

AN ABSTRACT OF THE THESIS OF

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Signature redacted for privacy.

Abstract approved:

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Several additives have been used in research and on an industrial scale to improve the pulp yield and to increase the rate of delignification. One such additive is 1,4-dihydro- 9,10-dihydroxyanthracene (DDA), also called soluble anthraquinone. This chemical is widely used in Japan and some other countries, especially with the eucalyptus species; however, there is little information on this additive in the literature for pulping softwoods. The behavior of this chemical in the kraft pulping of Douglas-fir (Pseudotsuga menziesii), a predominant species of the northwest, was studied using DDA and the more common anthraquinone (AQ) additives. DDA was found to be a superior additive compared to AQ as the total pulp yields improved by 1 to 2% over AQ or 3 to 4% over control kraft, for kappa numbers below 90 (at 0.1% additive level). A decrease of 80 to 400 in the H-Factor is possible during cooking for pulps

with kappa numbers between 25 and 80. For cooks producing pulps with kappa number of 90 or higher, DDA was actually detrimental. The brightness of the unbleached DDA pulps improved by 1 to 2% (TAPPI) over the AQ and control pulps.

No significant difference was found in the beating performance of the three types of pulps and also there was no significant difference in the pulp viscosities or the strength properties of the handsheets made from these pulps.

Kraft Pulping of Douglas-fir with Soluble Anthraquinone

by

Tapas Dutta

A THESIS

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degree of

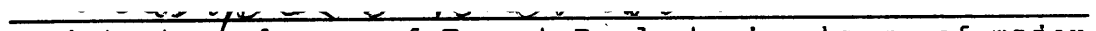
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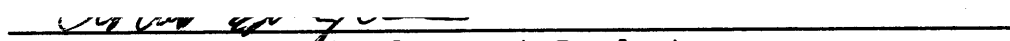
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Kraft Pulping of Douglas-fir with Soluble Anthraquinone

INTRODUCTION

It has been almost 14 years since the patents for pulping wood with anthraquinone (AQ) and the disodium salt of 1,4-dihydro-9,10-dihydroxy anthracene (DDA or SAQ) were filed in Japan. However, the catalytic effect of AQ during kraft pulping, was first made public in 1977 in Canada. The response from the pulp and paper industry was rapid and since then there has been a substantial research work and industrial application. The application of these chemicals in kraft pulping in Japan is particularly widespread, where almost all the pulp mills use these pulping additives.

The reason for the widespread use of these additives in Japan is the extremely high cost of wood chips, fuel, etc. in Japan as compared to other major pulp producing countries like the United States, Canada, Finland and Sweden. It is essential for the Japanese pulp and paper industry to utilize their resources to the fullest extent.

Worldwide more than 70 mills have continuously or intermittently used AQ pulping and over 100 mills have at least performed trials. About 18 countries, in addition to Japan, have been reported to have mills using AQ.

Information on the pulping of softwoods in the presence of DDA is quite limited. Therefore, the objective was to study the effect of this chemical on the kraft pulping of Douglas-fir (Pseudotsuga menziesii), which is the major

species of the northwest. The results have been compared with cooking in the presence of AQ and cooking without any additive (control).

The net economic benefits can be calculated in a simple manner by taking into account the increase in pulp yield and the cost of chemicals. However, the actual benefit varies substantially from mill to mill depending upon the limiting factor of production. Since the principal use of AQ is for the manufacture of textile vat dyes throughout the world, its price depends largely on the prevailing AQ demand in the textile industry.

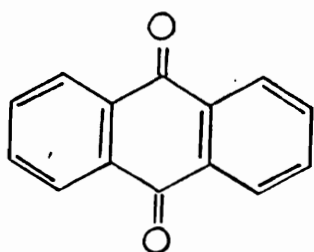
Before going into further detail, it is useful to look into the structure of these additives and see the mechanism by which they improve the yield and lead to a faster rate of delignification. The structures of these chemicals are shown in Figure 1.1 and the mechanisms are shown in Figures 1.2 and 1.3, respectively.

The major difference in mechanism of these two chemicals is, that in the case of DDA, the redox cycle starts with the reduction of lignin instead of the oxidation of the carbohydrates as in the case of anthraquinone.

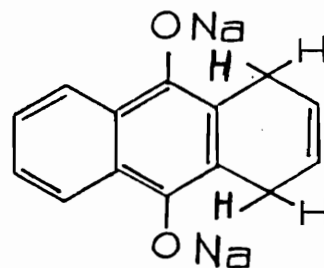
Attempts have been made to explain the difference between the efficacies of these chemicals on the basis of redox potential, solubility, hydrophilicity, xylophilicity, normal and half wave potential, and their chemical stability in alkaline media.

Another advantage of using quinone additives is that the

FIGURE 1.1: Structures of the two quinone additives



ANTHRAQUINONE
(AQ)



DISODIUM SALT OF 1,4-DIHYDRO-
9,10-DIHYDROXYANTHRACENE
(DDA)

FIGURE 1.2: The reaction mechanism of anthraquinone

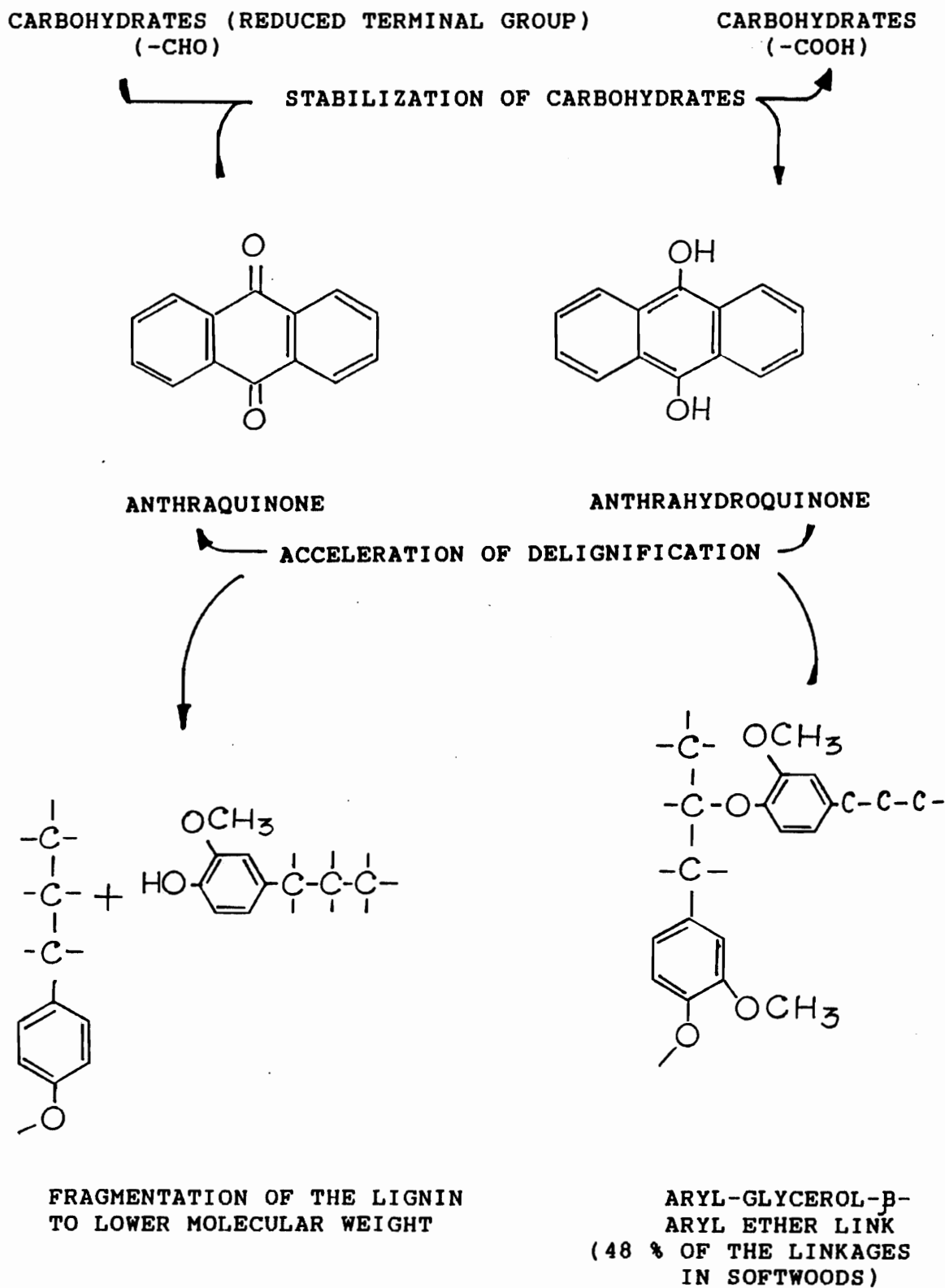
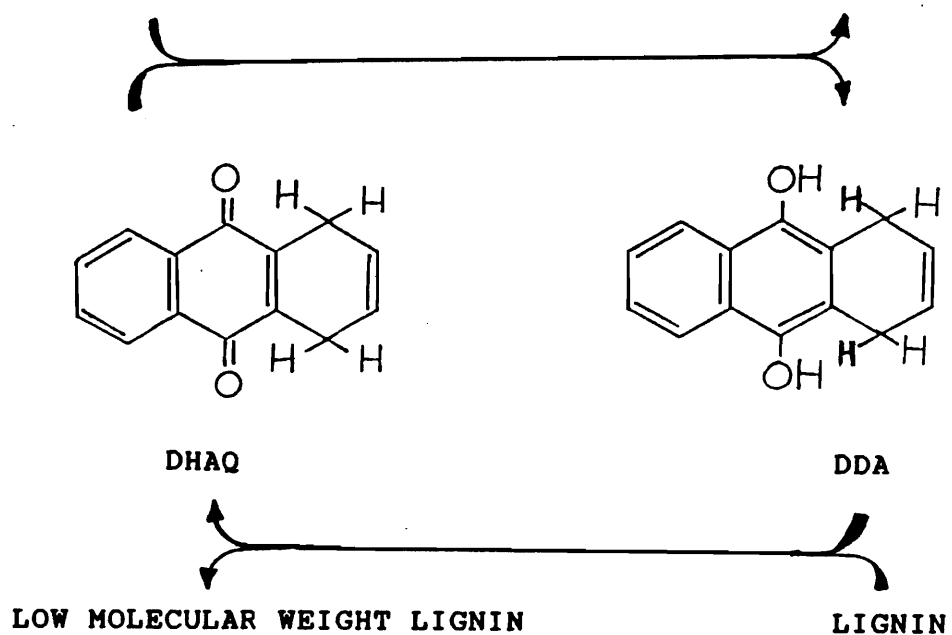


FIGURE 1.3: The reaction mechanism of DDA

CARBOHYDRATES (-CHO)

CARBOHYDRATES (-COOH)



DHAQ : 1,4-DIHYDRO-9,10-ANTHRACENEDIONE

DDA : 1,4-DIHYDRO-9,10-DIHYDROXYANTHRACENE

sulfidity of the cooking liquors can be reduced. This means that air pollution due to the sulfur compounds can be reduced by pulping with these additives. The reduced kappa number of the pulp also leads to a reduced consumption of bleach water which in turn leads to a reduced load on the effluent treatment plant.

On an industrial scale, a production gain as large as 9% has been reported in Japan by using a quinone additive during pulping.

