1]Rated by Miller's standard (76)

[2]Probability P .05 --

Probability .05 P .01 *

Probability .01 P .001 **

Probability .001 P ***

A. Density

The densities as shown in Table 3, showed that there was a significant difference between the samples chosen in this study. The highest density sample was taken from the base of the tree and the other two samples were both from the top.

B. Penetrability

Heartwood samples were tested for penetration of copper sulfate after they had been dried in the oven. The high density sample showed the greatest penetration while the low density sample showed the least penetration. The intermediate density was only slightly more penetrable than the low density sample. As Phillips (5) stated, the degree of pit aspiration is related to moisture content and the number of unaspirated pits increased with greater cell wall thickness. The results agreed with Phillips' suggestion that high density wood should have greater cell wall thickness than low density wood (5, 43). The aspirated pits in wood form during drying of wood (43), but the high density sample was made of thicker walled cell that have stiffer pit membranes which oppose the forces of surface tension to form aspirated pits more than the lower density sample (5, 28). It could be considered that aspirated pits could occur mostly in the thinner walls of the low density of wood during the drying process.

C. Heartwood to Sapwood Ratio

Significant differences between the heartwood to sapwood ratio were found between the samples. The high density sample which was most easily penetrated showed the highest percent of heartwood, and the low density wood contained more heartwood than the intermediate sample did. The ratio of heartwood to sapwood did not relate to variation in the densities and heartwood penetrabilities of wood.

TABLE 4. CHEMICAL CONSTITUENTS IN WOOD

Wood Density	Klason lignin %	Alcohol-Benzene Solubility %	Alcohol Solubility %	Carbohydrate* Content %
Low	26.1	2.6	0.29	70.1
Intermediate	24.5	2.3	0.22	73.0
High	26.7	4.4	0.33	68.6
F	1017.5	21.1	No Statistical Test	No Statistical Test
Probability	***	*		

*Carbohydrate content = 100 - Klason lignin - Alcohol-benzene solubility - Alcohol solubility (%)

Note: Klason lignin and solubilities are based on total wood substance.

D. Lignin

The Klason lignin contents of the different samples as shown in Table 4, were significantly different. The intermediate density sample contained much less Klason lignin than the other two samples. The Klason lignin contents varied with the ratio of heartwood and sapwood. The highest amount of heartwood was associated with the highest amount of lignin, which may be due to incrustation of lignin like substances that occurred during heartwood formation (60).

E. Extractives Content

Slightly significant differences were noted between the amounts of alcohol-benzene and alcohol soluble extractives present in the wood samples and the highest percent of heartwood correlated with the highest quantity of extractives. However, the extractives content did not influence the heartwood penetrabilities of the samples, since the highest wood density sample also had the highest amount of extractives.

Pulping Results

A. Pulp Yields

As shown in Figure 2, an increase in temperature decreased the pulp yields and the yields decreased with

increased pulping time. It is also shown by the analysis of variance in Table 5 that the treatment (H factor) had a highly significant effect on the yields, but the variations of wood samples had a relatively small effect on the yields. This relationship is also shown in Figures 4 and 5, where it is difficult to see any significant difference between the wood samples relative to the yields at different levels of the H factor.

TABLE 5. ANALYSIS OF VARIANCE OF YIELD

Source	df	SS	MS	F
Sample	2	7.61	3.80	4.85*
Treatment	11	971.00	88.27	112.59**
H Factor	1	774.48	773.48	992.92**
Remainder	10	196.52	19.65	25.19**
Temperature	2	724.57	362.29	464.47**
Time	3	237.12	79.04	101.33**
Temperature * Time	6	9.31	1.55	1.99N.S.
Residual	22	17.25	0.78	

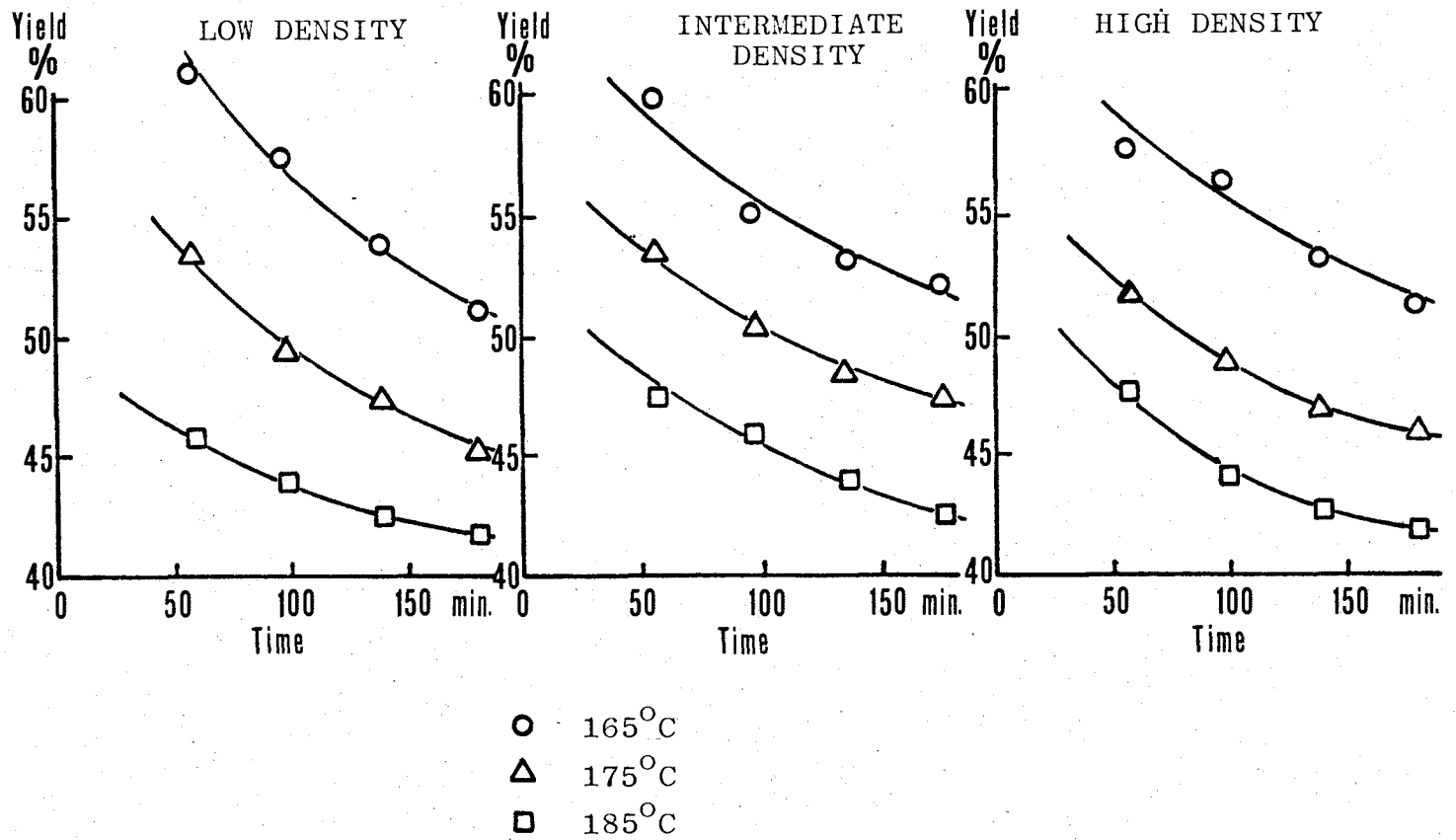

Figure 2. Yield vs. cooking time of different wood density samples

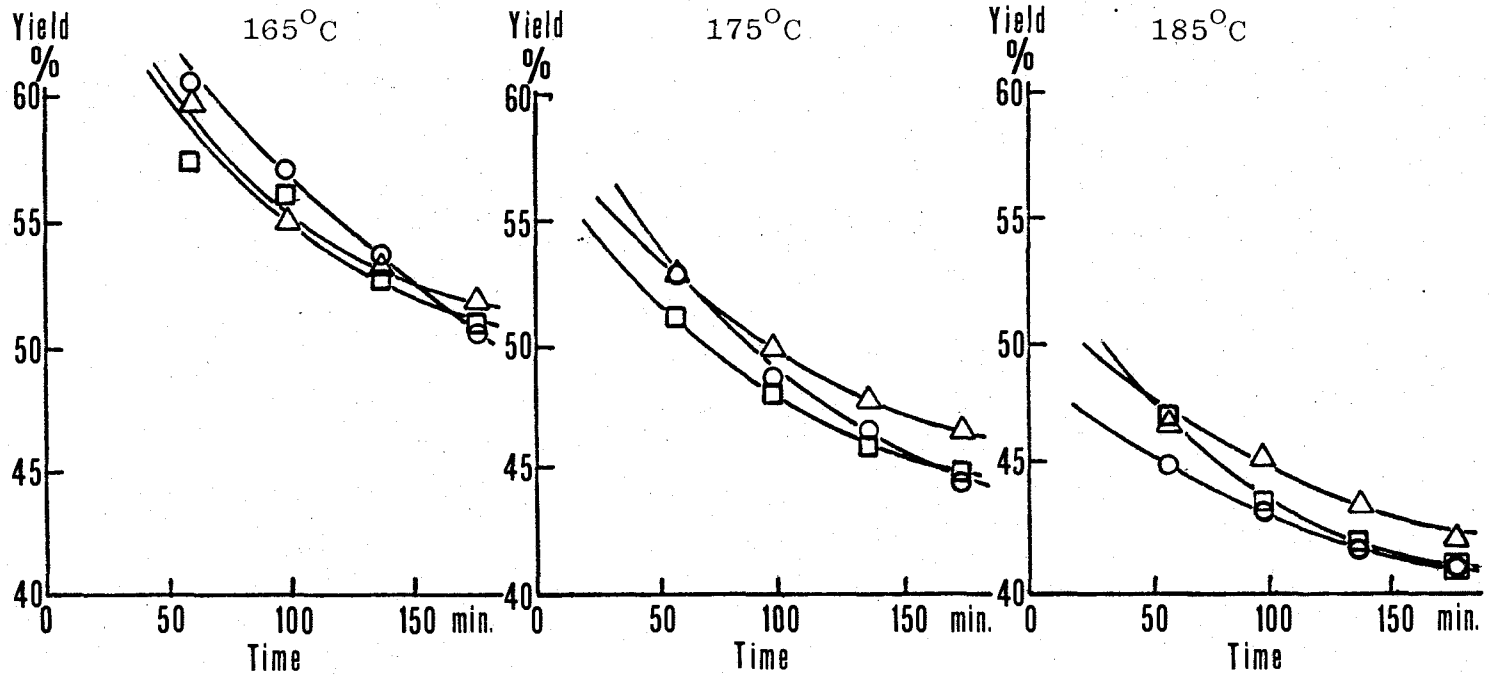

Figure 3. Yield vs. cooking time at different cooking temperatures

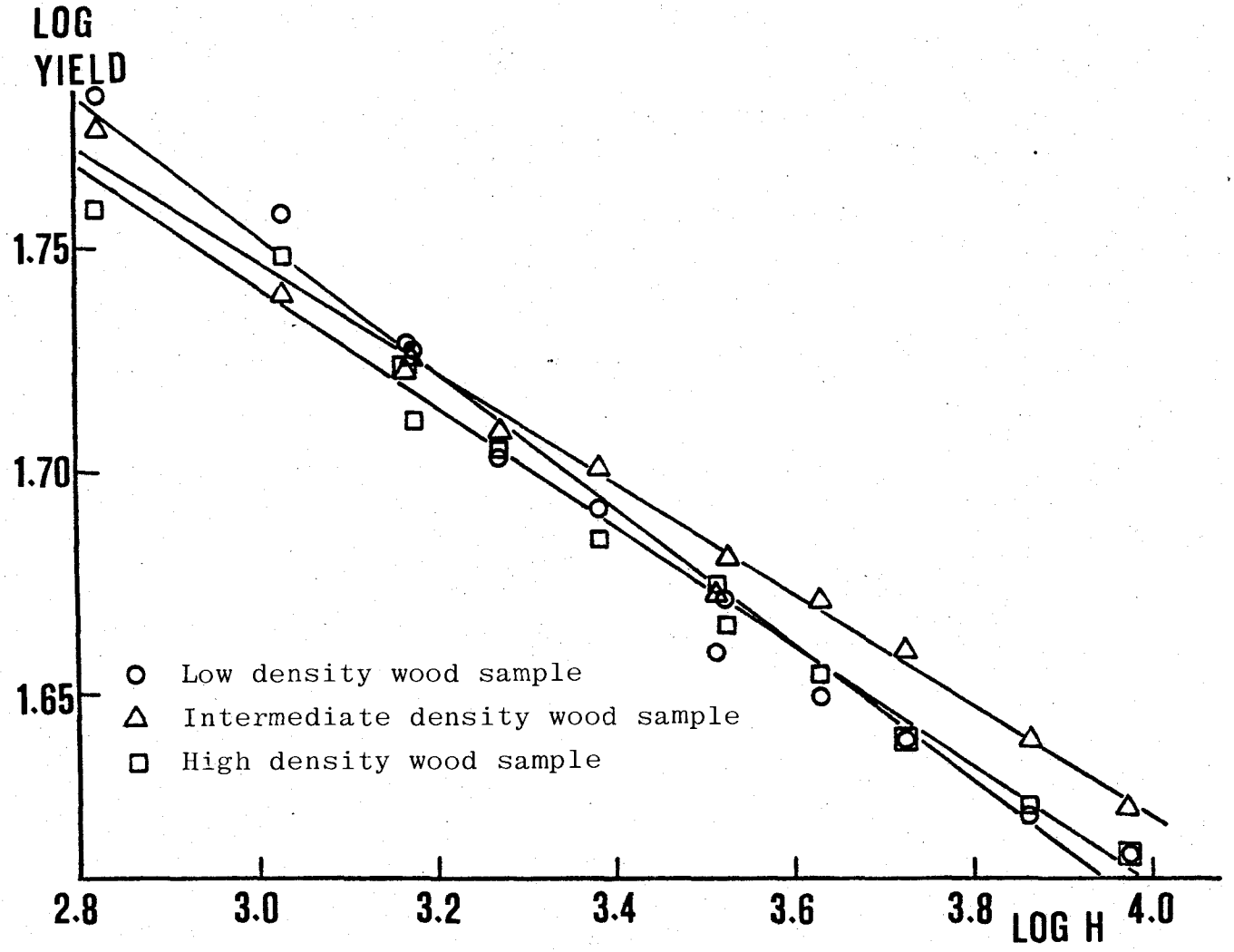

Figure 4. Log yield vs. log H factor

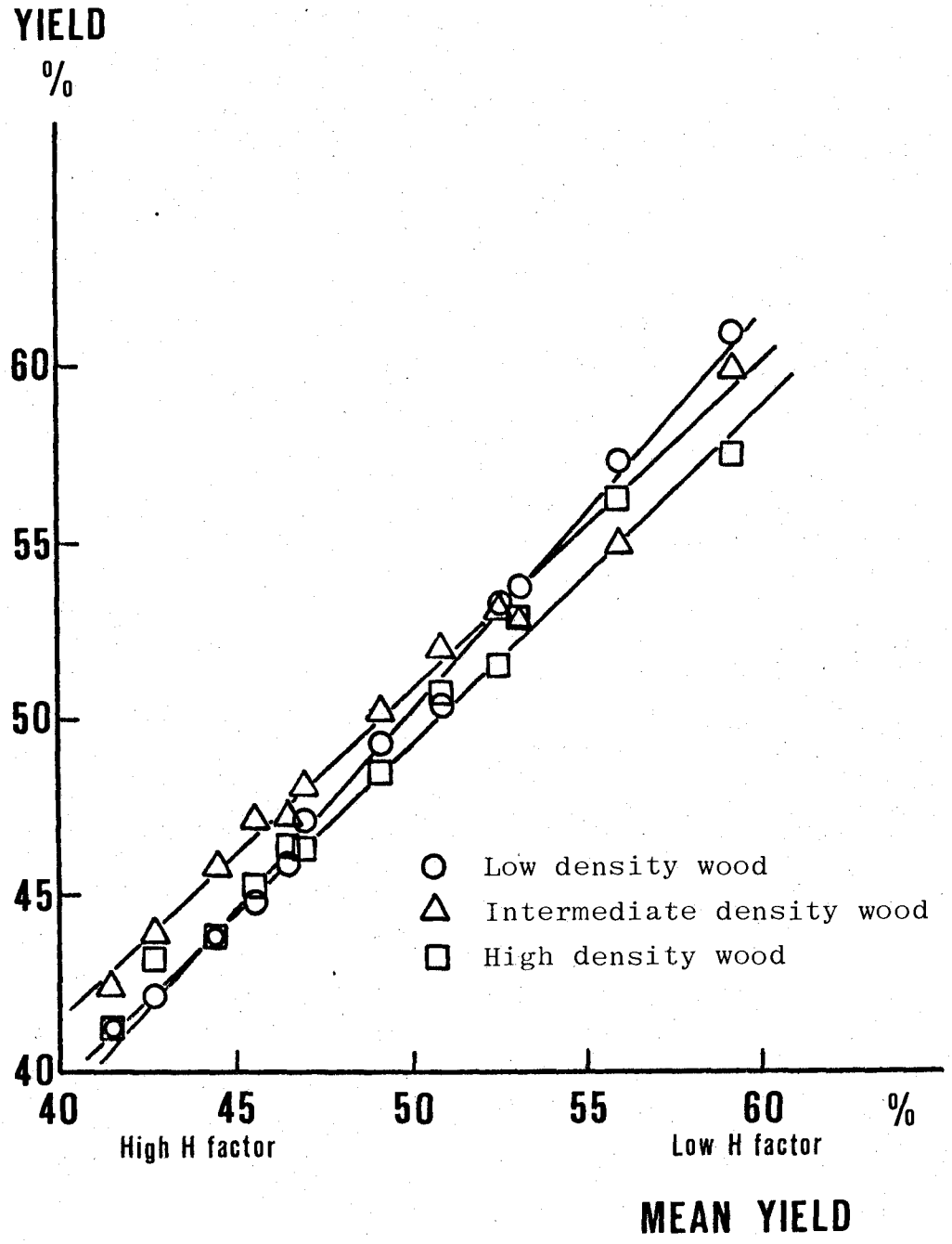

Figure 5. Yield vs. mean yield

Comparing the overall averages of yields of every pair of samples by the paired "t" test analysis as shown in Table 6, significant differences were found only between the intermediate density and the high density wood samples. The high density wood had the lowest pulping yield and the intermediate density had the highest pulping yield.

TABLE 6. PAIRED "t" TEST FOR YIELD

Wood Sample	Mean	Mean	t	Probability
(1)-(2)	49.13	49.73	1.48	--
(1)-(3)	49.13	48.60	1.43	--
(2)-(3)	49.73	48.60	3.69	**

Note: (1) Low density wood sample
(2) Intermediate density wood sample
(3) High density wood sample

The comparison of pulp yields of the different wood samples at the same temperature is shown in Figure 3. At the low temperature ($165^{o}C$), the low density wood showed the highest yield while the high density wood showed the lowest yield in the early stages of pulping. These relationships also occurred at the higher temperatures, but at the higher cooking temperature, they occurred earlier in the cooking period. They agree with the relationships of wood density and heartwood penetrability as shown in Table 15. The

wood penetrability, which had a significant correlation with wood density (r^2 = 0.988), was negatively correlated with the yield in the early stages of pulping. The wood with higher penetrability gave the lower yield, but the relationship occurred only at the beginning of the cooking period, and the higher the temperature, the shorter the cooking time at which this relationship that held true. It could be considered that the penetrability of wood had an influence on the pulping yield only during the penetration period of pulping liquor, but the penetrability did not show a significant effect on the overall pulping yield.

B. Kappa Numbers

As shown in Figure 6., the Kappa numbers also showed a relationship similar to that of the yields with the pulping times and temperatures. The higher cooking temperatures produced the lower Kappa numbers and the Kappa numbers decreased with increasing cooking time.

Table 7 shows that the temperature and time had a highly significant effect on the Kappa number. The variation in properties of the wood samples show more significant influence on the Kappa numbers than on the pulp yields.

TABLE 7. ANALYSIS OF VARIANCE OF KAPPA NUMBERS

Source	df	SS	MS	F
Sample	2	1213.7	606.5	26.8**
Treatment	11	27872.3	2533.8	112.1***
H Factor	1	19669.1	19669.1	870.3**
Remainder	10	8203.2	820.3	36.3**
Temperature	2	19835.1	9917.6	438.8**
Time	3	7054.5	2351.5	104.1**
Temperature * Time	6	982.7	163.8	7.3**
Residual	22	497.4	22.6	

It can be seen clearly in Figure 8 that there were differences in the Kappa numbers of each wood sample at any H factor. The intermediate density wood pulp sample always had the lowest Kappa number while the low density wood pulp sample always had the highest Kappa number. This same relationship is also shown in Figure 9 where the low H factor tended to have greater effect on the spread of Kappa numbers of the wood samples than the high H factor did. Since the lignin content of pulp decreases with increasing H factor, there is less variation in lignin contents of the pulps of the three samples because the lignin contents are approaching zero.