LITERATURE REVIEW

HISTORY

Kraft pulp was invented by Carl F. Dahl in Danzig, Germany in 1884⁽¹⁾. The use of sodium sulfate (kraft process) instead of carbonate (soda process) was actually introduced in 1879, as the make-up chemical to cover the losses in the process⁽²⁾. The first kraft pulp in the United States was made in 1909⁽¹⁾ and by the 1920's this pulping technology was well established. The main reasons were the excellent strength properties of the pulp produced and its comparatively insensitivity to variations in wood condition and its applicability to all wood species^(1,2). Kraft pulping, which uses sodium sulfide as a part of the cooking liquor, emits odoriferous reduced sulfur compounds^(1,2) and attempts have been made since its implementation to reduce the use of sulfur compounds without affecting the strength properties of the pulp.

After the discovery of recovery boilers in the 1930's⁽³⁾, the kraft process became well established. Since then, there have been several major improvements in the equipment⁽⁴⁾, but there have been only a few changes in the process itself.

REACTIONS OF CARBOHYDRATES DURING ALKALINE PULPING⁽²⁾

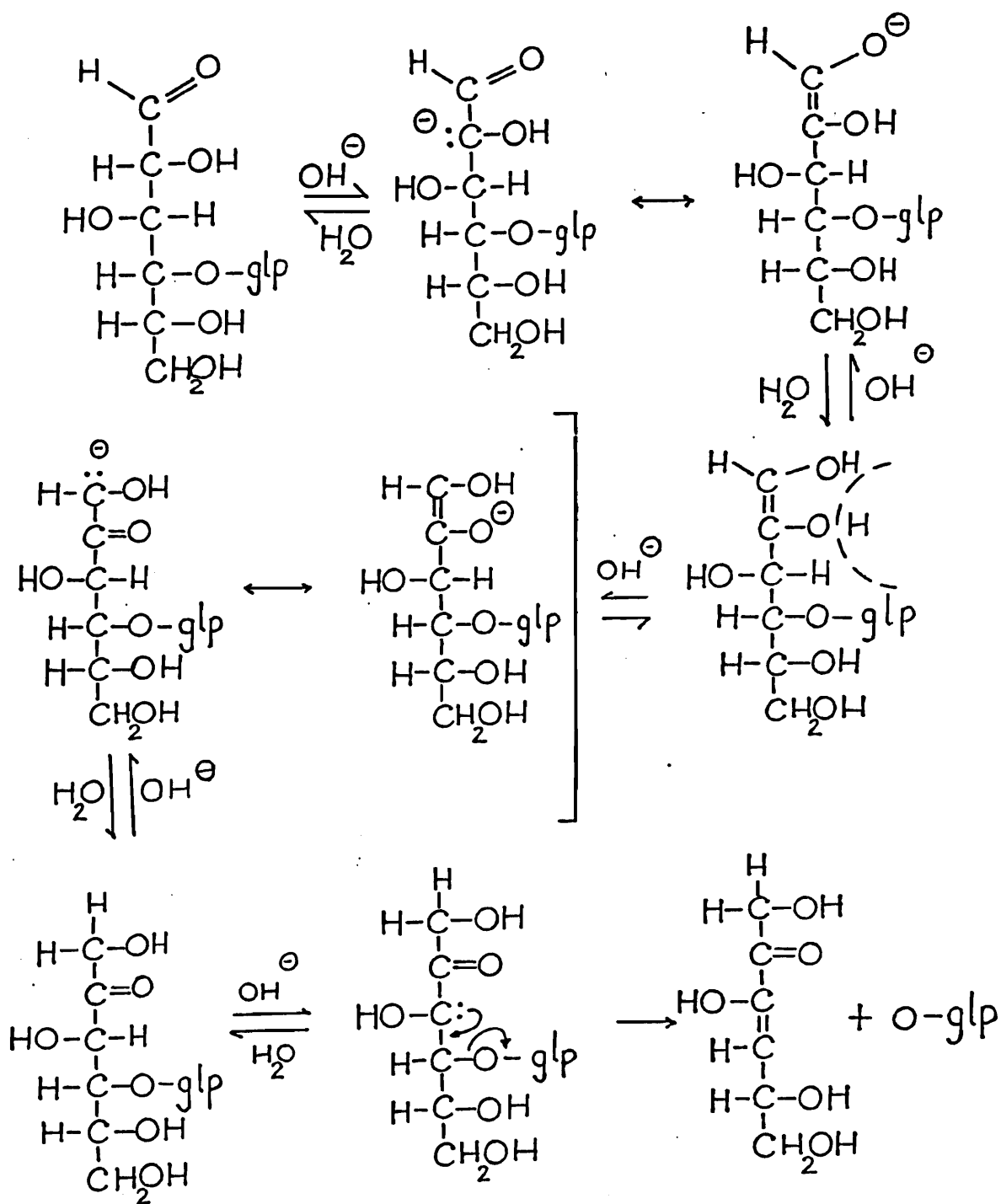
During alkaline cooking, carbohydrates undergo a number

of complicated reactions as follows :

1. Alkaline swelling, causing physical changes in the fiber wall.
2. Alkaline dissolution of carbohydrate matter without chemical degradation.
3. Reprecipitation of dissolved carbohydrates and their adsorption on the fiber structure.
4. Alkaline hydrolysis of acetyl groups.
5. Alkaline peeling, a reaction sequence involving enolization, hydrolysis of β -alkoxycarbonyl bonds and further degradation of the products of hydrolysis, including isomerization, as well as hydrolysis to hydroxy acids.
6. Stopping reactions, involving dehydration and fragmentation or intramolecular rearrangements to alkali-stable configurations.
7. Alkaline hydrolysis of β -glycosidic bonds to shorter fragments which are exposed to further degradation by alkaline peeling.

Of these, the peeling reaction is responsible for most of the alkali consumption and yield losses. This reaction is shown in figure 2.1. It starts as the enolization of carbonyl groups of end units in the carbohydrate chains, followed by isomerization to β -alkoxy-carbonyl configurations. These are extremely sensitive to hot alkali and undergo rapid decomposition, whereby the end unit is split off, and a new aldehyde-containing end unit is formed, which

FIGURE 2.1: The peeling reaction



glp: glucopyranose unit

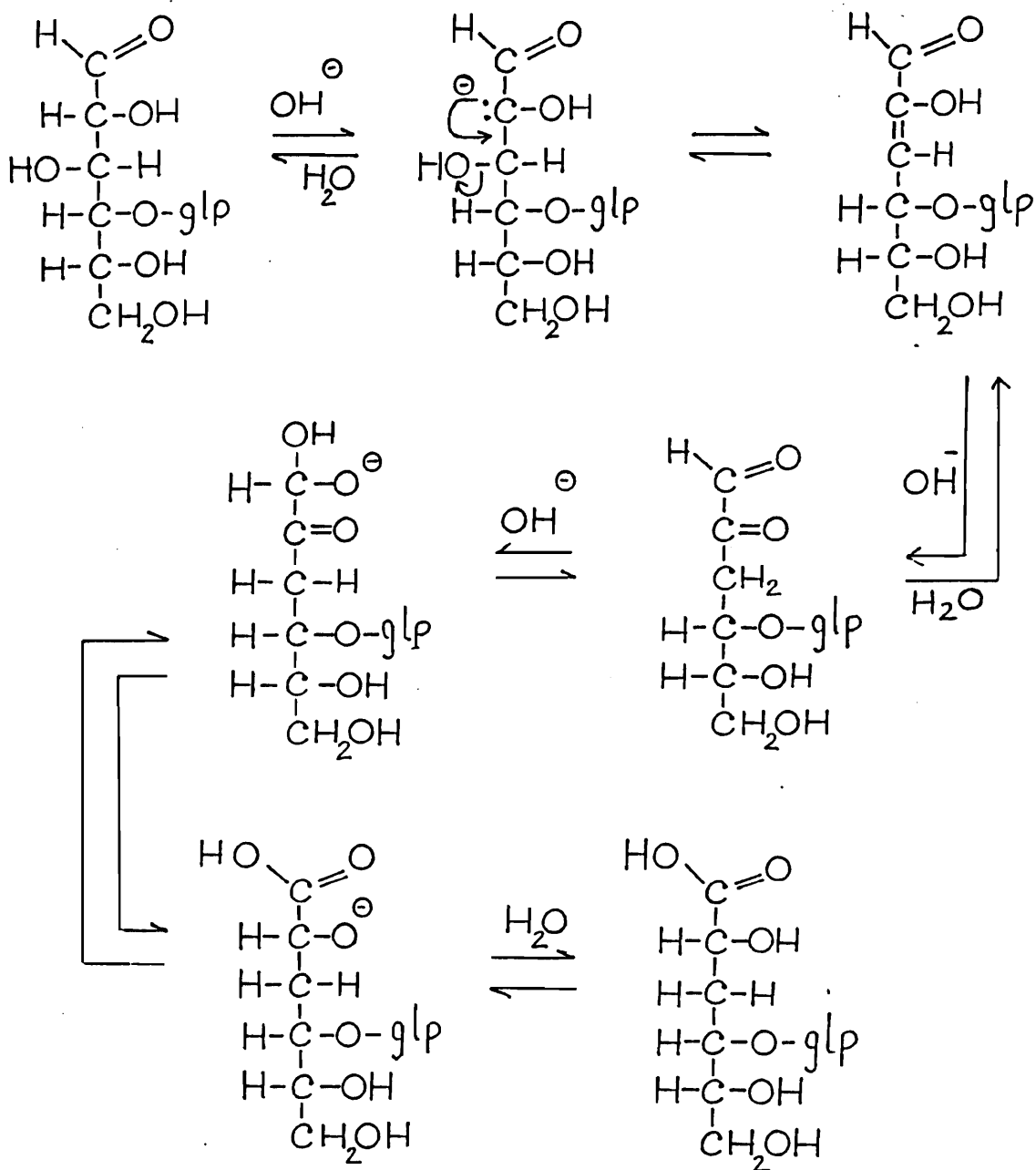
in its turn can be split off in the same manner. The peeling proceeds until an average of 50-65 monomers are cleaved from every starting point until finally another reaction, called the 'stopping reaction', provides the end unit with a configuration stable to alkali. The termination of the peeling reaction is shown in figure 2.2.

The two obvious ways to minimize alkaline peeling would be to either reduce the end group to an alcohol group or to oxidize it to an acid group. As already shown in the mechanism of the quinone additives, they stabilize the reducing end group of the cellulose chain by oxidizing it to an acid group, so that a minimum number of glucose monomers are lost by the action of alkali.

WHY USE THE KRAFT PROCESS FOR DOUGLAS-FIR

The kraft process is well established for Douglas-fir, but it can not be easily pulped by the acid sulfite process^(2,5,6). It is believed that one reason why Douglas-fir can not be easily pulped by the acid sulfite process is the presence of the phenolic extractive dihydroquercetin. This extractive tends to reduce bisulfite to thiosulfate, which reduces the stability of the cooking acid⁽²⁾. This in turn leads to high screen rejects and high kappa number of the pulp. The pulp comes out of the digester yellow in color⁽⁵⁾ which is thought to be due to the oxidation of the dihydroquercetin to quercetin⁽²⁾.

FIGURE 2.2: Termination of the peeling reaction



ADDITIVE PULPING

Several modifications of the kraft pulping process have been examined by scientists around the world. The basic objective has been improvement in pulp yield by stabilizing the carbohydrates so that they are lost only to the minimum extent by the peeling reaction. These include H₂S pre-treatment of wood chips⁽⁷⁾, polysulfide process and use of additives during pulping.