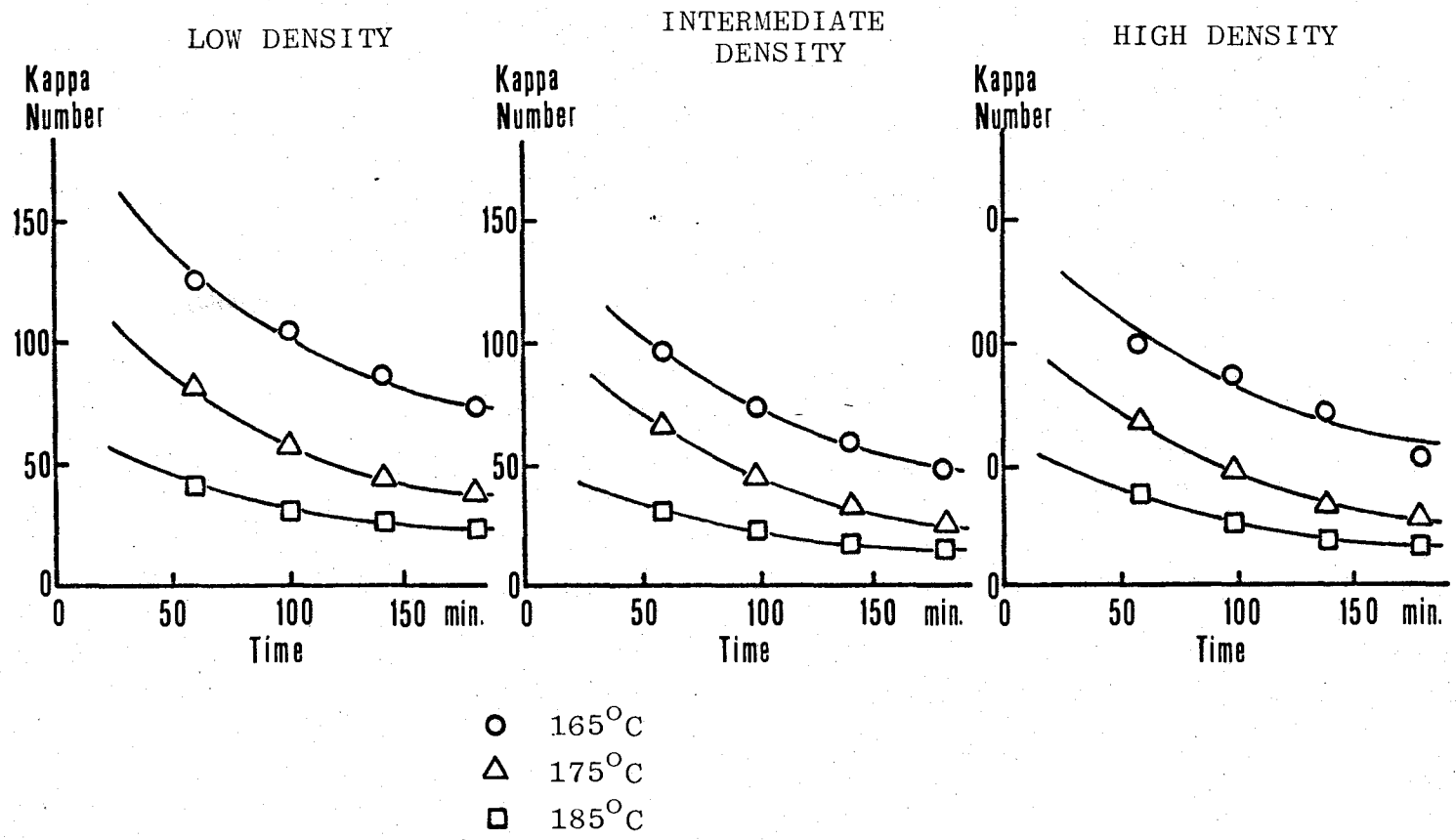

Figure 6. Kappa number vs. cooking time of different wood density samples

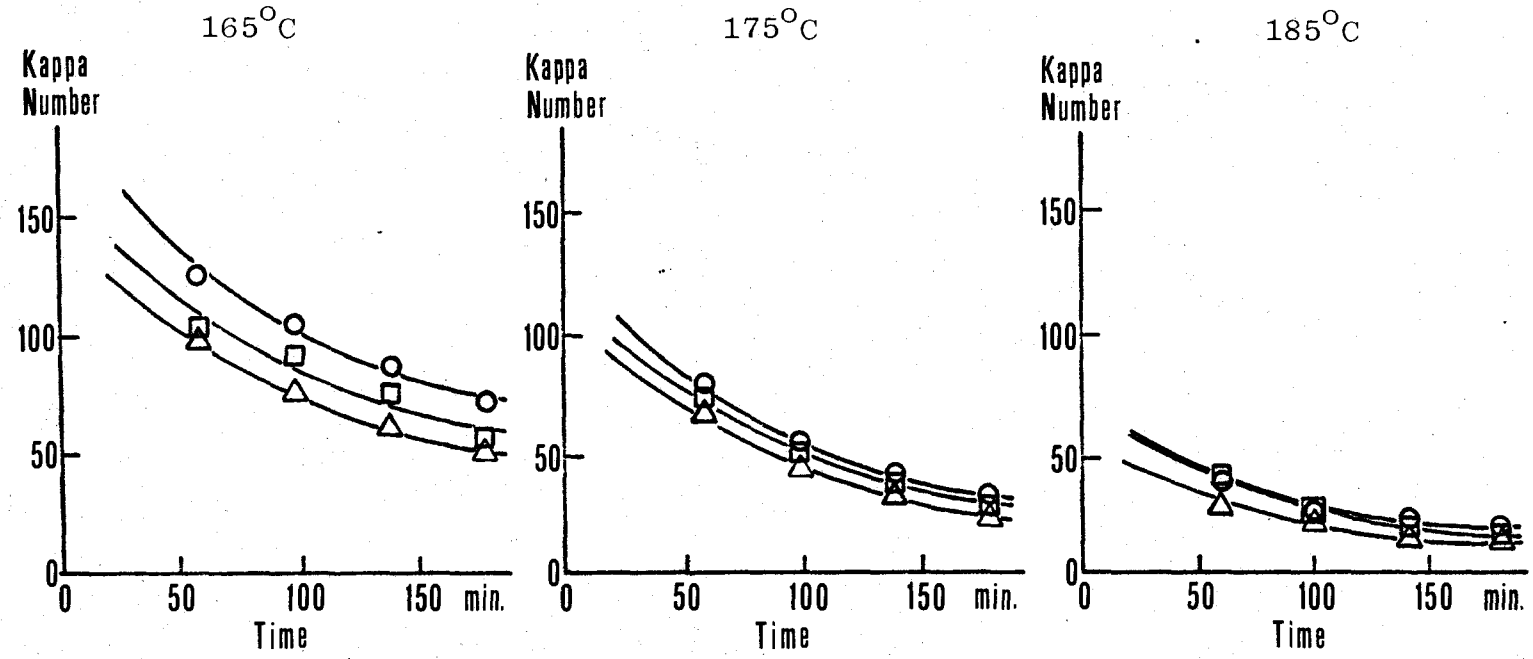

Figure 7. Kappa number vs. cooking time at different cooking temperatures

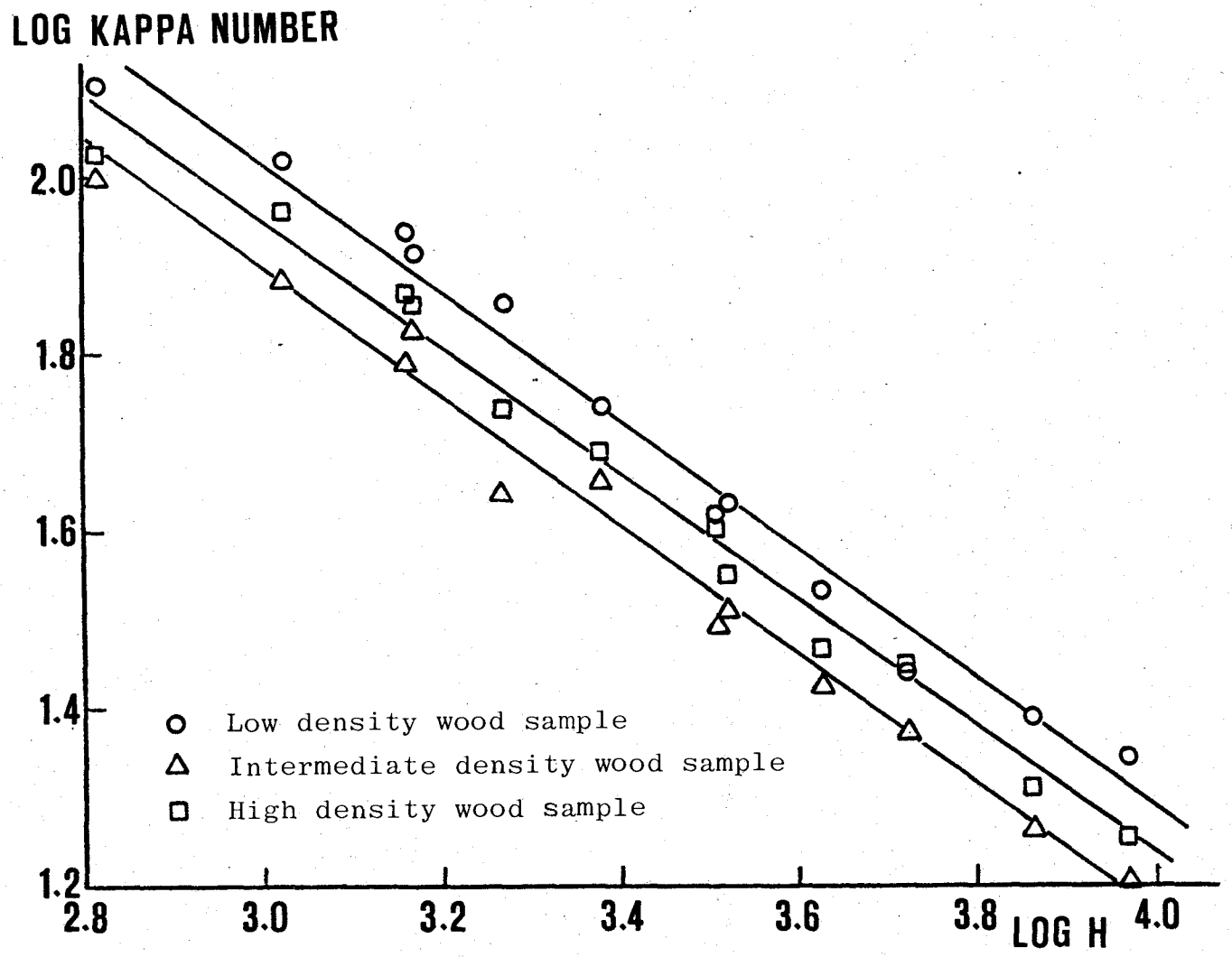

Figure 8. Log Kappa number vs. Log H factor

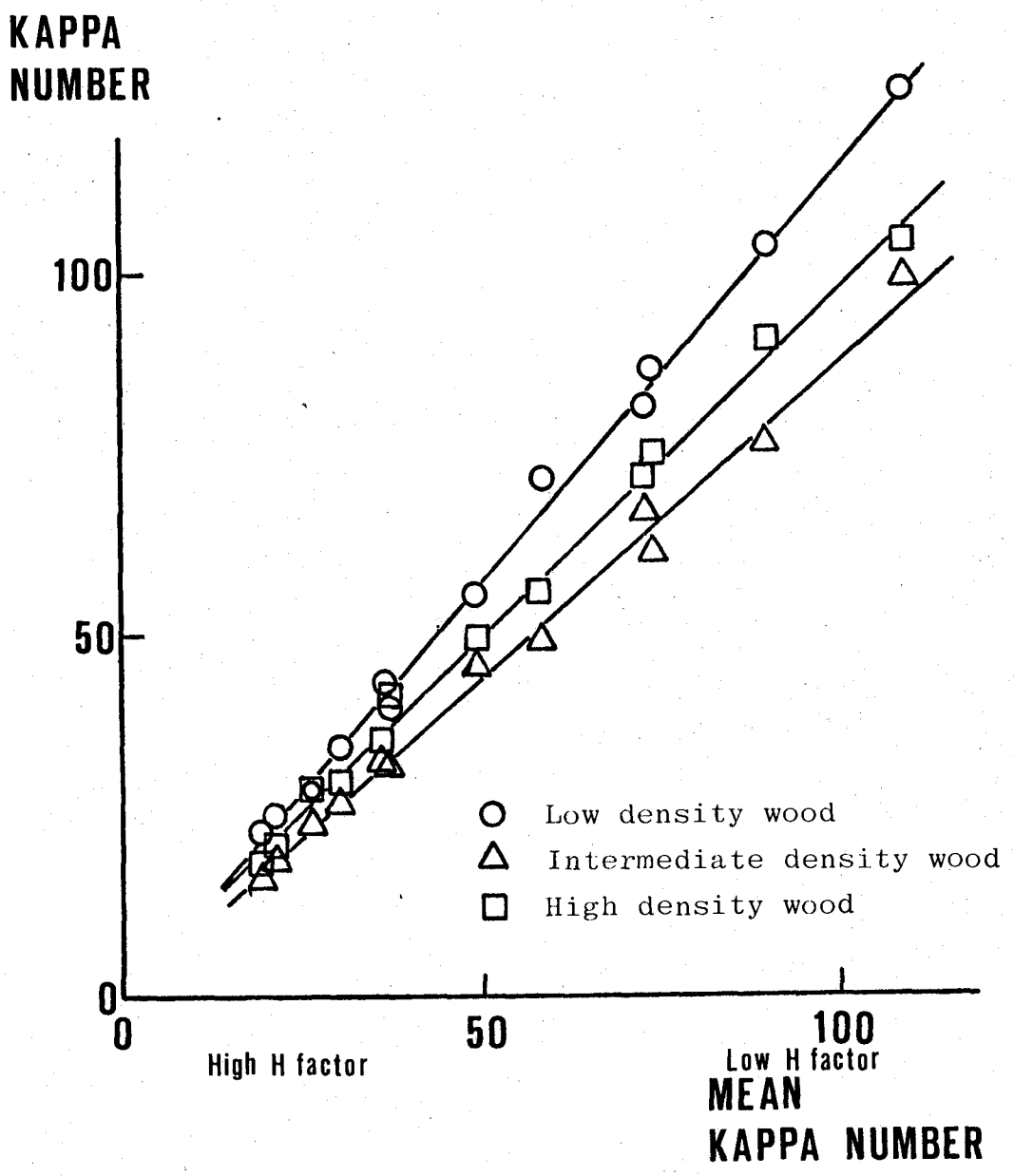

Figure 9. Kappa number vs. mean Kappa number

TABLE 8. Paired "t" TEST FOR KAPPA NUMBER

Wood Sample	Mean	Mean	t	Probability
(1)-(2)	59.53	45.35	5.67	***
(1)-(3)	59.53	51.43	4.30	***
(2)-(3)	45.35	51.43	4.94	***

Note: (1) Low density wood sample

(2) Intermediate density wood sample

(3) High density wood sample

From the paired "t" test data as shown in Table 8, the overall averages of the Kappa numbers of the different wood samples were significantly different. The intermediate density wood sample had the lowest Kappa numbers and the low density wood sample had the highest Kappa numbers. The same relationships also occurred at each cooking temperature as shown in Figure 7. Comparing the relationships in the correlation table (Table 15), it was noted that although the intermediate density wood had an intermediate level of heartwood penetrability, it had the highest quantity of sapwood. Sapwood is more easily penetrated by liquids than heartwood (39). The easy penetration of cooking liquor into sapwood may be responsible for the lowest Kappa numbers in the intermediate density sample. Moreover, the intermediate density wood also had the lowest Klason lignin content. This low quantity of lignin in wood may

affect the Kappa number, since starting with the lowest amount of lignin in wood, pulping at constant conditions would probably result in the lowest amount of lignin in pulp as expressed by the Kappa number. Comparing the high density and the low density woods, the low density wood had less lignin and more sapwood than the high density wood. The penetrabilities of the high and the low density woods were highly different. It appears that the difference between the Kappa numbers of these two samples was mainly due to the difference in the penetrabilities of wood when pulped at the same conditions.

C. Fluorescence

The fluorescent intensities were related to pulping times and temperatures as shown in Figures 10 and 11. As was true for the pulp yields and the Kappa numbers, the treatments of temperature and time had highly significant effects on the fluorescent intensities as shown in Table 9. The analysis of variance showed that the quality of wood had a significant effect on the fluorescent intensity. In contrast to Figure 12 and 13, the fluorescent intensity did not show clearly difference between each wood sample at different level of the H factor. However, if the fluorescent intensity data at 185^{o}C were neglected, it is shown in Figure 14 and 15 that there were differences between the fluorescent intensities of the liquors from

TABLE 9. ANALYSIS OF VARIANCE OF FLUORESCENCE

Source	df	SS	MS	F
Sample	2	.24007	.12004	36.18**
Treatment	11	1.32322	.12029	36.26**
H Factor	1	.82411	.82411	248.23**
Remainder	10	.49911	.04991	15.03**
Temperature	2	.90877	.45439	136.86**
Time	3	.25840	.08613	25.94**
Temperature * Time	6	.15605	.02601	7.83**
Residual	22	.07300	.00332	

each wood sample. It may be due to the fact that although the fluorescent intensities showed a linear relationship with the cooking time and temperature at the 165 and 175^{o}C temperatures, it had a curvi-linear relationship with the cooking time and temperature at 185^{o}C (Figure 10, 11 and Table 10). This was proven by a duplicate pulping experiments at 185^{o}C.

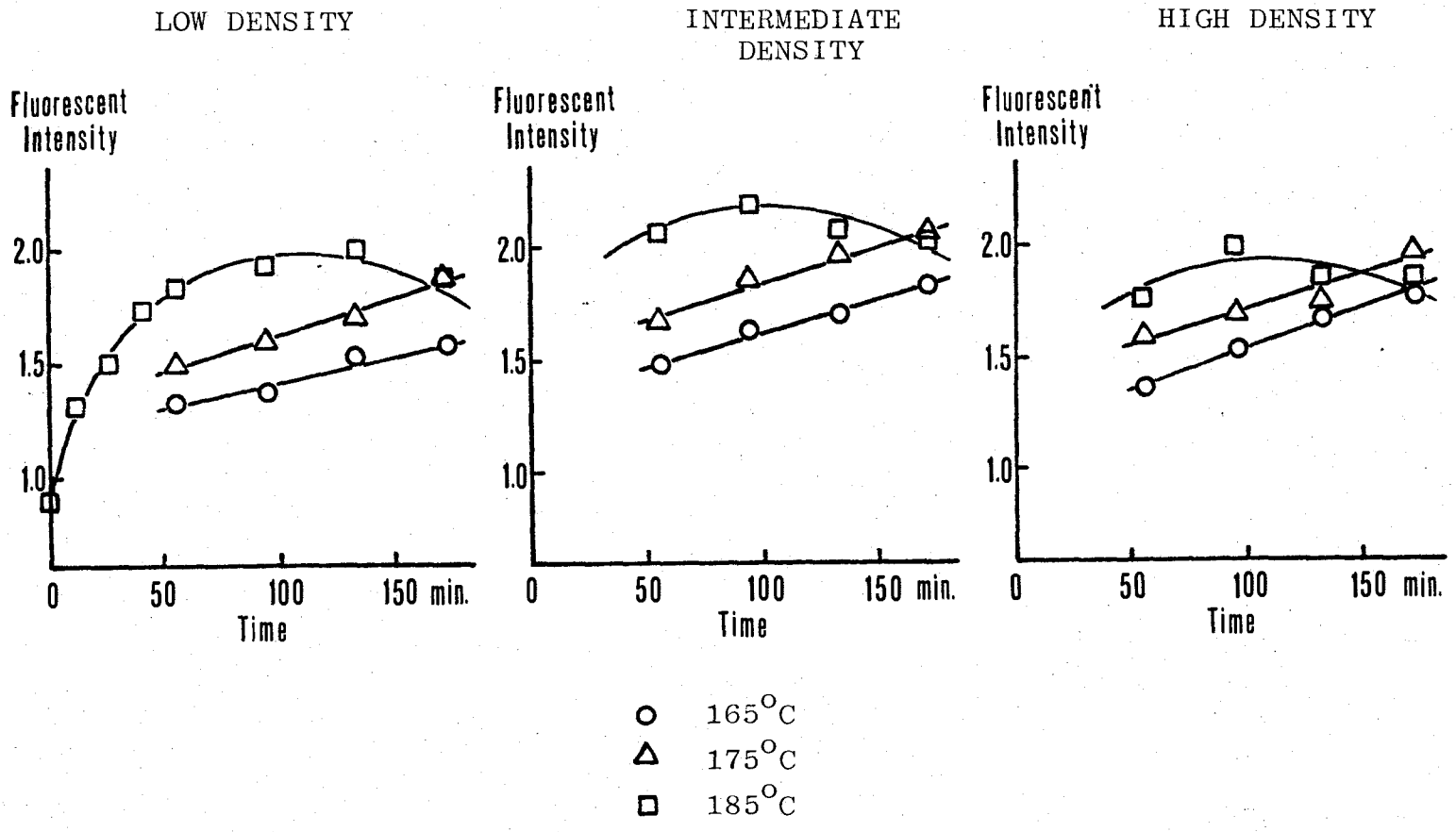

Figure 10. Fluorescent intensity vs. cooking time of different wood density samples

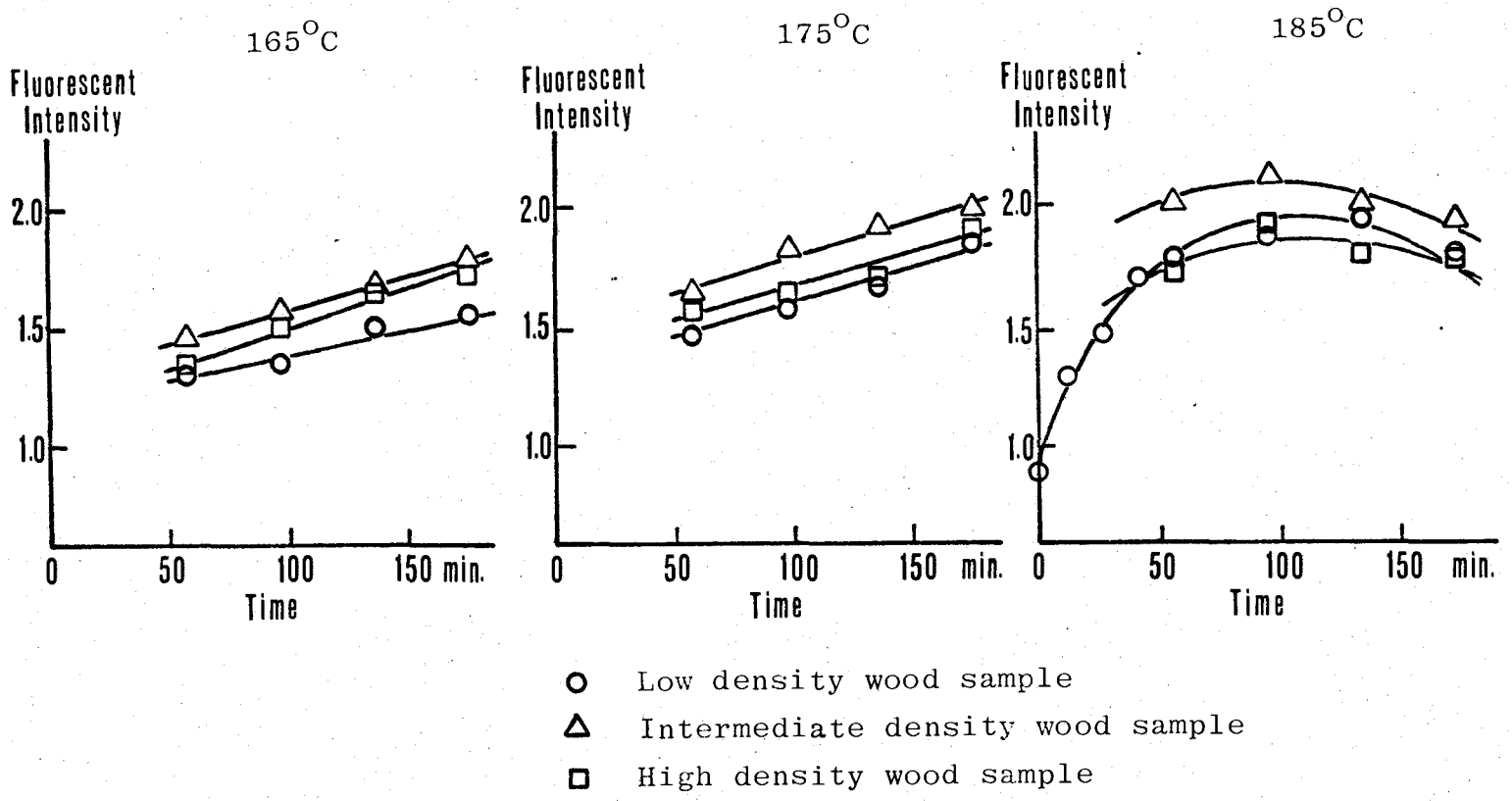

Figure 11. Fluorescent intensity vs. cooking time at different cooking temperatures