A major breakthrough in pulping technology came in 1977 when the catalytic effect of anthraquinone was first made public in Canada⁽⁸⁾. In fact quinone additives like anthraquinone and 1,4-dihydro-9,10-dihydroxy anthracene (DDA or SAQ) were actually used in pulping in Japan prior to 1977. Patents for the use of these chemicals were filed in Japan in October 1974 and December 1976, respectively^(9,10).

Anthraquinone cannot be called a true catalyst as it can be recovered only partially after pulping. According to Fullerton et al.⁽¹¹⁾, anthraquinone undergoes condensation reactions in the reduced anthrahydroquinone form with the lignin derived quinone methides and this is the most likely reason for AQ's effectiveness as a pulping catalyst. This may also explain why AQ is only partially recoverable after pulping.

In some cases quinone additive pulping has produced benefits greater than those observed in laboratory tests. In Japan, production gains as high as 9% have been reported by the use of DDA in kraft pulping of eucalyptus⁽¹²⁾. The most

probable cause for better yields industrially than in laboratory tests is the build up of AQ levels due to recycling of black liquor in industrial production. This would lead to higher than applied charges of AQ, which means less AQ may be needed on industrial scale to obtain a given effect than laboratory studies suggest⁽¹³⁾.

Since 1977, when the results of AQ pulping were first presented to the public⁽⁸⁾, it attracted great interest in the pulp and paper industry⁽¹⁴⁾. Research and mill trials were subsequently carried out to study effectiveness and mechanism of AQ action⁽¹⁵⁻¹⁹⁾, and also to see if the use of AQ led to any problems during scaleup⁽¹²⁾. A large number of other quinone derivatives were also tested for effectiveness and possible use as a pulping additive^(15,18). Donnini et al.⁽¹⁵⁾ studied over 300 pulping additives and concluded that anthraquinone was the most cost effective pulping catalyst.

1,4-Dihydro-9,10-dihydroxyanthracene or DDA is produced by dissolving tetrahydroanthraquinone (THAQ) in caustic soda solution or in white liquor^(10,21). AQ is conventionally produced as an important intermediate in the dyestuffs industry from anthracene extracted from coal tar⁽²¹⁾. The other process for producing AQ starts with catalyzed gas phase oxidation of naphthalene to naphthoquinone. Naphthoquinone is then subjected to Diels-Alder synthesis with butadiene, giving tetrahydroanthraquinone, which can be easily converted to anthraquinone⁽²¹⁾.

ADVANTAGES OF DDA

One great advantage of using DDA rather than AQ is the fact that DDA is much easier to handle. It is supplied in liquor form, whereas AQ is a powder and insoluble in white liquor. This makes AQ quite difficult to be used on a commercial scale^(9,12,20). Also, it has been reported that the catalytic effects of AQ depends to a great extent on the uniformity of its distribution through out the digester⁽²¹⁾. Difficulties encountered due to improper mixing of the additive can be partially eliminated by using DDA.

PROBLEM WITH DDA

However, some problems have been reported in the literature regarding the use these quinone additives on an industrial scale^(9,10,12). It has been reported that the dilute black liquor drained from the digesters contains active quinones of about 30% of the total quinone additives. DDA also forms AQ gradually by oxidation through catalytic actions with lignin. AQ thus recovered in the drain sometimes causes deposits in the multiple effect evaporators, heat exchangers, pipelines etc. Precipitated AQ attaches to the digester wall forming a scale composed of AQ and the adhesive oily components in the drain as the viscosity increases with cooling. These scales have been reported to be relatively soft and consist of about 65% AQ and 35% oily components in the drain⁽⁹⁾.

According to a report on procedures of scale removal⁽¹²⁾,

these deposits can be removed by circulating 9% aqueous sodium hydroxide at a temperature of about 80°C. In some cases the results are improved by subjecting AQ scales to reductive dissolution with hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) under alkaline condition⁽⁹⁾.

MECHANISMS

Two fundamental functions of quinone as cooking additive are⁽¹⁰⁾:

1. Acceleration of delignification by cleavage of the β -phenylester bonds.
2. Stabilization of cellulosic materials by oxidation of terminal aldehyde groups of polysaccharides.

Accelerated delignification may lead to one or more of the following benefits:

1. Lowering of cooking temperature saving energy.
2. Shortening of cooking time saving energy.
3. Reduction of active alkali saving chemicals or speeding throughput in the recovery furnace.
4. Low kappa number of pulp reducing bleaching process waste water.
5. Lowering of sulfidity reducing odor problem.

Stabilization of carbohydrates will lead to improvement of pulp yield and possibly an improvement in pulp strength properties.

The difference between the efficiency of these additives have been explained on the basis of redox potential, solubility⁽²²⁾, hydrophilicity⁽²³⁾, xylophilicity⁽¹⁶⁾, normal⁽²⁴⁾ and half wave potential⁽²⁵⁾, and the chemical stability in alkaline media⁽²⁶⁾.

The reaction mechanisms^(9,10,21) of the two quinone additives (AQ and DDA), are shown in figures 1.2 and 1.3 respectively. These two additives have the following 'redox potentials'⁽²¹⁾:

AQ: 0.15 V

DDA: -0.13 V

Nakano et al⁽⁹⁾ studied the reaction mechanism of DDA in the cooking process for guaiacyl-glycerol- β -guaiacylester which was used as a model compound of lignin, and found that DDA also functioned as a redox catalyst.

The mechanism of DDA action is quite similar to that of AQ except that, due to the lower redox potential, the redox cycle starts with reduction of lignin instead of oxidation of carbohydrates⁽²¹⁾.

Although it appears from figure 1.2 that only cellulosic materials reduce AQ and lignin oxidizes AHQ in the redox reversible cyclic reaction, actually both cellulosic and lignin derivatives can reduce AQ and oxidize AHQ⁽⁹⁾.

EXPERIMENTAL PROCEDURES

WOOD CHIPS

Douglas-fir chips of industrial quality were obtained from a local pulp mill. The same supply of chips was used for the complete set of experiments.

Chips were screened on a Hatton screen arrangement having the following classification from top to bottom:

Over-Long	:	45 mm diameter holes
Over thick	:	10 mm slots
Accept	:	7 mm diameter holes
Pin-Chips	:	3 mm diameter holes
Fines	:	-3 mm

The accept chips (i.e. -10 +7 mm fraction) were used in these experiments. When using small digesters, chip homogeneity is very important to ensure uniform results. Chips were manually sorted for defective pieces, knots or bark.

The chemical composition of the wood chips is shown in Appendix B.

COOKING LIQUOR

Kraft cooking liquor was made up by mixing NaOH stock and Na₂S stock solutions together with distilled water to the desired active alkali and sulfidity.

Cooking liquor was always made fresh just prior to the cooking, and was heated to 80 °C before charging it to the digester. This temperature is close to an operating mill's

white liquor temperature, and also the oxidation of DDA is reduced due to less dissolved oxygen in the heated liquor.

CHIP CONDITIONING

The effect of DDA is reduced if low moisture content chips are used for cooking without rewetting⁽²⁷⁾. Therefore, chips were first air-dried to 20 to 30% moisture content by spreading them on a sheet. These chips were then mixed up to make a uniform sample and were kept in polyethylene bags. Air drying to a 20-30% moisture content is very important in order to minimize error caused by differences in moisture content among the chips.

Whenever required, a batch of uniformly air-dried chips were taken, weighed and conditioned to a 40-45% moisture content prior to cooking. Chips were rehydrated by adding the calculated amount of warm water and holding the sample overnight. By this time all the water is absorbed by the wood chips⁽²⁷⁾. Moisture content was again checked after mixing the chips thoroughly.

Moisture content of the wood chips is very important as the quinone compounds diffuse slowly in wood chips, particularly in dry chips.

MIXING OF DDA WITH THE COOKING LIQUOR

As noted previously, DDA was mixed with the white liquor at 80°C immediately prior to cooking to minimize oxidation of DDA by reducing its contact with dissolved oxygen.

DDA was added and mixed gently so as to avoid drawing air into the liquor. Vigorous stirring may cause oxidation. To minimize the contact of DDA with oxygen, it was sealed under nitrogen gas after each use.

COOKING PROCEDURE

A weight of 50 gm (o.d. basis) of the conditioned chips, were used for each experiment. Pulping was done in four stainless steel digesters, each with a capacity of 500 ml. The digesters were heated by immersion in a hot oil bath, preheated to the desired cooking temperature. Mixing was done by rocking the oil bath. Suspended-basket cooking, where the testing basket is suspended inside the digester having exactly the same cooking conditions is most appropriate for these kind of studies. However, suspended basket cooking was not possible under the conditions of these experiments.

The cooking conditions were as under:

Cooking Temperature: 170°C
Time to Temperature: Essentially instantaneous
Time at Temperature: Variable while studying the effect of time and 120 minutes otherwise.

White Liquor Sulfidity: Variable while studying the effect of sulfidity and 25% otherwise.

Alkali Charge: 20% on o.d. wood

Liquor/Wood ratio: 7:1
Additive Concentration: 0.025 to 0.5% based on the o.d. wood while studying the effect of additive concentration and 0.1% otherwise.

Yield was determined after drying the pulp at $105 \pm 3^{\circ}\text{C}$. Kappa number and viscosities were determined according to TAPPI standards (T 236 os-76 and T 254 pm-76, respectively). For the larger batches a C-E-H sequence was used to test the bleachability of the pulps and brightness was measured as per TAPPI standards (T 217 os-48).

The liquor to wood ratio was higher than that normally used commercially. This was necessary in order to dip all the chips in the liquor in the digester to ensure uniform cooking.

For each cook, the digester was charged with the appropriate amount of chips and cooking chemicals, sealed and inserted in the oil bath for the desired time. At the end of the cook the digester was removed, cooled rapidly in water and opened. Spent chemical was decanted from the chips and the chips were defibered with about one liter of water in a kitchen blender. The pulp was washed in a Buchner funnel with an additional one liter of water. Excess water was removed by suction and the pulp was air-dried before further testing.

Large batch cooks were carried out in digesters capable of handling 1 Kg of o.d. chips. The cooking conditions were

similar to smaller experimental cooks except for a lower liquor to wood ratio. This was possible because the cooking liquor is circulated in these digesters.

TESTING OF PULP PROPERTIES

The following TAPPI Test methods⁽²⁹⁾ were used for testing of pulp and preparation and testing of pulp handsheets. Five handsheets were made to test the strength properties for each type of pulp and each level of freeness.

- T 236 os-76: Kappa number of pulp
- T 254 pm-76: CED disperse viscosity of pulp
(falling ball method)
- T 217 os-48: Brightness of pulp
- T 248 pm-74: Laboratory beating of pulp
(PFI mill method)
- T 227 os-58: Freeness of pulp
- T 205 om-81: Forming handsheets for physical testing of
pulp
- T 220 om-83: Physical testing of pulp handsheets
- T 211 om-80: Ash in wood and pulp
- T 222 om-83: Acid-Insoluble lignin in wood and pulp
- T 410 om-83: Grammage of paper and paper board
- T 403 os-76: Bursting strength of paper
- T 414 om-82: Internal tearing resistance of paper
- T 494 om-81: Tensile breaking properties of paper and
paper board
- T 511 om-83: Folding endurance of paper (MIT)

STATISTICAL DESIGN

A 'Randomized Block Design' was chosen for the experiments and the statistical analyses. Different batches of three cooks each, were taken as blocks. The three treatments were applied to the digesters at random in each batch. The statistical analyses and effect of blocking (i.e. whether blocking was effective or not) are shown in the 'Results and Discussion' section.