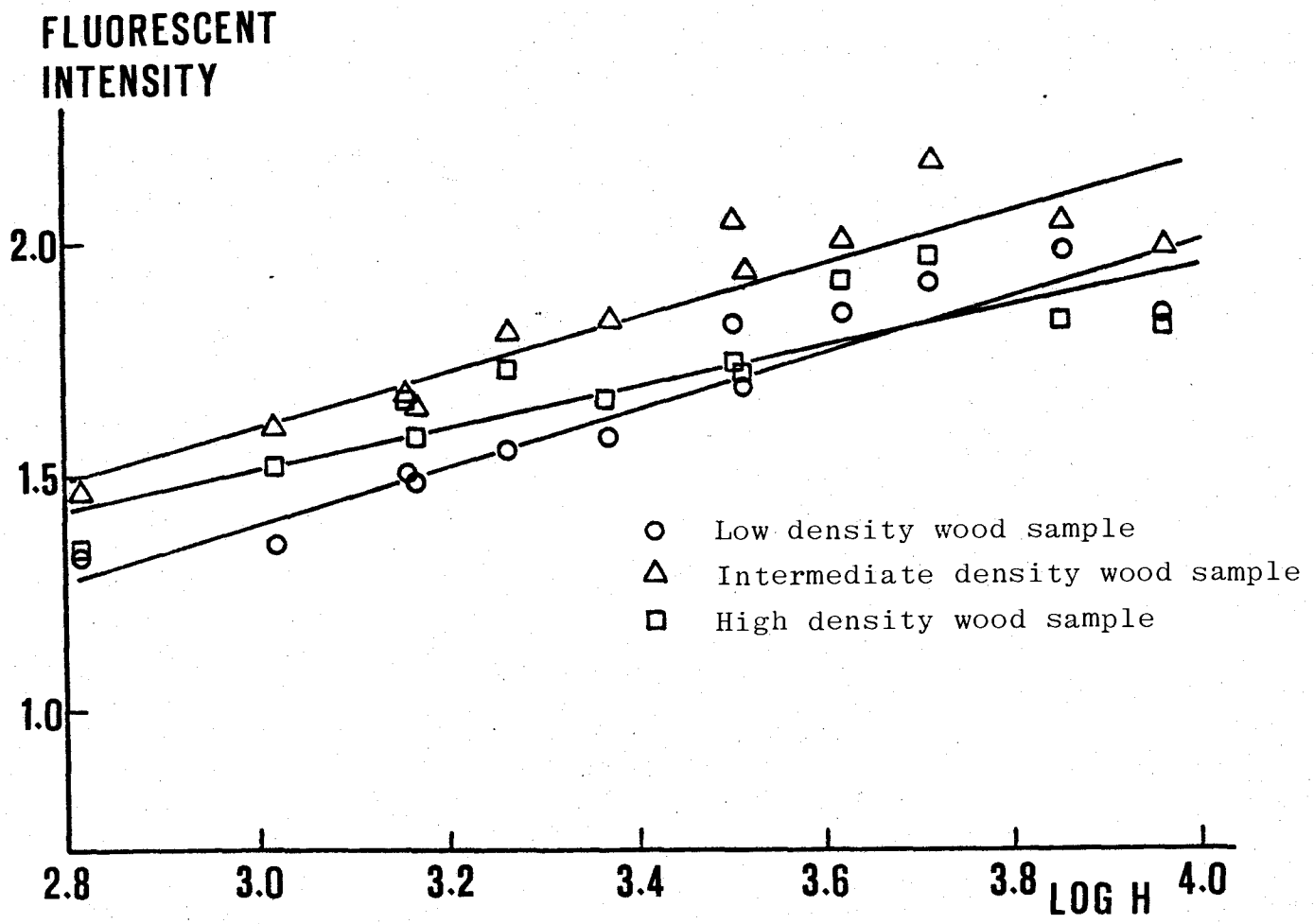

Figure 12. Fluorescent Intensity vs. Log H factor

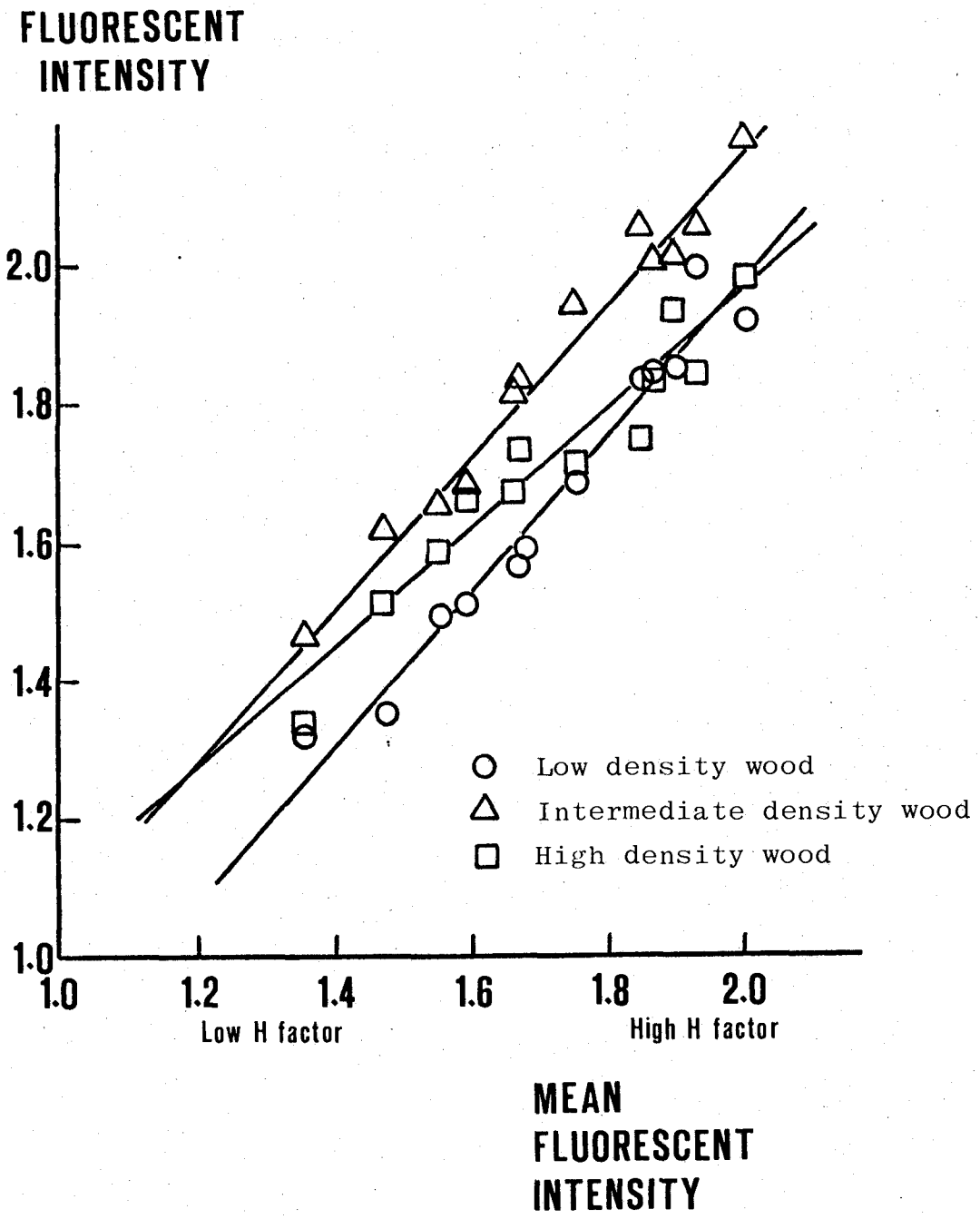

Figure 13. Fluorescent intensity vs. mean fluorescent intensity

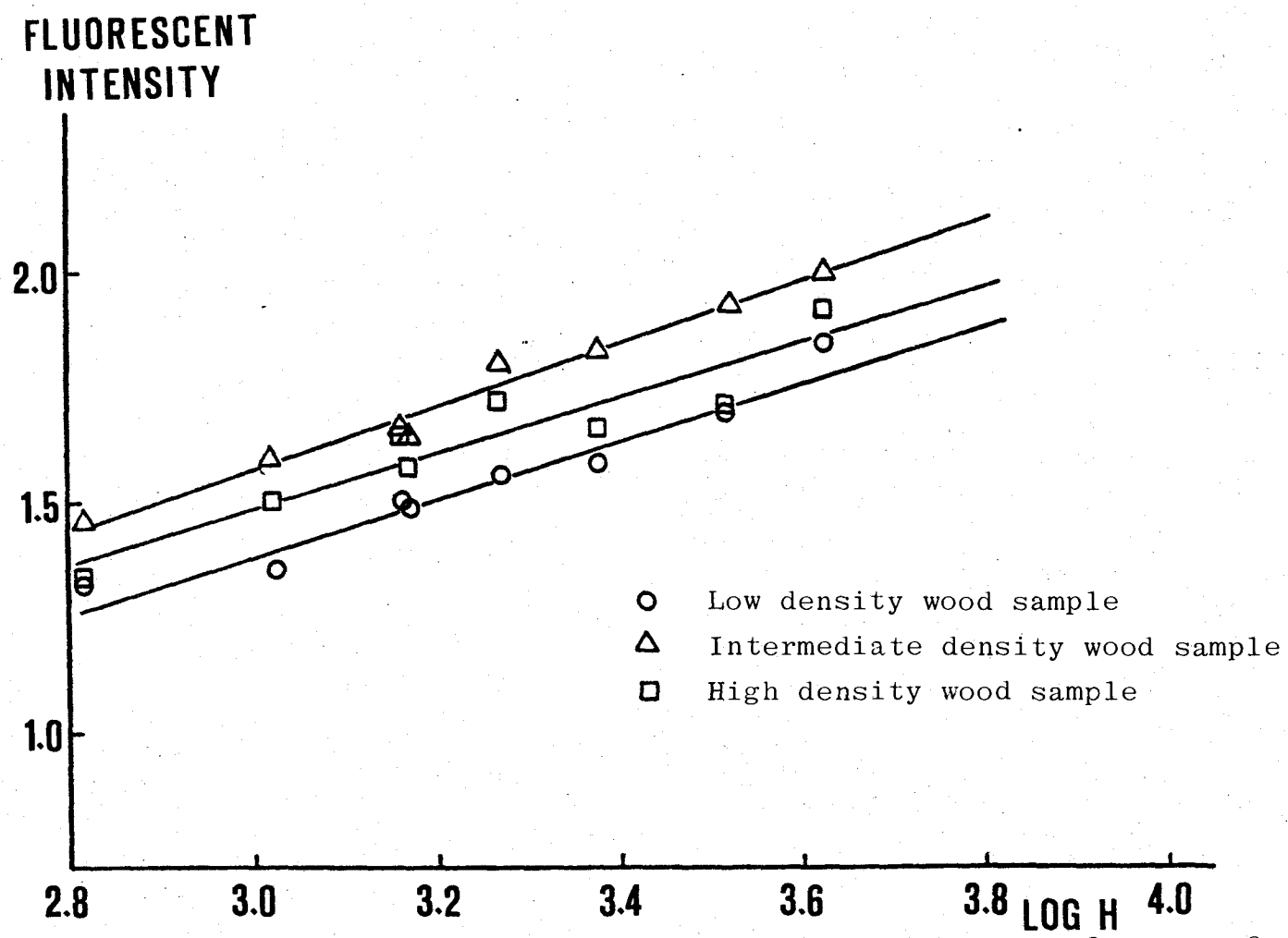

Figure 14. Fluorescent intensity vs. Log H factor at 165^{o} and 175^{o}C

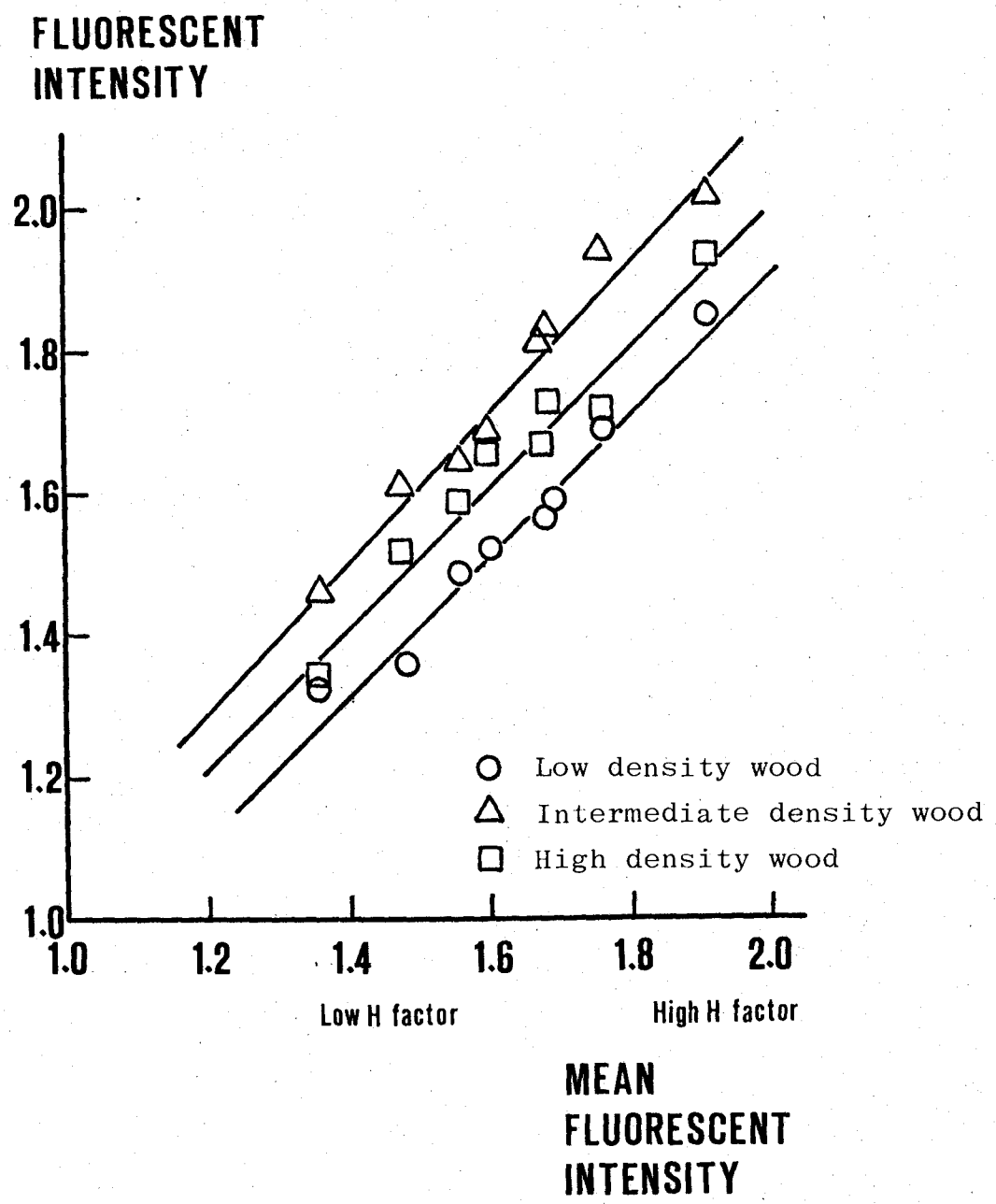

Figure 15. Fluorescent intensity vs. mean fluorescent intensity at 165° and 175°C

TABLE 10. LINEAR REGRESSION ANALYSIS FOR FLUORESCENT INTENSITY

Wood Sample	Cooking Temperature ^{o}C	r^2
Low density	165	0.92
	175	0.98
	185	0.05
Intermediate density	165	0.99
	175	0.95
	185	0.22
High density	165	0.97
	175	0.90
	185	0.02

From the analysis of the paired "t" test as shown in Table 11, significant differences were found between each pair of wood samples at the 165^{o} and $175^{o}C$ cooking temperatures. However, when the fluorescent intensities of the $185^{o}C$ samples were included, no significant differences were found between the low density and the high density wood samples as shown in Table 12.

TABLE 11. PAIRED "t" TEST FOR FLUORESCENT INTENSITY AT 165, 175°C

Wood Sample	Mean	Mean	t	Probability
(1)-(2)	1.54	1.74	11.19	***
(1)-(3)	1.54	1.64	4.90	**
(2)-(3)	1.74	1.64	4.66	**

TABLE 12. PAIRED "t" TEST FOR FLUORESCENT INTENSITY OF ALL SAMPLES

Wood Sample	Mean	Mean	t	Probability
(1)-(2)	1.66	1.85	10.57	***
(1)-(3)	1.66	1.70	1.77	--
(2)-(3)	1.85	1.70	6.09	**

Note: (1) Low density wood sample

(2) Intermediate density wood sample

(3) High density wood sample

The relationships between the fluorescent intensities and the cooking times at each temperature seemed to agree with the relationships of the Kappa numbers to cooking times at the 165° and 175°C levels. The high Kappa number pulps correlated with the low fluorescent intensity liquors because a high Kappa number pulp contains a high amount of

lignin (95) and the low fluorescent intensity indicated a low amount of lignin in the waste liquor (98). As shown in Figure 11, the fluorescent intensity at 185°C of every pulping waste liquor tended to increase at the beginning of the period and tended to decrease at the end of the cooking period. This situation may be due to lignin condensation that may occur at the high cooking temperatures when high rates of delignification occur (23, 98).

D. Kappa Number-Yield Relationship

As shown in the previous figures, the intermediate density of wood sample always showed the highest degree of delignification of all wood samples, indicated by its lowest Kappa numbers and highest fluorescent intensities. Considering the relationship between the Kappa numbers and the pulp yields as shown in Figure 16, there were no clear distinctions between the high density and the low density wood samples. But the intermediate density wood sample showed a clear difference from the other two samples, and also had a better relationship than those of the other two. It can be seen that the intermediate density wood pulp had a higher yield at the same Kappa number, or conversely a lower Kappa number at the same yield. It may be due to the fact that the intermediate density wood contained the lowest amount of Klason lignin, and this was responsible for the lowest amount of lignin left in the pulp. The intermediate

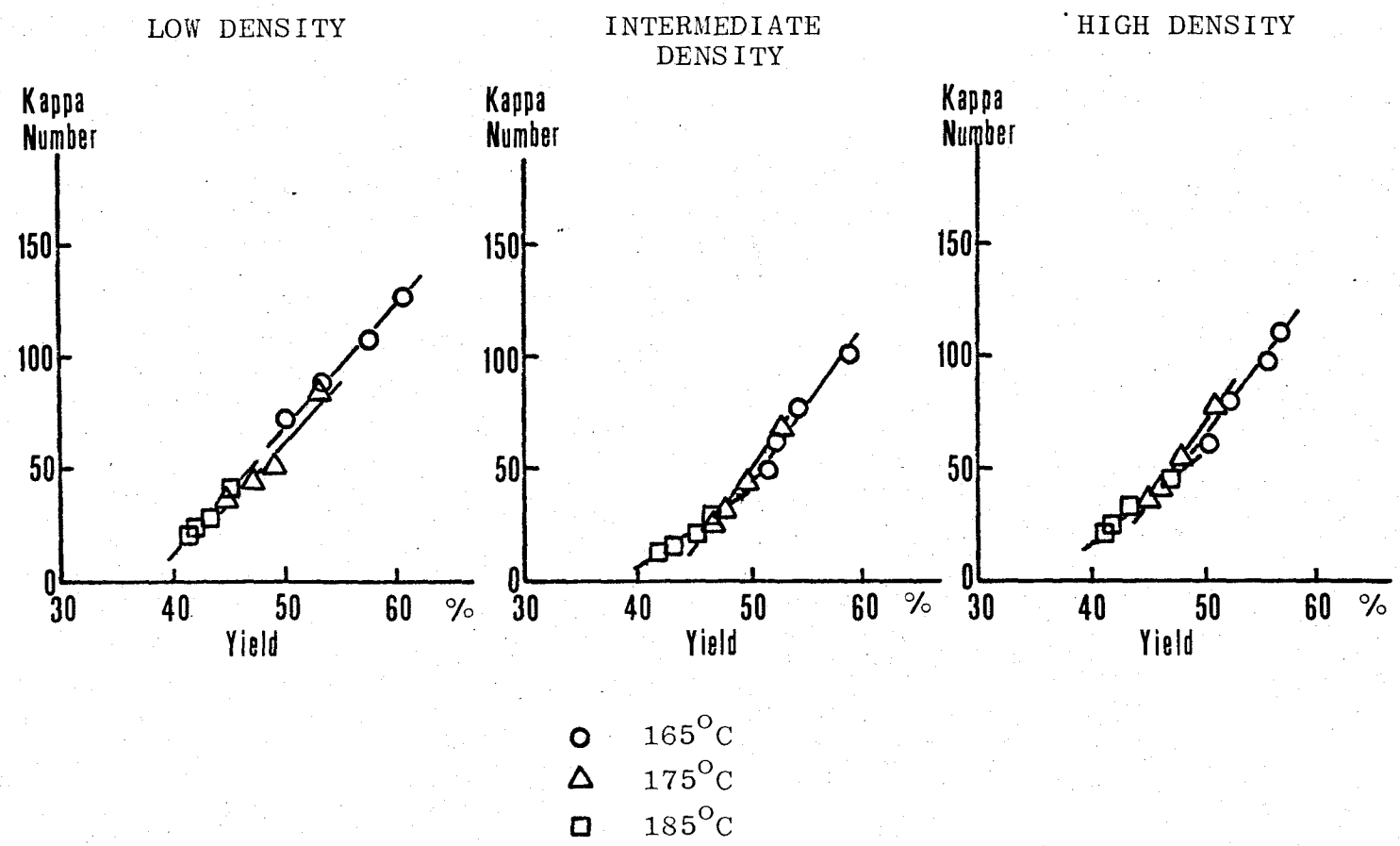

Figure 16. Kappa number vs. yield of different wood density samples

density wood sample has the highest carbohydrate content as shown in Table 4, which probably was responsible for the better Kappa number-yield relationship of the intermediate density wood sample.

Reaction Rates and Activation Energies

Table 13 shows that the cooking times had a significant effect only on reaction rates and activation energies of pulping, but they had only a slight effect on reaction rates and activation energies of delignification. In contrast, the cooking temperature had a significant effect on the rate of delignification and a highly significant effect on the activation energies of the pulping and delignification reaction rates. But no significant effect on the rate of pulping were found by cooking temperature. As was true for yields, Kappa numbers, and fluorescent intensities, no singificant effects on the reaction rates and activation energies were found due to wood quality variations.

As shown in Table 14, no significant differences in pulping reaction rates and pulping activation energies were found between the different wood samples. There are only some significant differences between the rates and activation energies of delignification of the low density wood sample and those of the other two samples. No significant differences were found between the rates and energies of

the intermediate density and the high density wood samples.

TABLE 13. ANALYSIS OF VARIANCE FOR REACTION RATES AND ACTIVATION ENERGIES

	Pulping Reaction			
	Rate (K_1)		Activation energy (E_1)	
	F	P	F	P
Wood Sample	0.01	--	0.04	--
Time	192.55	***	17.10	***
Temperature	0.21	--	9.53	***

	Delignification			
	Rate (K_2)		Activation energy (E_2)	
	F	P	F	P
Wood Sample	0.42	--	0.29	--
Time	3.27	*	0.41	--
Temperature	6.81	**	79.76	***

Note: P = Probability

TABLE 14. PAIRED "t" TEST FOR RATES OF REACTION AND ACTIVATION ENERGIES

	Wood Sample	Mean	Mean	t	Probability
K_1	(1)-(2)	3.70	3.58	0.86	--
	(1)-(3)	3.70	3.71	0.10	--
	(2)-(3)	3.58	3.71	0.85	--
K_2	(1)-(2)	6.85	8.23	3.76	**
	(1)-(3)	6.85	8.15	2.86	*
	(2)-(3)	8.23	8.15	0.20	--
E_1	(1)-(2)	33066	32959	1.10	--
	(1)-(3)	33066	32994	0.82	--
	(2)-(3)	32959	32994	0.31	--
E_2	(1)-(2)	33843	34087	2.97	*
	(1)-(3)	33843	34072	2.21	*
	(2)-(3)	34087	34072	0.27	--

Note: $K_1(\times 10^{-3})$ Rate of Pulping reaction

$K_2(\times 10^{-3})$ Rate of Delignification

E_1 Activation energy of Pulping reaction (cal/mole)

E_2 Activation energy of Delignification (cal/mole)

(1) Low density wood sample

(2) Intermediate density wood sample

(3) High density wood sample

Table 15 (Correlation Table) showed that the low density wood had less heartwood and Klason lignin than the high density wood. However, the low penetrability of the low density wood did not show much effect on the delignification rate compared to the high density wood. The significant differences of the rates and the activation energies of delignification found between these two wood samples may be due to the difference in their penetrabilities at the same cooking conditions. Although there was only a slight difference in the penetrabilities of low and intermediate density woods, the latter contained the highest quantity of sapwood. Moreover, as noted by Rydholm (83), the delignification rate varies with the lignin content in wood, and the intermediate density wood had the least amount of lignin. These two qualities of the intermediate density wood may be responsible for the highest rate of delignification of the three samples. It is possible that the high penetrability of heartwood of the high density wood may have some effect on the delignification rate, since, although it contained more lignin and more heartwood than the intermediate density wood, there were no significant differences between the reaction rates and between the activation energies of delignification of these two samples.

TABLE 15. CORRELATION TABLE

Low ——→ Intermediate ——→ High

1. Low density wood sample
2. Intermediate density wood sample
3. High density wood sample

	Yield			Kappa Number			Fluorescent Intensity		
	2	3	1	2	1	3	1	3	2
Density	1	2	3	1	2	3	1	2	3
Permeability	1	2	3	1	2	3	1	2	3
Heartwood/ Sapwood	2	1	3	2	1	3	2	1	3
Klason lignin	2	1	3	2	1	3	2	1	3
Extractive	2	1	3	2	1	3	2	1	3

	K_1			E_1			K_2			E_2		
	2	1	3	2	3	1	1	3	2	1	3	2
Density	1	2	3	1	2	3	1	2	3	1	2	3
Permeability	1	2	3	1	2	3	1	2	3	1	2	3
Heartwood/ Sapwood	2	1	3	2	1	3	2	1	3	2	1	3
Klason lignin	2	1	3	2	1	3	2	1	3	2	1	3
Extractive	2	1	3	2	1	3	2	1	3	2	1	3

Note: K_1 Rate of pulping reaction
E_1 Activation energy of pulping reaction
K_2 Rate of delignification
E_2 Activation energy of delignification

Pulp Testing

A. Bauer-McNett Fiber Classification

The Bauer-McNett fiber classification test classifies fibers by fiber length and fiber thickness. As shown in Table 16, the pulp from the high density wood contained the highest amount of the fiber retained on the 20 mesh screen while the pulp from the low density wood contained the lowest amount of fiber retained on the 20 mesh screen. This suggests that the high density wood produced the longest and thickest fiber while the low density wood produced the shorter and thinnest fiber.

TABLE 16. AVERAGE BAUER-MC NETT FIBER CLASSIFICATION

Wood Sample	1*	2	3	4	5
Low density	35.98	36.28	17.99	5.89	3.86
Intermediate density	59.61	20.00	12.94	4.31	3.14
High density	61.26	21.21	11.32	3.57	2.65

*Note: 1. % of fibers on 20 mesh
2. % of fibers on 35 mesh
3. % of fibers on 65 mesh
4. % of fibers on 150 mesh
5. % of fibers past 150 mesh

B. Physical Strength Properties of Pulp Samples

1. Constant Beating

As shown in Table 17, the lowest density wood pulp sample showed the highest bursting strength, tensile strength, and folding endurance, but the lowest tearing strength, while the high density wood pulp showed the lowest of these strength properties except it had the highest tearing strength. Note that the bursting strength of the low density wood pulp decreased at the highest level of beating. This may be due to the thin cell walls of the low density wood pulp where severely beaten and the fiber had almost broken, causing lower bursting strength.

2. Constant Freeness

As shown in Table 18 and Figures 17-20, the same results found at constant beating were found at constant freeness. As stated, the high density wood pulp has thicker cell walls (50) and the Bauer-McNett fiber classification also showed approximately the same results. The thinner walled fibers had a stronger tendency to collapse than the thicker walled fibers (1), thus forming better fiber to fiber bonding. The higher fiber bonding of the thin wall fiber produced the higher tensile strength, bursting strength,

TABLE 17. PHYSICAL STRENGTH PROPERTIES OF PULP AT CONSTANT BEATING

CONSTANT BEATING DATA

		WOOD DENSITY		
		LOW	MEDIUM	HIGH
PROPERTY	BEATING	1-1C-1	2-1C	2-3C-1
CSF	250	516	607	633
	500	284	469	451
	750	136	317	268
BRIGHTNESS	250	18.1	20.7	17.0
	500	17.3	19.3	17.0
	750	15.9	19.2	17.1
BULK	250	1.333	1.765	1.686
	500	1.267	1.506	1.593
	750	1.218	1.447	1.499
BURST	250	61.6	47.7	43.3
	500	74.1	60.9	46.8
	750	58.9	63.5	50.3
TEAR	250	107.2	196.3	242.5
	500	87.2	185.3	216.9
	750	82.8	175.8	191.3
FOLD	250	1105	426	316
	500	1587	640	493
	750	1826	747	670
BREAKING LENGTH	250	12974	10071	8893
	500	11876	11687	9410
	750	13093	11550	9928

TABLE 18. PHYSICAL STRENGTH PROPERTIES OF PULP AT CONSTANT CSF

CONSTANT FREENESS DATA

PROPERTY	CSF	WOOD DENSITY: LOW 1-1C-1	MEDIUM 2-1C	HIGH 2-3C-1
BEATING	600	128	265	295
	400	375	613	569
	200	642	891	843
BRIGHTNESS	600	20.7	20.5	17.0
	400	17.7	19.3	17.0
	200	16.5	19.0	17.1
BULK	600	1.507	1.732	1.669
	400	1.300	1.479	1.567
	200	1.239	1.419	1.453
BURST	600.	49.1	49.4	43.9
	400	67.9	62.1	47.8
	200	65.5	68.7	55.2
TEAR	600	124.0	195.5	237.9
	400	97.2	181.0	209.8
	200	84.7	164.5	171.7
FOLD	600	776	448	348
	400	1346	689	542
	200	1723	960	866
BREAKING LENGTH	600	10528	10319	8986
	400	12425	11625	9554
	200	12567	12320	10739