RESULTS AND DISCUSSION

A dramatic decrease in kappa number and an increase in the pulp yield, due to faster delignification and stabilization of the carbohydrate fraction occurred when either additive was used.

The kappa number and total pulp yield relationship is shown in Figure 4.1. During the initial stages of cooking, i.e. for pulps with high kappa numbers, DDA appeared to have a detrimental effect as the kappa number was higher for a given pulp yield, compared to AQ and even conventional kraft cooks. However, when the kappa number was below 90, DDA showed a positive effect, and it was observed that for the same yield, the DDA kappa number was 7-20 points lower compared to AQ or conventional kraft cooks.

Low kappa number pulp reduces the load on the bleach plant and thus reduces chemical usage and waste water. This can be quite important for mills with restricted capacity in the bleach and waste water treatment plants.

The kappa number and total pulp yield relations for the pulps could be best described by the following equations:

$$\begin{aligned} \text{yield} &= 39.8 + 0.2 * \text{kappa number}, && \text{for control pulps} \\ &= 39.0 + 0.28 * \text{kappa number} + 0.0006 * (\text{kappa number})^2, && \text{for AQ pulps, and} \\ &= 39.6 + 0.35 * \text{kappa number} + 0.0013 * (\text{kappa number})^2, && \text{for DDA pulps.} \end{aligned}$$

The decrease in kappa number as the cook proceeded, is shown in Figure 4.2. In general, it can be said that for a

cook to the same kappa number, about 5-15 and 20-25 minutes of cooking time can be saved by using DDA, compared to AQ and conventional kraft cooks, respectively. Since the cooks were carried out at 170°C, this corresponds to a H-factor saving of 80-400.

These results can be interpreted in different ways. The maximum benefits can be obtained if the limiting factors of a particular mill are studied. Mill personnel need to assign importance to the potential advantages per their mill's operating conditions. The various advantages may be one or more of the following:

Savings of active alkali : For pulp mills where the capacity of the chemical recovery unit is limited, savings in active alkali may be profitably achieved. Alkali saving has been reported to be the most effective from the point of view of overall economy of pulp production⁽⁹⁾. Although I did not carry out the experiments at different levels of alkali charge, it has been reported by other workers⁽⁹⁾ that addition of 0.03% of DDA (on o.d. weight of wood) reduces active alkali in the range of 1 to 1.5%. Saving in active alkali will also reduce amount of weak black liquor and hence reduce the load of recovery plant evaporators. A reduction in active alkali will also reduce fuel oil consumption of the lime kiln.

Lowering of cooking temperature or cooking time : As noted, a saving of 80-400 in the H-factor was possible depending upon the kappa number of the pulp. This can result

in either a lower cooking temperature or a shorter cooking time. The optimum option will differ depending upon the particular mill condition. Lowering the cooking temperature would obviously result a saving in the steam used for the heating of digesters. At the same time the life of the digesters can be extended by using a lower cooking temperature. Among other advantages is the reduced scaling in the heating tubes of the digester and safer operation due to lower steam pressure.

Shortening of cooking times means increase in pulp production by having a higher throughput in any of the digesters.

Increase in pulp yield : All other things being similar, the AQ additive pulping resulted in an increase of 1 to 2% in the total pulp yield as compared to control, and DDA additive pulping resulted in an increase of 3 to 4% depending upon the kappa number and other pulping conditions.

SULFIDITY:

Kraft pulping, which is the most widely used pulping process in the world, emits strong malodorous reduced sulfur by-products which form during cooking. This is because of the presence of Na_2S in the cooking liquor. With DDA and AQ additive pulping, the sulfidity of the cooking liquor can be reduced to some extent while maintaining the same rate of delignification and pulp yields. Some mills increase the amount of quinone during the seasons when the wind blows

towards populated town areas, and reduce the sulfidity of the cooking liquor⁽⁹⁾.

The effect of sulfidity on kappa number for both DDA and AQ additives is shown in Figure 4.3. The positive effects of DDA was more pronounced at lower sulfidity levels. It is assumed that in this case DDA acts to assist delignification, the role normally taken on by the sulfide nucleophile. It can be concluded that the additive would substantially benefit soda pulping.

ADDITIVE CONCENTRATION

The effect of additives at various concentration levels was also studied with the results shown in Figure 4.4. It is seen that regardless of the additive level, DDA was more effective than AQ in reducing the kappa number. The effect seemed to be more pronounced at higher additive levels but the differences were fairly constant at an additive concentration of 0.1% or higher (on o.d. wood).

SAQ being soluble, can be fed in the system rather accurately with very simple equipment like a storage chest and a metering pump.

It has been reported⁽⁵⁾ that the efficacy of an additive is proportional to the square root of the additive charged. This implies that a plot of the square root of the additive charged and the inverse of the kappa number should result in a straight line. The plot of our results (Figure 4.5) confirms this; although, it is not a strict linear relationship.

CELLULOSE SOLUTION (0.5 % CED) VISCOSITY

The viscosity of the dissolved cellulose as a function of kappa number is shown in Figure 4.6. It was expected that the cellulose viscosities would be higher in the case of DDA, as it stabilizes the carbohydrates more efficiently. However, it is seen that the viscosity figures are scattered more or less around a straight line. It is known that the drop in viscosity is due to the random cleavage of the cellulose chain. It can be interpreted that the additives were not able to prevent the random cleavage of the cellulose chain even though they were able to stabilize the carbohydrates by altering the functional group at their reducing end.

UNBLEACHED PULP BRIGHTNESS:

The unbleached pulp brightness of the AQ and control kraft pulps were of the same magnitude, whereas an improvement of 1 to 2 points was observed in the case of pulping with DDA. This indicates that a saving in the cost of bleaching chemicals might also be possible. When the same amount of bleaching chemicals were applied the brightness of the DDA pulps were always 1 to 2 points higher. The relationship between the kappa number and the unbleached pulp brightness is shown in Figure 4.7.

In mills where relatively high kappa number pulp is produced, pulp with a higher kappa number may be produced as a result of the brightness improvement.

MATHEMATICAL MODELS AND STATISTICAL ANALYSES:

The development of mathematical models to correlate the pulping responses with the independent variables is very important because of the complexity of the pulping system. Linear and non-linear equations were developed by regression techniques for the prediction of kappa number and yield in the presence of the additives (see Table 10). The non-linear equations gave better fits and may be used to predict the kappa numbers or yield. These models can be very helpful for controlling the independent variables for a target yield or kappa number, within the range of the data.

A multiple range analysis of the data by 95% Fisher's Protected Least Significant Difference (FPLSD) method suggested significant difference in the kappa numbers for the three types of cooks i.e. control, AQ, and the DDA.

The Analysis of Variance (ANOVA) is as follows:

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Total	32	18324.82		
Batch	10	14618.27	1461.83	80.1
Treatment	2	3341.48	1670.74	91.5
Error	20	365.07	18.25	

Following interpretations can be made from this ANOVA:

1. Critical F-value from F-table at 0.05 level with numerator and denominator degrees of freedom being 2 and 20, is: $F_{0.05}(2, 20) = 3.49$ which is less than 91.5.

Therefore, it can be concluded that the differences among the treatment means are significant at 5% level.

2. $F_{0.05}(10, 20) = 2.35$ which is less than 80.1.

Therefore, blocking was effective in reducing error.

3. The 95% confidence intervals would be:

72.1 to 77.5 for control pulps,

53.6 to 59.0 for AQ pulps, and

48.7 to 54.1 for DDA pulps.

BEATING AND HAND-MADE PULP SHEET PROPERTIES:

BEATING PERFORMANCE:

To determine the performance of the pulp when it is converted to paper, the physical testing of the laboratory beaten and hand made pulp sheets provide significant information. Laboratory beating of pulp is a method for simulating commercial refining practices.

Figure 4.8 shows the fall in freeness (CSF) as a function of beating. All three types of pulp followed more or less similar paths, suggesting that there isn't any significant difference in the beating performance and that approximately the same energy would be required to bring all three pulps to the desired level of freeness. After a freeness of 500 CSF, it appears that the fall in freeness in the case of the control pulp is a little faster than the quinone additive pulps. However, the differences are too small to arrive at any conclusions.

FOLDING ENDURANCE:

This test is used to estimate the ability of the paper to withstand repeated bending, folding and creasing and for predicting the deterioration of paper upon aging. A lot of 'within-sample' variation was observed in this test. This is mainly because of the nature of the test. The folding stresses are applied to a very small area of the paper and failure occurs at this point unlike the normal tensile test where failure occurs at the weakest point of the test strip. The fold test operates cumulatively, the reduction in strength at the test point being approximately exponential. For this reason, it is considered that the log of the number of folds is a better measure of folding endurance than the number of folds.

The results are shown in figure 4.9. The quinone additive pulps appear to have slightly lower values, though no reason can be assigned to it. However, as already mentioned, the variations were too large to come to any conclusion statistically.

BURSTING STRENGTH:

This test simulates some end use requirements. It measures resistance to rupture. The development of the bursting strength as the beating proceeds, is shown in Figure 4.10. All the three pulps appeared to follow similar paths; the values for AQ pulp being little higher. The burst

index of the DDA pulp appeared to drop slightly after a freeness of 400 CSF.

TEARING STRENGTH:

In this test several sheets of the paper are torn through a fixed distance by means of the pendulum of the tear tester and the work done in tearing is measured by the loss in potential energy of the pendulum.

This strength property was the only one that decreased as the pulp was beaten. This is because tearing strength is directly related to the fiber length. As the beating proceeds, the fibers are shortened due to some cutting. Shortening of fiber length due to cutting during the beating operation can be minimized by adjusting several variables but it can not be avoided completely. The results of this test are shown in Figure 4.11. After a freeness of 400 CSF, the DDA pulps seemed to have slightly more tear strength (as indicated by the tear index), otherwise the three pulps behaved similarly.

TENSILE STRENGTH:

Tensile strength is indicative of the serviceability of papers such as wrapping and bag papers which are subjected to direct tensile stress. The tensile strength of printing papers is also important as tensile resistance is required during printing and converting operations. Tensile strength is indicated by 'Breaking Length', which has been defined in

appendix A. Tensile strength and bursting strength are related to each other, and tend to behave similarly as the beating proceeds. The results are shown in Figure 4.12. The breaking length of the control pulp appeared to decrease slightly after a freeness of 350 CSF. Tensile strength developed as the beating proceeded, due to fibrillation and more exposure of the fiber surface area for hydrogen bonding. However, if the beating is carried out for longer periods the strength decrease due to loss in fiber length.

A NOTE ABOUT FUTURE RESEARCH WITH DDA

It is known that peeling reaction is responsible for most of the alkali consumption during pulping⁽²⁾. Therefore, titration of the black liquor can be carried out to check the exact alkali consumption during control, AQ, and DDA pulping. This will provide significant information regarding actual behavior of DDA during pulping. Also, pulping of cotton in presence of DDA will provide more knowledge about the effect of this chemical on pure cellulose. This will also help in understanding the mechanism of DDA action in a better way.

Similarly, it will be interesting to know whether DDA stabilizes the hemicelluloses more effectively than AQ. Hemicellulose content of the control, AQ, and DDA pulps can be checked after carrying out the experiments under exactly similar conditions to find this. All above tests would provide a better understanding of the peeling reaction.