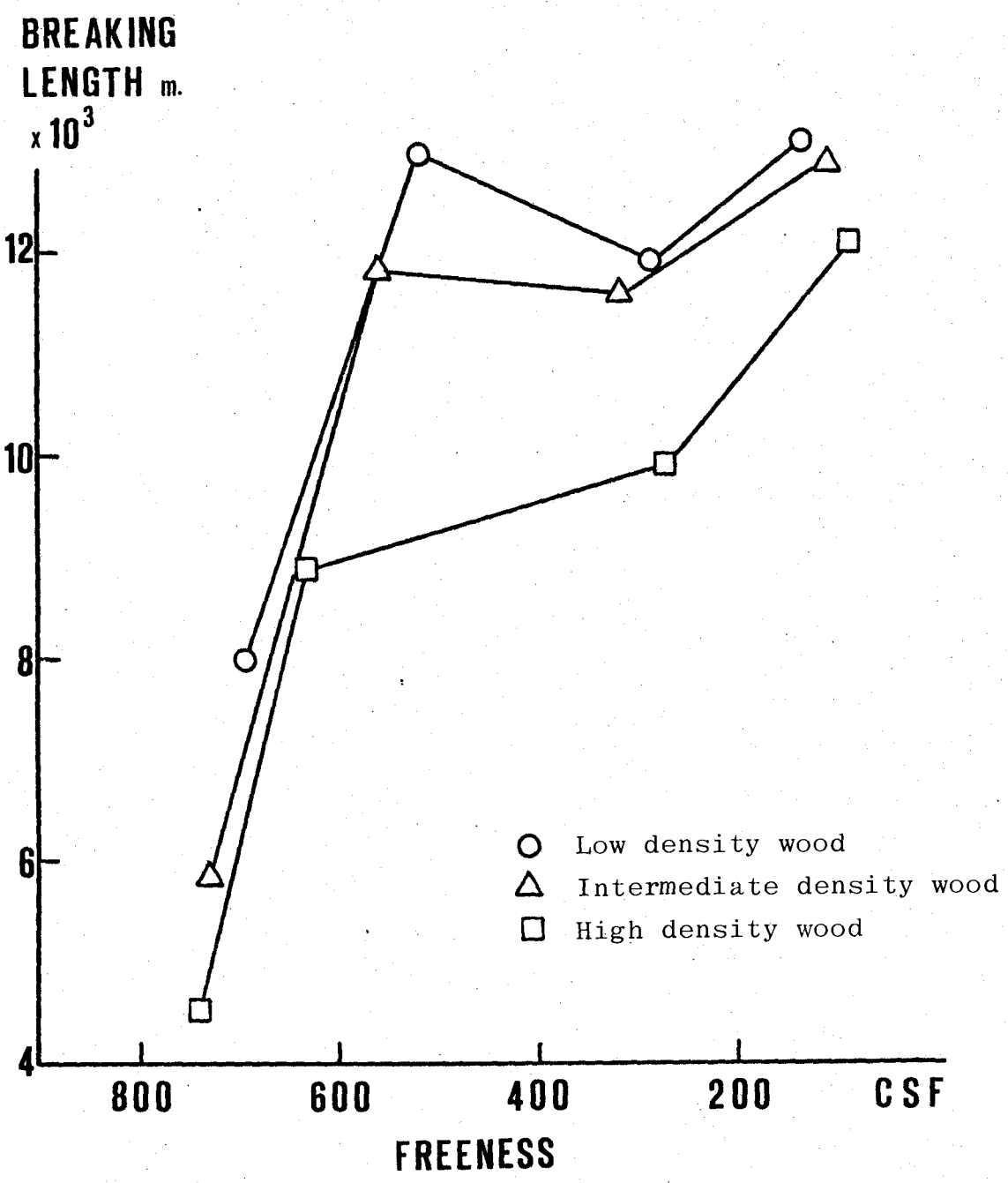

Figure 17. Breaking length vs. CSF

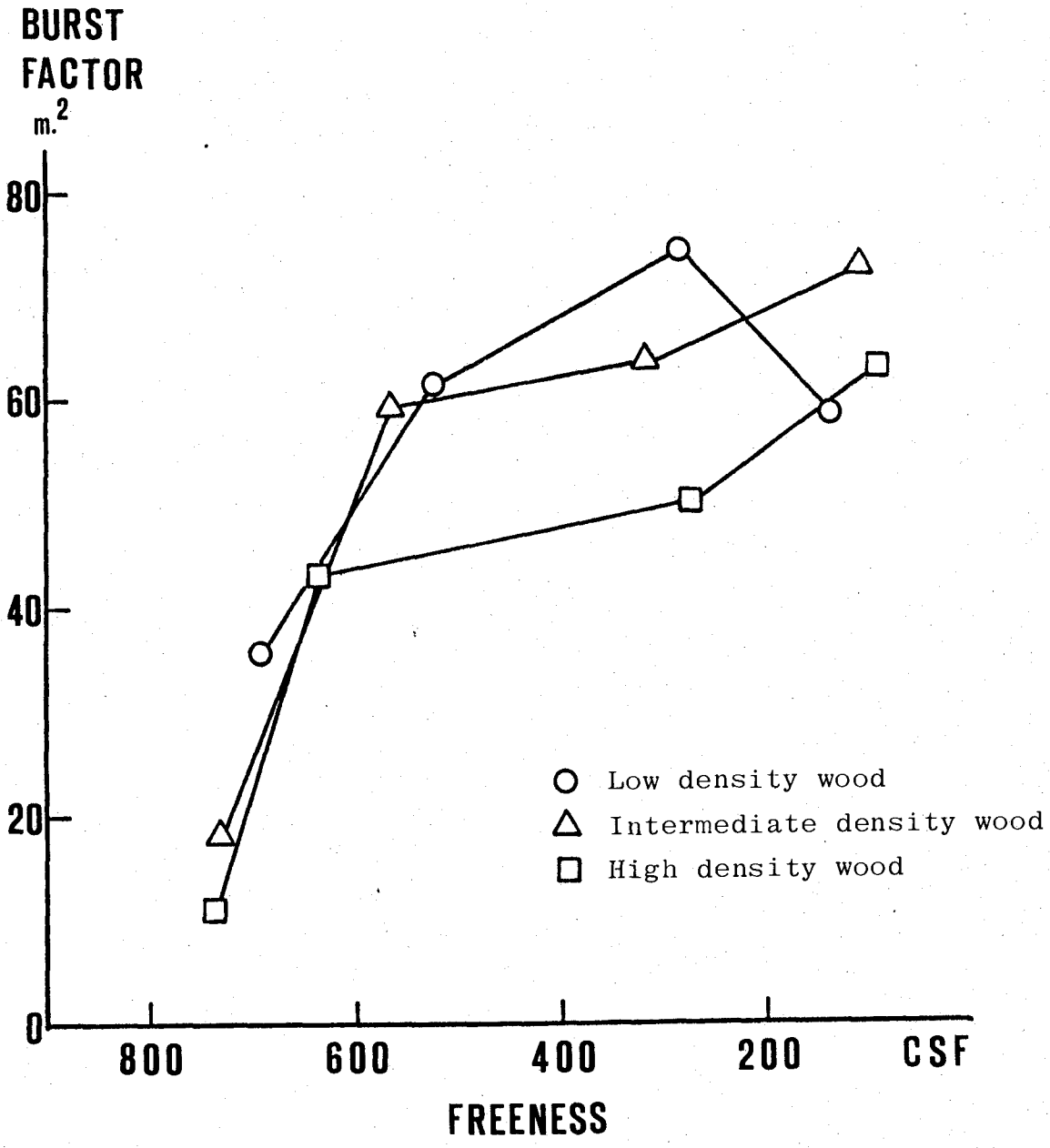

Figure 18. Burst factor vs. CSF

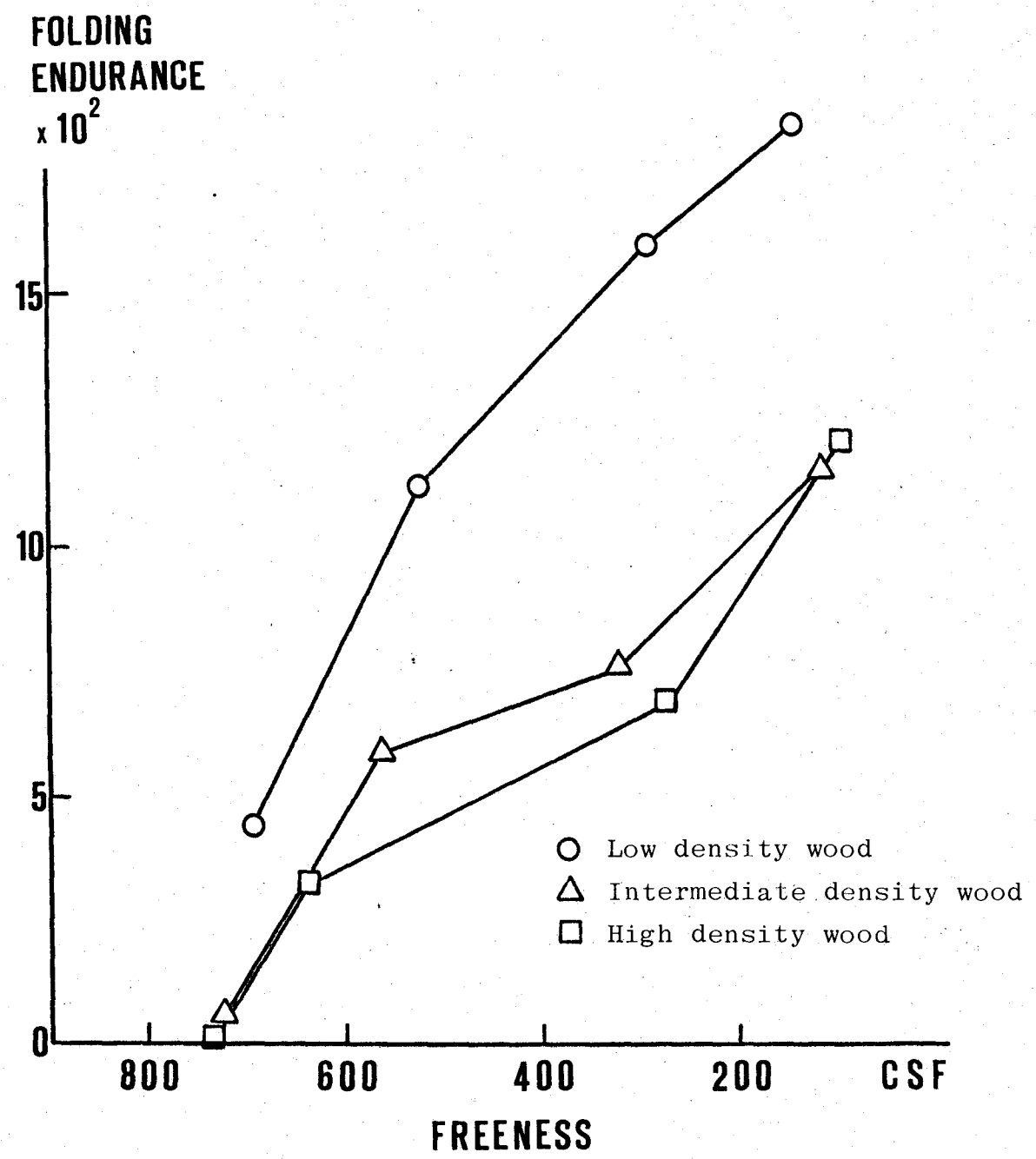

Figure 19. Folding endurance vs. CSF

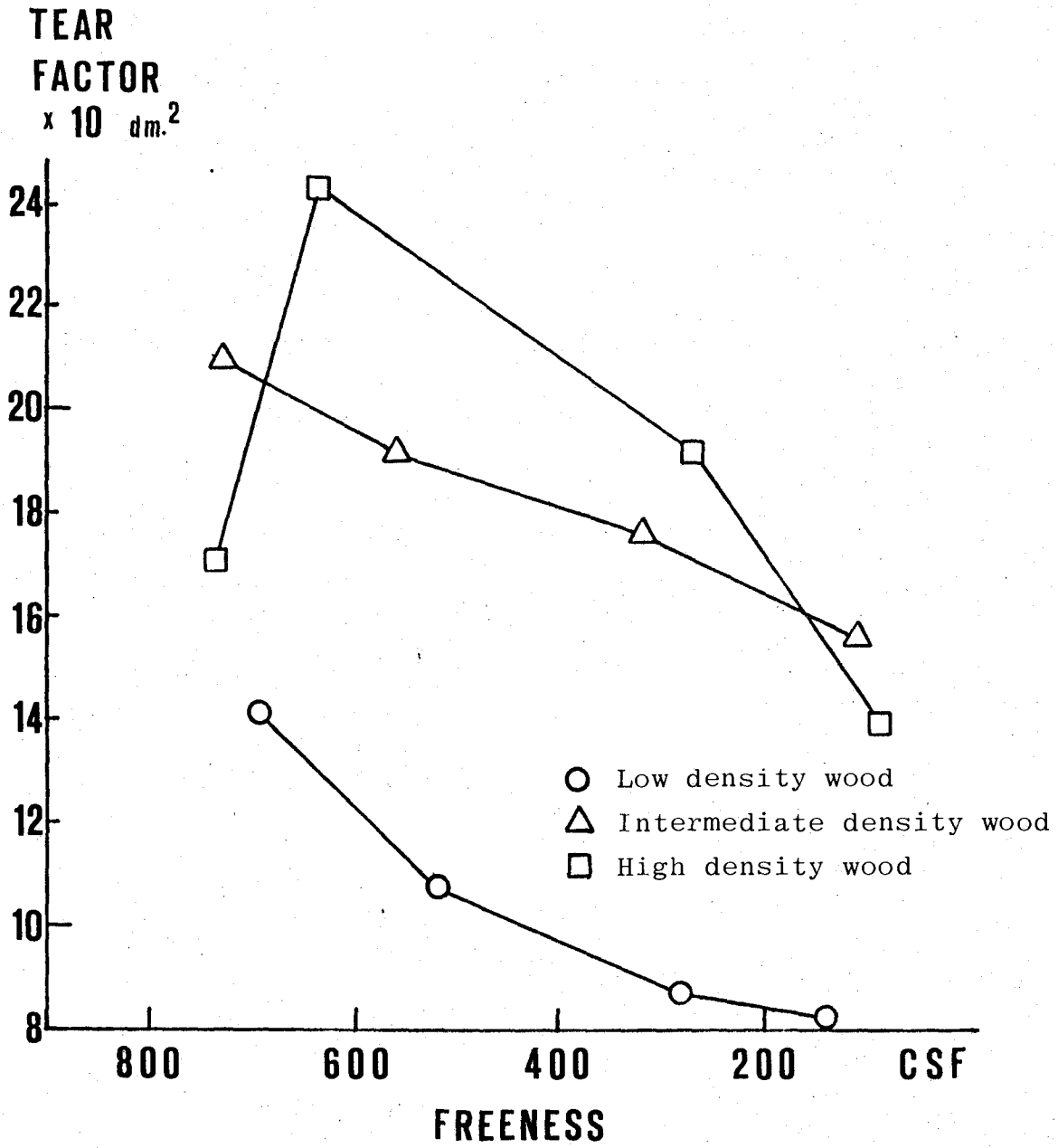

Figure 20. Tear factor vs. CSF

and folding endurance. For tearing strength, the results agree with the former reports (7, 32, 99), that thicker walls and longer fibers produce higher tearing strength.

TABLE 19. LINEAR REGRESSION OF BULK TO STRENGTH PROPERTIES OF PULP

	r^2		
	Low density	Intermediate density	High density
Log Beating	0.994	0.996	0.988
CSF	0.794	0.668	0.718
Brightness	0.994	0.994	0.900
Burst	0.771	0.986	0.980
Tear	0.960	0.721	0.003
Fold	0.919	0.836	0.756
Breaking Length	0.902	0.980	0.966

2. Constant Bulk

Significant linear relationships between the bulks and logarithms of beating, brightness, folding endurances, and breaking lengths of each wood sample were found as shown in Table 19. However, there was lower correlation in certain properties such as CSF and bursting strength of the low density wood,

folding endurance and tearing resistance of the intermediate density and the high density wood samples. There was no linear relationship between bulk and the tearing resistance of the high density wood pulp because it had a curvi-linear relationship with the CSF as shown in Figure 20.

Table 20 shows the strength properties of the wood pulp at constant bulk, the intermediate density showing the highest bursting strength, tearing strength, folding endurance and breaking length with the low density wood pulp showing almost the lowest of these properties at the same bulk, It can be noted that the high density wood pulp tended to have higher tearing resistance than the intermediate density wood pulp when the bulk decreased. Also the low density wood pulp tended to have higher folding endurance than the other two and higher breaking lengths than the high density wood pulp when the bulk decreased. The higher strength properties of the intermediate density wood pulp compared to the high density wood pulp may be due to the thinner cell walls of the intermediate density wood pulp that could collapse more readily than the high density wood pulp fibers as explained in the previous discussion. However, the strength properties of the low density wood pulp at 1.75 and 2.00 cm^3/g of bulk and also the

TABLE 20. PHYSICAL STRENGTH PROPERTIES OF PULP AT CONSTANT BULK

LINEAR REGRESSION DATA

PROPERTY	BULK	WOOD DENSITY LOW 1-1C-1	MEDIUM 2-1C	HIGH 2-3C-1
LOG BEATING	1.25	2.788	3.493	3.568
	1.50	1.220	2.682	2.800
	1.75	-0.349	1.870	2.032
	2.00	-1.918	1.059	1.264
CSF	1.25	277	211	153
	1.50	532	338	295
	1.75	787	464	437
	2.00	1042	591	579
BRIGHTNESS	1.25	16.7	18.0	16.2
	1.50	20.6	19.4	17.1
	1.75	24.5	20.8	18.0
	2.00	28.4	22.2	18.9
BURST	1.25	65.9	76.8	65.6
	1.50	49.6	63.2	53.6
	1.75	33.2	49.6	41.6
	2.00	16.8	36.0	29.6
TEAR	1.25	89.1	164.0	183.5
	1.50	119.9	175.1	184.7
	1.75	150.7	186.2	186.0
	2.00	181.5	197.3	187.2
FOLD	1.25	1588	1025	1023
	1.50	897	791	780
	1.75	206	557	537
	2.00	-484	324	294
BREAKING LENGTH	1.25	12833	13607	12222
	1.50	10158	11800	10503
	1.75	7482	9994	8784
	2.00	4806	8188	7065

1.25 cm^3/g of the intermediate and the high density wood pulps have to be neglected because they were out of the scale of the experiment.

At the constant bulk at 1.50 cm^3/g, the high density wood pulp had the highest tearing strength and the low density had lowest value. These results agree with the Bauer-McNett data and previous reports (31, 99) that the longest fibers (the high density wood pulp) had the highest tearing strength and the shortest fibers (the low density wood pulp) produced the lowest tearing strength. The low density wood pulp had the highest folding endurance which may be due to the ability of its fibers to collapse as previously explained. But the breaking length and the bursting strength tended to decrease, possibly due to the thin walled fibers that probably broke down with severe beating.

SUMMARY

Three significant differences in the properties of the three wood density samples of Douglas-fir were noted in the study. The high density sample was the most penetrable while the low density wood had the least penetrability, which may be due to pit aspiration that occurred during drying conditions. The high density wood that contained thicker cell walls could have stiffer pit membranes that resist more strongly the surface tension forces that cause pit aspiration than the lower density sample. Significant differences between the heartwood to sapwood ratios were noted. The intermediate density wood sample had the highest quantity of sapwood while the high density wood sample had the lowest quantity of sapwood. The quantity of Klason lignin and the extractive content varied with the ratio of heartwood and sapwood. The high quantity of lignin in heartwood may be due to development of lignin like substances during heartwood formation.

No significant effect on the reaction rates and activation energies of the overall pulping reactions and delignification reactions were noted due to differences in the wood qualities of Douglas-fir. Temperature seemed to have the most significant effect on the reaction rates and the energies of activation of delignification. The cooking time had the most significant effect on the rates and the energies of activation of the pulping reaction.

However, wood quality seemed to have more effect on delignification than on the pulping reaction.

At constant H factor, the wood penetrabilities and Klason lignin contents had a significant effect on the Kappa numbers of the pulps. In the beginning stages of cooking, variations in the penetrability of wood apparently affected the penetration of cooking liquor, but this tended to decrease at the higher temperatures and the longer cooking times.

The fluorescent intensity of waste liquor showed a linear relationship with cooking times at 165^{o} and $175^{o}C$. The results agreed with the relation of the Kappa numbers to the cooking times at these temperatures. The fluorescent intensity of waste liquor increased rapidly in the beginning stages and tended to decrease toward the end of the cooking period at $185^{o}C$. This may be due to condensation of lignin at high cooking temperatures and longer periods of time.

Although wood quality variations showed less effect on pulping reactions than the process variables of time and temperature, the density of wood could be considered as an approximate indicator of physical strength properties of pulp from that wood. The low density wood sample produced pulp with high tensile strength, bursting strength, and folding endurance due to its thinner cell wall fibers. These fibers had a tendency to collapse better during

drying than the thicker walls of the high density wood pulp, and gave better fiber bonding. The high density wood pulp can be considered as having higher tearing strength than low density wood pulp.

CONCLUSIONS

1. Wood quality variations in Douglas-fir affect on the reaction rates of pulping and delignification less than the process variables of time and temperature do.

2. Variations in wood quality affect the delignification reactions more strongly than the overall pulping reactions.

3. Temperature is the most important factor controlling the rate of delignification.

4. Time is the most important factor controlling the rate of overall pulping reaction.

5. Penetrability of the wood apparently has an effect on the initial penetration rate of liquor. Wood of high penetrability provides faster initial rate of penetration, but the difference decreases at longer times and higher temperatures of cooking.

6. High sapwood content wood delignifies more rapidly than low sapwood content wood because of the high penetrability of sapwood and the limited penetrability of heartwood.

7. A low Klason lignin content wood produces a low Kappa number pulp at constant H factor.

8. Wood containing easily penetrable heartwood apparently delignifies more rapidly than wood containing low penetrable heartwood at constant H factor.

9. Variations in the extractive contents of Douglas-fir have no effect on the reaction rates of pulping or delignification.

10. Linear relationships exist between the fluorescent intensities of the waste liquors and the cooking times at low and medium temperatures.

11. Lignin condensation may affect the fluoroemtric response of waste liquor at higher temperatures.

12. Wood density can be considered as an approximate indicator of the strength properties of pulp. Low density wood pulp has higher folding endurance, tensile strength, and bursting strength, but lower tearing strength than high density wood pulp.

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APPENDICES

APPENDIX TABLE 1

COOKING DATA OF LOW DENSITY WOOD SAMPLE

Cook No.	Temperature °C	Time min.	Yield %	Kappa Number	Fluorescent Intensity
1	165	60	60.76	124.6	1.32
2	165	100	57.28	103.7	1.35
3	165	140	53.64	86.3	1.51
4	165	180	50.54	71.3	1.55
5	175	60	53.26	81.2	1.48
6	175	100	49.16	55.0	1.58
7	175	140	47.04	43.0	1.68
8	175	180	44.84	34.3	1.84
9	185	60	45.66	40.1	1.82
10	185	100	43.80	27.8	1.91
11	185	140	42.18	24.7	1.98
12	185	180	41.28	22.3	1.84

APPENDIX TABLE 2

COOKING DATA OF INTERMEDIATE DENSITY WOOD SAMPLE

Cook No.	Temperature ^{o}C	Time min.	Yield %	Kappa Number	Fluorescent Intensity
13	165	60	59.68	98.6	1.46
14	165	100	54.86	75.9	1.60
15	165	140	52.84	61.3	1.67
16	165	180	51.80	49.1	1.80
17	175	60	53.22	66.6	1.64
18	175	100	50.16	45.1	1.83
19	175	140	48.04	32.2	1.93
20	175	180	46.98	26.4	2.00
21	185	60	47.24	31.2	2.04
22	185	100	45.80	23.4	2.17
23	185	140	43.78	18.5	2.04
24	185	180	42.26	15.9	1.99

APPENDIX TABLE 3

COOKING DATA OF HIGH DENSITY WOOD SAMPLE

Cook No.	Temperature °C	Time min.	Yield %	Kappa Number	Fluorescent Intensity
25	165	60	57.44	103.7	1.34
26	165	100	56.10	90.7	1.51
27	165	140	52.80	74.4	1.65
28	165	180	50.72	55.5	1.72
29	175	60	51.50	71.1	1.58
30	175	100	48.44	48.9	1.66
31	175	140	46.28	35.3	1.71
32	175	180	45.24	29.3	1.92
33	185	60	47.44	41.3	1.74
34	185	100	43.82	28.0	1.97
35	185	140	42.28	20.6	1.83
36	185	180	41.26	18.4	1.82

APPENDIX TABLE 4

Physical Strength Properties of Low Density Wood Pulp

COOK NO. 1-1C-1 MONTREE

YIELD	=	41.80
SCREENINGS	=	0.98
KAPPA	=	32.71

ORIGINAL DATA

INTERVAL	1	2	3	4
BASIS WEIGHT	59.850	63.100	59.450	61.100
CSF	688	516	284	136
BEATING	0	250	500	750
BRIGHTNESS	23.5	18.1	17.3	15.9
BULK	1.689	1.333	1.267	1.218
DENSITY	0.592	0.750	0.789	0.821
BURST	36.0	61.6	74.1	58.9
TEAR	141.7	107.2	87.2	82.8
FOLD	432	1105	1587	1826
BREAKING LENGTH	7964	12974	11876	13093

APPENDIX TABLE 5

Physical Strength Properties of Intermediate Density Wood Pulp

COOK NO. 2-1C MONTREE

YIELD	=	46.88
SCREENINGS	=	0.94
KAPPA	=	30.98

ORIGINAL DATA

INTERVAL	1	2	3	4
BASIS WEIGHT	76.100	72.450	73.650	74.100
CSF	724	560	317	109
BEATING	0	350	750	1000
BRIGHTNESS	24.1	19.3	19.2	18.9
BULK	2.326	1.541	1.447	1.397
DENSITY	0.430	0.649	0.691	0.716
BURST	18.6	59.4	63.5	72.7
TEAR	209.4	191.1	175.8	155.6
FOLD	51	576	747	1126
BREAKING LENGTH	5826	11769	11550	12920

APPENDIX TABLE 6

Physical Strength Properties of High Density Wood Pulp

COOK NO. 2-30-1 MONTREE

YIELD	=	47.01
SCREENINGS	=	2.65
KAPPA	=	31.81

ORIGINAL DATA

INTERVAL	1	2	3	4
BASIS WEIGHT	55.050	56.900	60.100	60.950
CSF	734	633	268	86
BEATING	0	250	750	1000
BRIGHTNESS	20.5	17.0	17.1	17.2
BULK	2.392	1.686	1.499	1.376
DENSITY	0.418	0.593	0.667	0.727
BURST	11.7	43.3	50.3	63.5
TEAR	171.0	242.5	191.3	138.9
FOLD	12	316	670	1195
BREAKING LENGTH	4541	8893	9928	12097