FIGURE 4.1:

The kappa number and total pulp yield relationship (cooks at 170 °C, 25% sulfidity and 20% alkali charge)

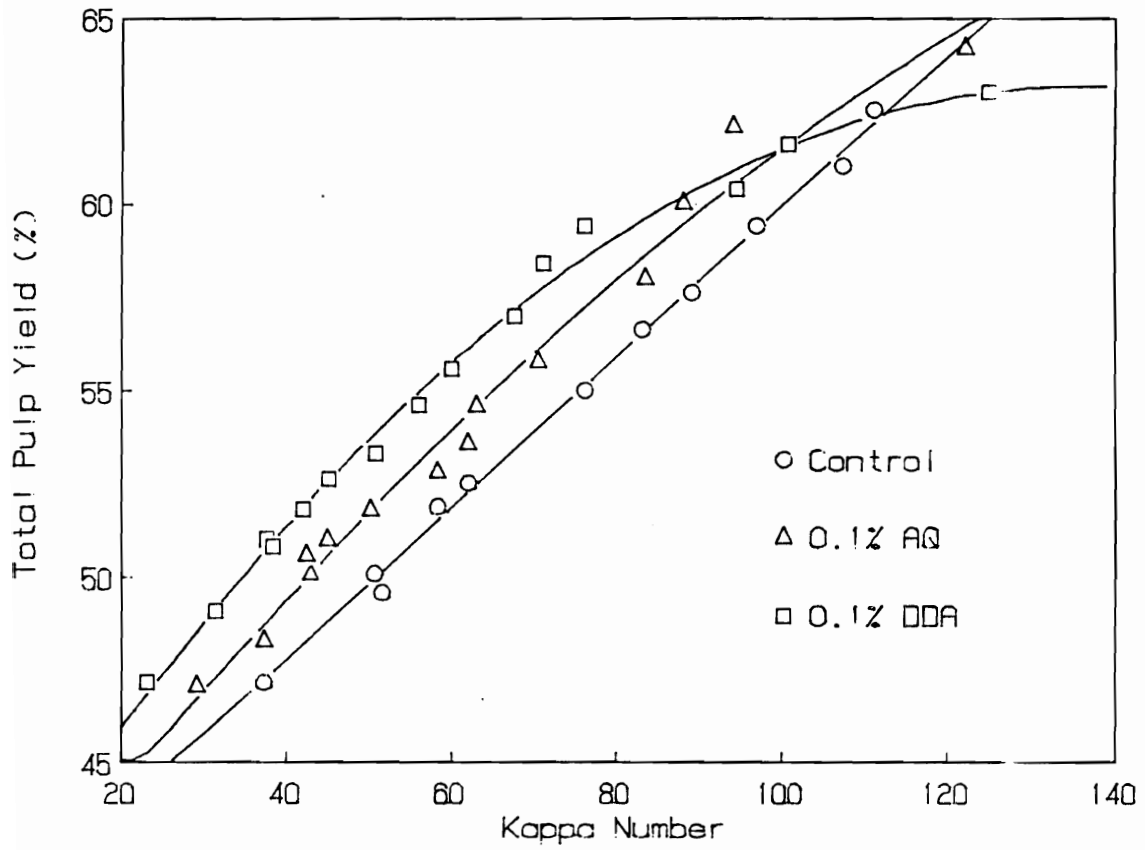


FIGURE 4.2:

The time at temperature and kappa number relationship
(cooks at 170 °C, 25% sulfidity and 20% alkali charge)

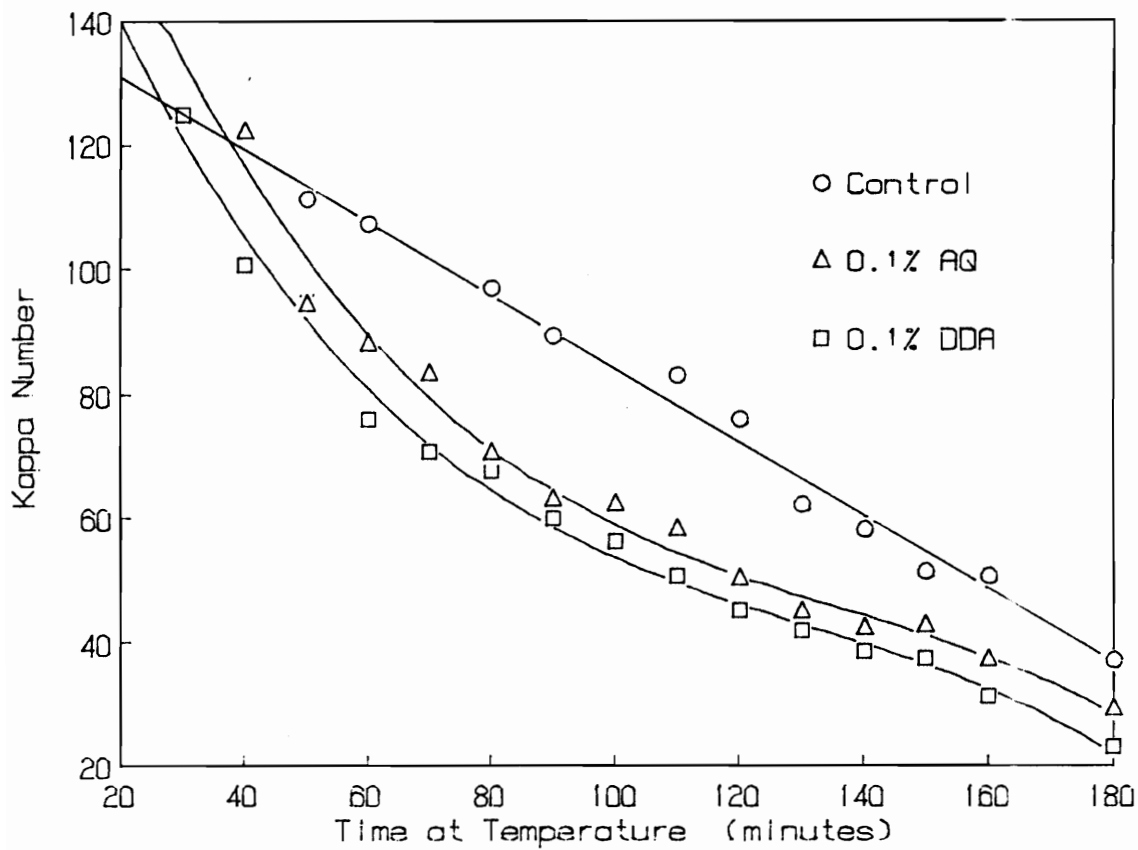


FIGURE 4.3:

The effect of sulfidity on kappa number in the presence of DDA and AQ additives (2 hours, 170 °C, 0.1% additive)

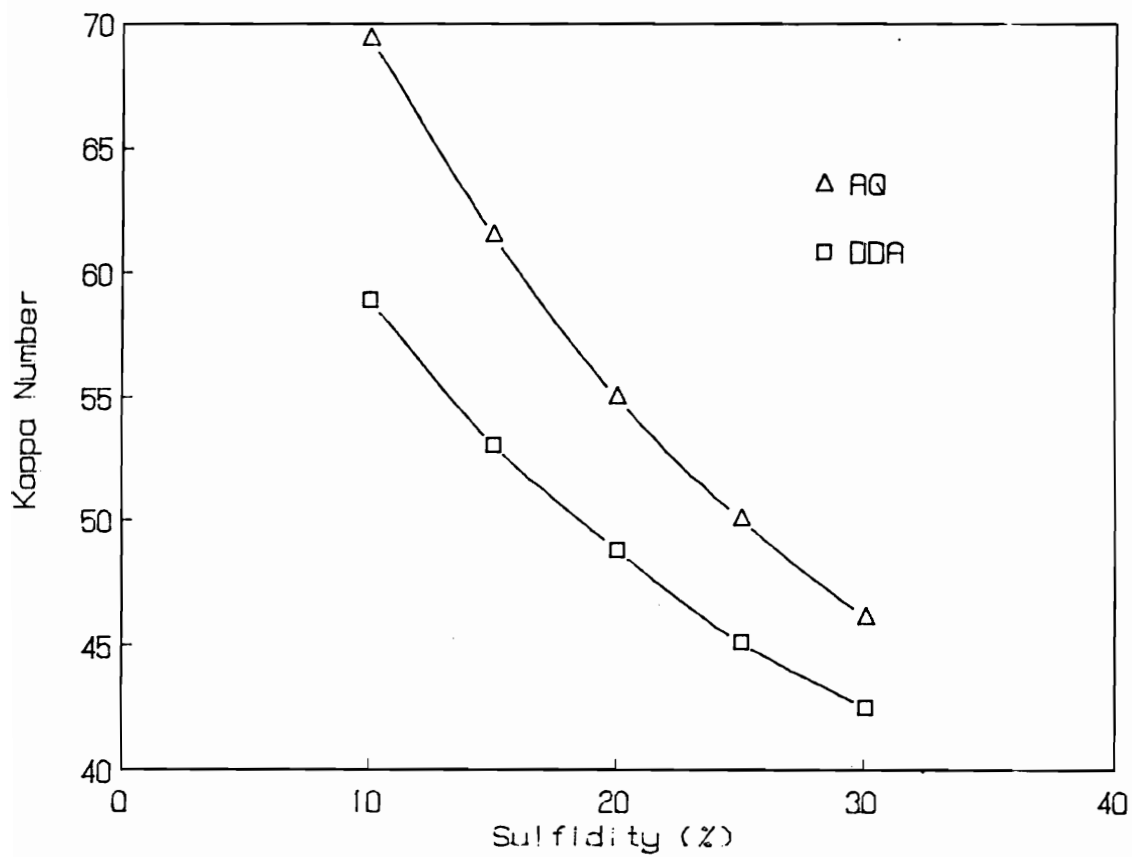


FIGURE 4.4:

The effect of DDA and AQ additive concentrations on kappa number (2 hours at 170°C and 25% sulfidity)

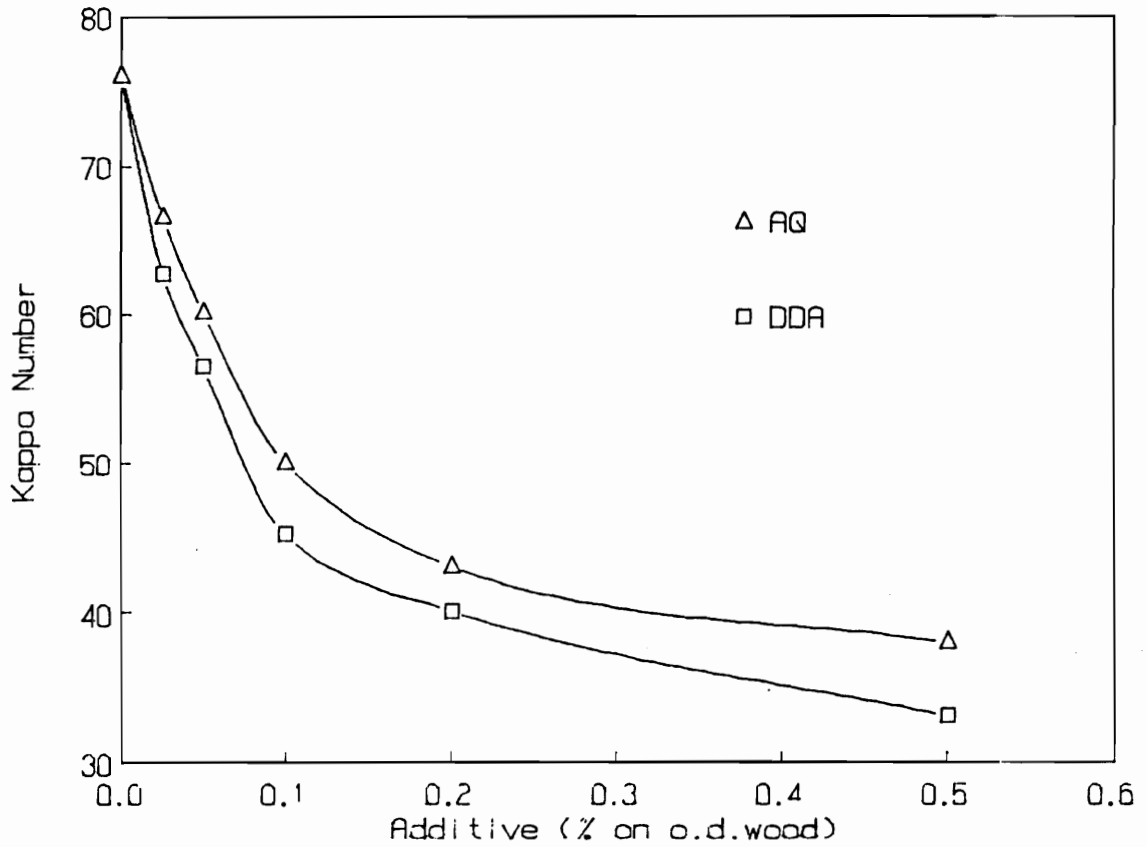


FIGURE 4.5:

The square root relationship between kappa number and additive concentration (2 hours, 170°C, 25% sulfidity)

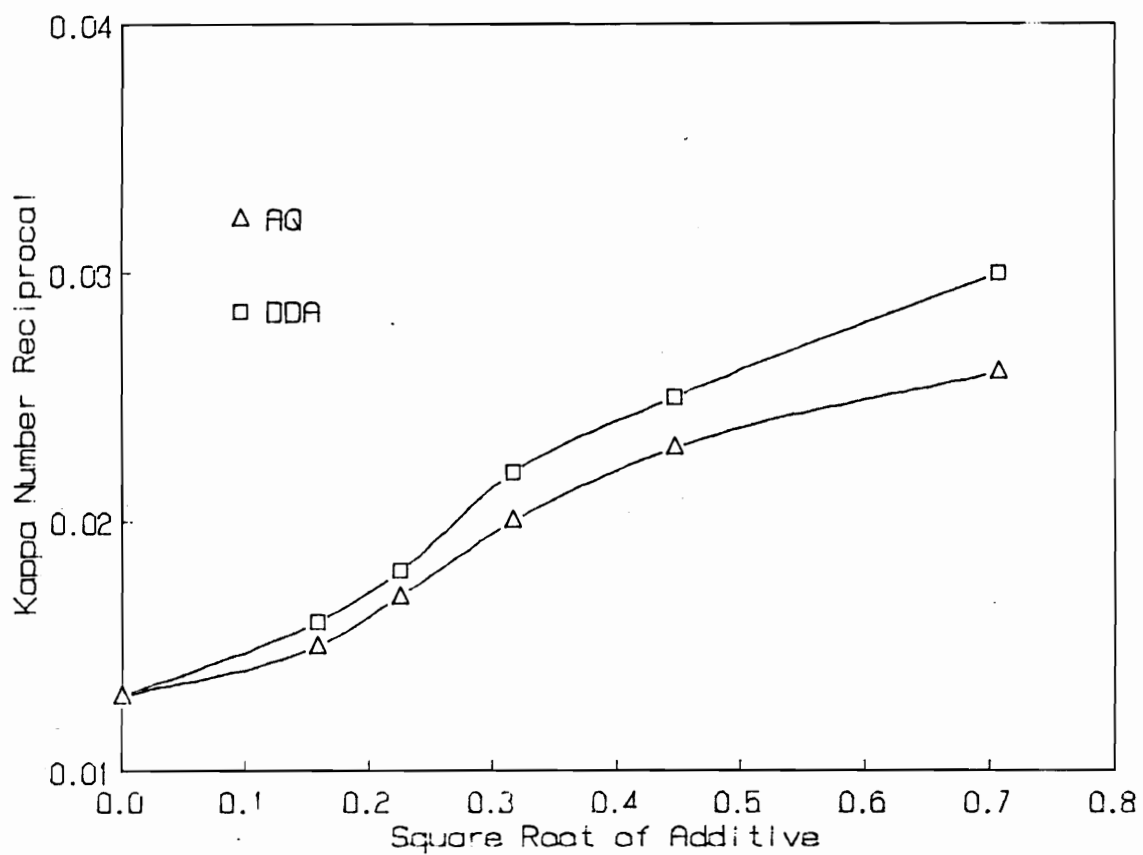


FIGURE 4.6.: The kappa number and unbleached pulp viscosity relation (cooks at 170°C and 25% sulfidity)

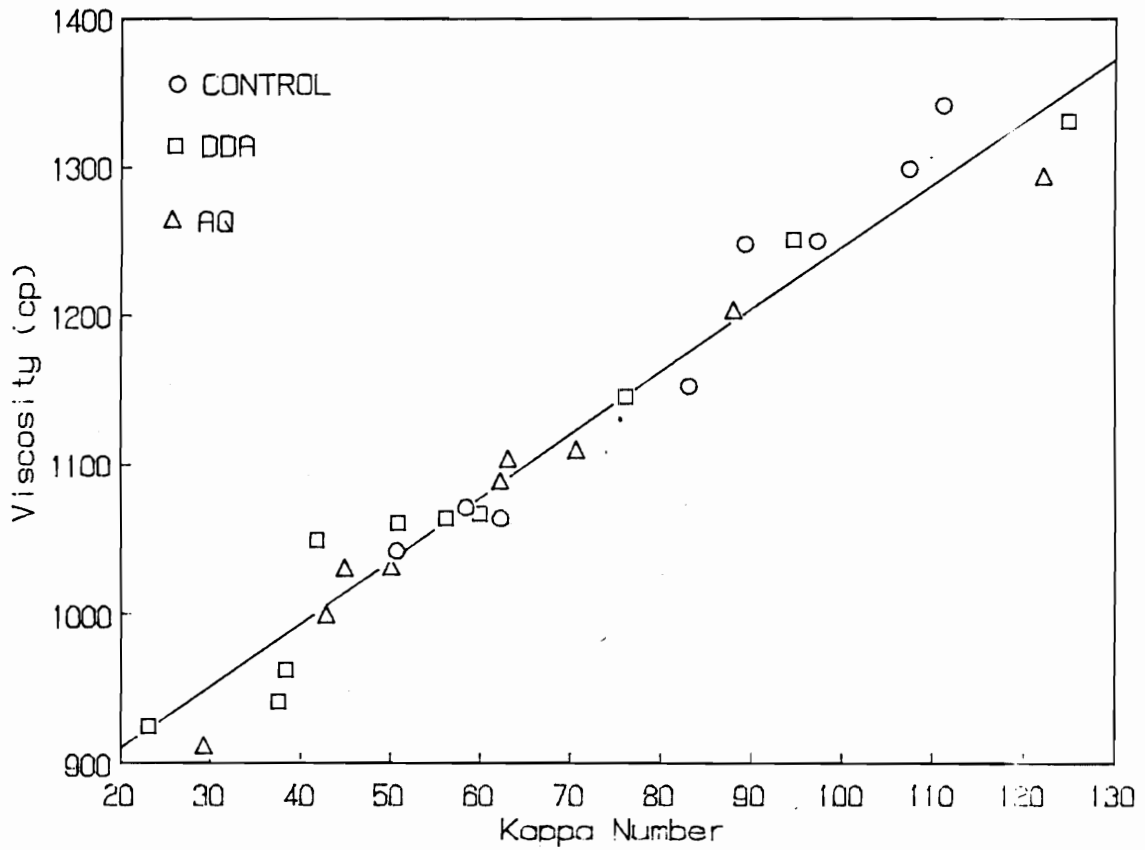


FIGURE 4.7.: The kappa number and unbleached pulp brightness relation (cooks at 170°C and 25% sulfidity)

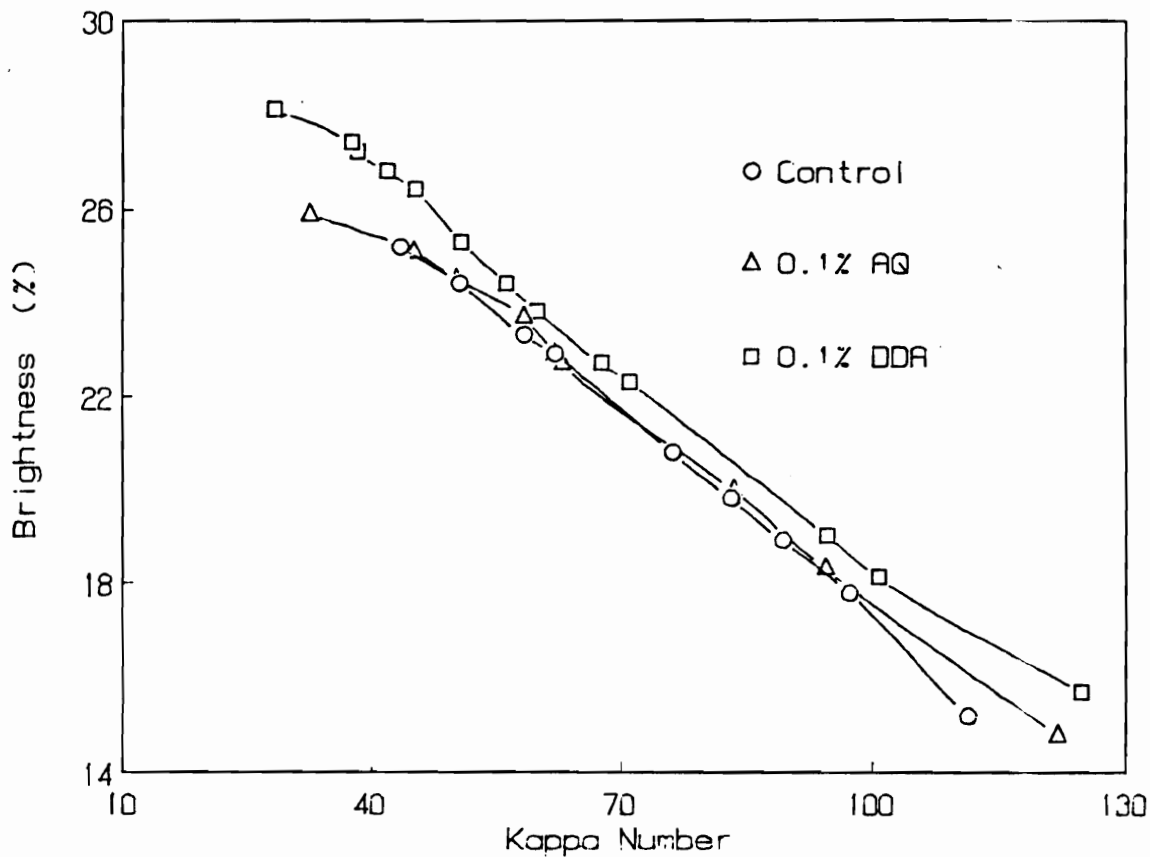


FIGURE 4.8.: Beating performance of the three types of pulp

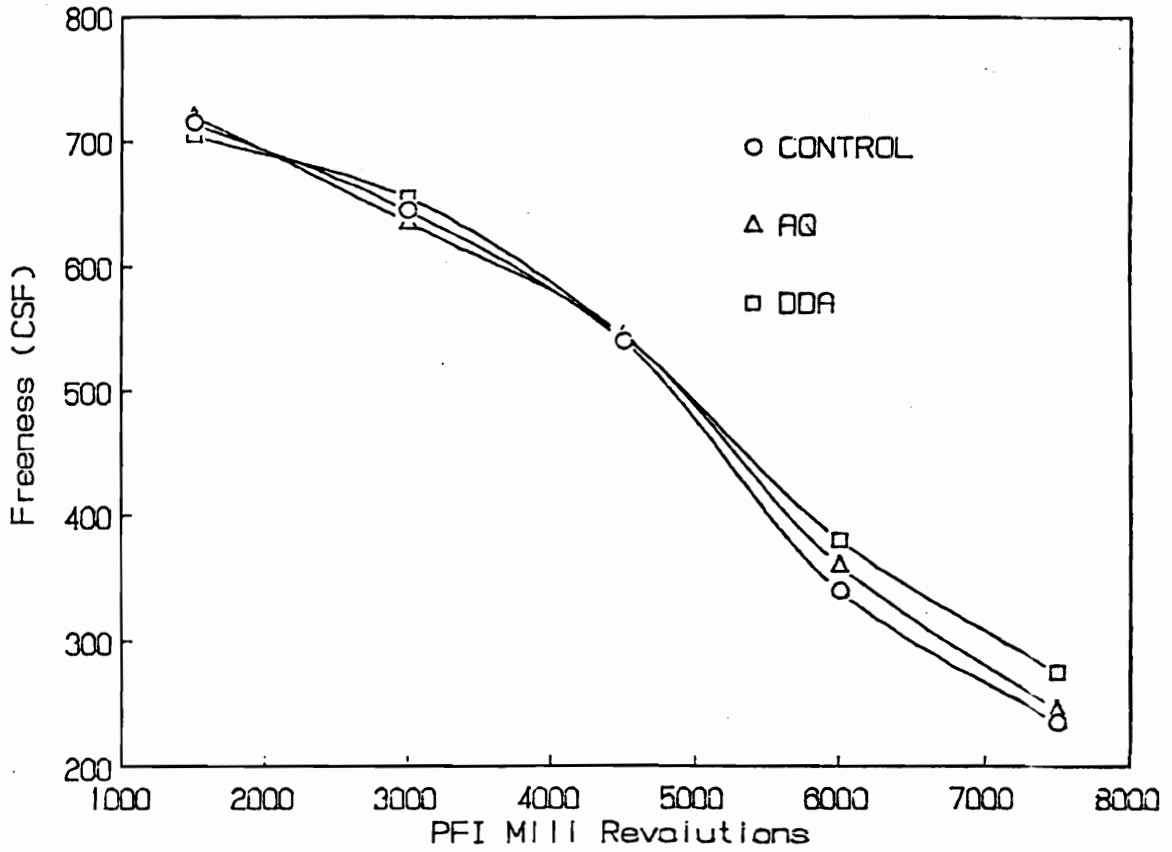


FIGURE 4.9.:

Folding endurance vs. freeness curve for the pulps

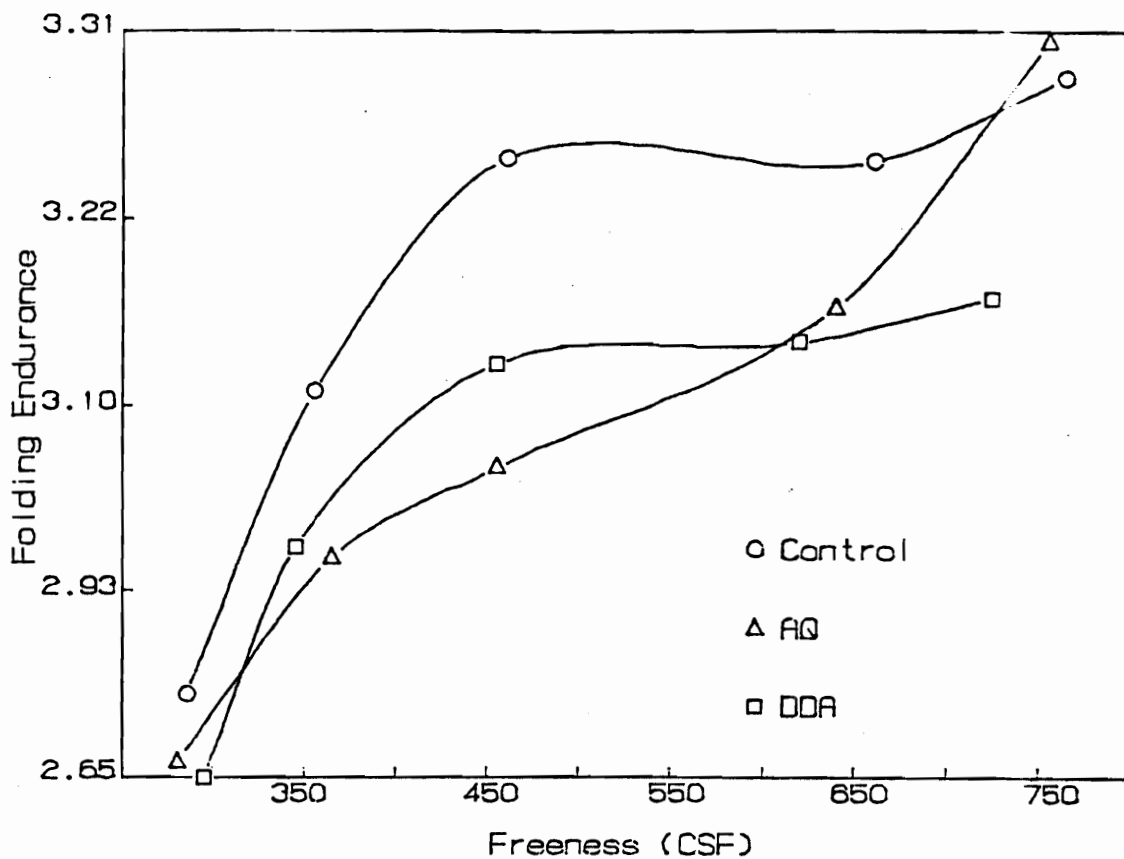


FIGURE 4.10.: Burst index vs. freeness curve for the pulps

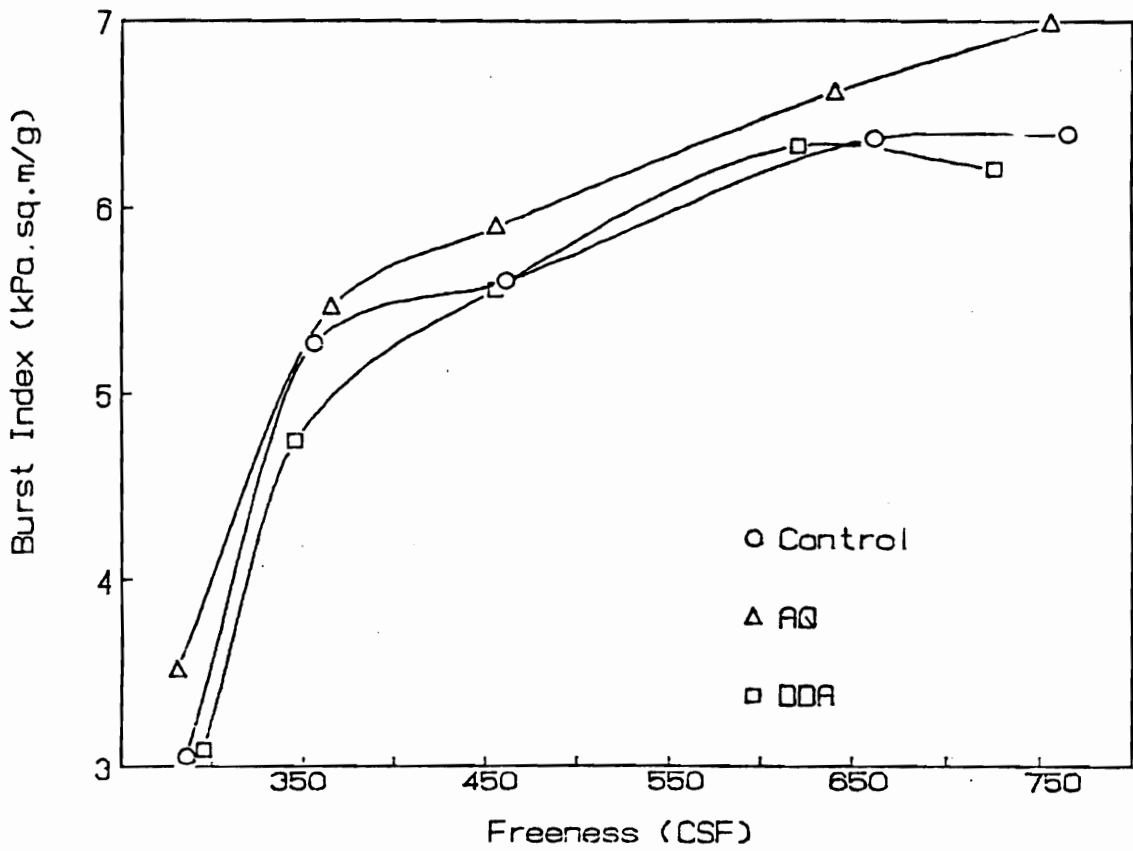


FIGURE 4.11.: Tear index vs. freeness curve for the pulps

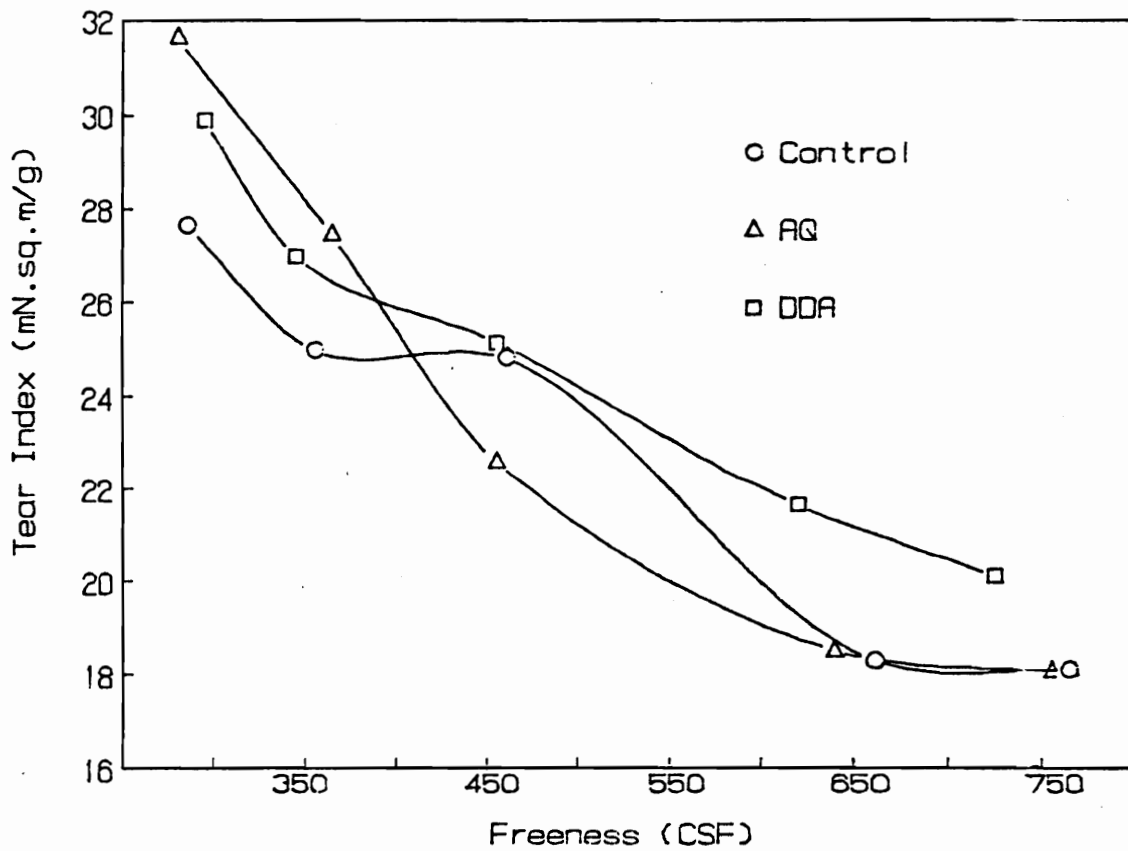
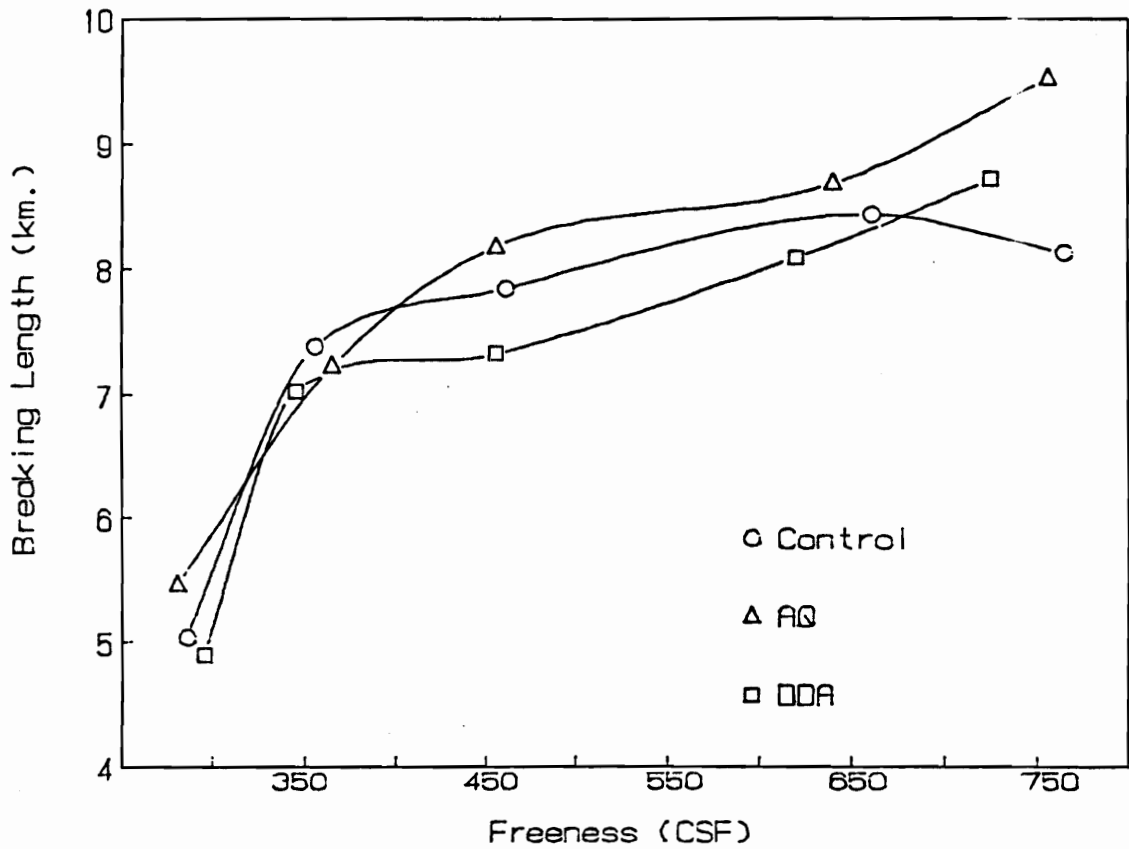


FIGURE 4.12.: Breaking length vs. freeness curve for the pulps



CONCLUSIONS

1. The quinone additives had measurable and statistically significant effect on the pulping rate and the pulp yield. DDA appeared to be a superior additive to AQ for pulps with kappa numbers below 90. An increase in total pulp yield of 1 to 2% as compared to AQ and 3 to 4% as compared to conventional kraft process was achieved by using DDA as a pulping additive.
2. A saving of about 80 to 400 in the H-factor is possible depending upon the desired kappa number of the pulp. This could lead to savings in cooking time, cooking temperature, or both; depending on the operating conditions of a given mill.
3. Both additives showed improved pulping at the lower sulfidity range, with DDA being superior to AQ.
4. The reduction in kappa number increased with higher additive concentration during pulping, to some extent. However, most of the positive effects of the quinone additive pulping were achieved at an additive concentration of 0.1% on o.d. wood.
5. There was no significant change in the pulp cellulose solution viscosity in the presence of additives.
6. Brightness of the unbleached pulp improved by 1 to 2 points in the case of pulping with DDA compared to control and AQ pulps.
7. All three types of pulps i.e. Control, AQ and DDA, behaved similarly in their beating characteristics.

The strength properties of the handsheets made from these pulps differed slightly but were not statistically significant.

TABLE 1: The total pulp yield and kappa numbers for the control kraft pulps

Cook Type	Cooking Time (minutes)	Total Pulp Yield (%)	Kappa No.
Control Kraft	50	62.5	111.1
	60	61.0	107.2
	80	59.4	97.0
	90	57.6	89.1
	110	56.6	83.0
	120	55.0	76.1
	130	52.5	62.0
	140	51.9	58.2
	150	49.6	51.4
	160	50.1	50.5
	180	47.2	37.1

Other important cooking conditions:

Cooking Temperature : 170 °C

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

TABLE 2: The total pulp yield and kappa numbers for the anthraquinone additive pulps

Additive	Cooking Time (minutes)	Total Pulp Yield (%)	Kappa No.
AQ	40	64.2	122.0
	50	62.1	94.2
	60	60.0	88.0
	70	58.0	83.3
	80	55.8	70.5
	90	54.6	62.9
	100	53.6	62.0
	110	52.8	58.1
	120	51.8	50.0
	130	51.0	44.9
	140	50.6	42.2
	150	50.1	42.7
	160	48.3	37.2
	180	47.1	29.1

Other important conditions:

Cooking Temperature : 170 °C

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

Additive percentage : 0.1% on o.d. wood

TABLE 3: The total pulp yield and kappa numbers for the DDA additive pulps

Additive	Cooking Time (minutes)	Total Pulp Yield (%)	Kappa No.
DDA	30	63.0	124.8
	40	61.6	100.7
	50	60.4	94.5
	60	59.4	76.0
	70	58.4	70.9
	80	57.0	67.5
	90	55.6	59.9
	100	54.6	56.0
	110	53.3	50.7
	120	52.6	45.1
	130	51.8	41.8
	140	50.8	38.3
	150	51.0	37.4
	160	49.1	31.2
	180	47.2	23.1

Other important conditions:

Cooking Temperature : 170 °C

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

Additive percentage : 0.1% on o.d. wood

TABLE 4: The cooking liquor sulfidity and kappa number results for the two quinone additive pulps

Sulfidity (%)	Kappa Number	
	AQ Pulp	DDA Pulp
10	69.4	58.9
15	61.5	53.1
20	55.0	48.8
25	50.0	45.1
30	46.1	42.5

Other important conditions:

Cooking Temperature : 170 °C

Cooking Time : 120 minutes

Alkali Charge : 20% on o.d. wood

Additive percentage : 0.1% on o.d. wood

TABLE 5: The additive concentration and kappa number results for the two quinone additive pulps

Additive Concentration (% on o.d. wood)	Kappa Number	
	AQ Pulps	DDA Pulps
0	76.1	76.1
0.025	66.5	62.7
0.05	60.1	56.5
0.1	50.0	45.1
0.2	43.0	40.1
0.5	38.0	33.1

Other important conditions:

Cooking Temperature : 170 °C

Cooking Time : 120 minutes

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

TABLE 6: The kappa number and unbleached pulp viscosity results for the three different types of pulp

Kappa Number			Unbleached Pulp Viscosity (0.5 % CED, cp)		
Kraft	AQ	DDA	Kraft	AQ	DDA
-----	---	-----	-----	-----	-----
111.1	122.0	124.8	1341	1292	1330
107.2	88.0	94.5	1298	1202	1251
97.0	70.5	76.0	1250	1108	1145
89.1	62.9	59.9	1248	1103	1067
83.0	62.0	56.0	1152	1088	1064
62.0	50.0	50.7	1064	1031	1061
58.2	44.9	41.8	1071	1030	1049
50.5	42.7	38.3	1042	999	962
	29.1	37.4		910	941
		23.1			925

Other important conditions:

Cooking Temperature : 170 °C

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

Additive percentage : 0.1% on o.d. wood

TABLE 7: The kappa number and unbleached pulp brightness results for the three different types of pulp

Kappa Number			Unbleached Pulp Brightness (%)		
Kraft	AQ	DDA	Kraft	AQ	DDA
111.1	122.0	124.8	15.2	14.8	15.7
97.0	94.2	100.7	17.8	18.3	18.1
89.1	83.3	94.5	18.9	20.0	19.0
83.0	62.9	70.9	19.8	22.7	22.3
76.1	62.0	67.5	20.8	22.9	22.7
62.0	58.1	59.9	22.9	23.7	23.8
58.2	50.0	56.0	23.3	24.5	24.4
50.5	44.9	50.7	24.4	25.1	25.3
43.2	32.4	45.1	25.2	25.9	26.4
		41.8			26.8
		38.3			27.2
		37.4			27.4
		28.3			28.1

Other important conditions:

Cooking Temperature : 170 °C

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

Additive Charge : 0.1% on o.d. wood

TABLE 8: Beating results of the three types of pulp

PFI Mill Revolutions	Freeness of the Pulp (CSF)		
	Kraft	AQ	DDA
1500	715	720	705
3000	645	635	655
4500	540	545	545
6000	340	360	380
7500	235	245	275

Pulping Conditions:

Cooking Temperature : 170 °C

Cooking Time : 120 minutes

Sulfidity : 25%

Alkali Charge : 20% on o.d. wood

Additive percentage : 0.1% on o.d. wood

TABLE 9: Strength properties of the pulps at different levels of freeness

Pulp Type	CSF	Folding Endurance	Burst Index (kPa.m ² /g)	Tear Index (mN.m ² /g)	Break. Length (km.)
Kraft	715	2.80	3.06	27.63	5.04
	645	3.11	5.27	24.96	7.38
	540	3.25	5.60	24.80	7.84
	340	3.25	6.37	18.31	8.44
	235	3.29	6.39	18.09	8.13
AQ	720	2.69	3.52	31.62	5.46
	635	2.96	5.46	27.43	7.22
	545	3.05	5.89	22.59	8.18
	360	3.16	6.62	18.51	8.69
	245	3.31	6.98	18.07	9.52
DDA	705	2.65	3.09	29.89	4.90
	655	2.97	4.75	26.96	7.03
	545	3.13	5.56	25.14	7.32
	380	3.14	6.33	21.63	8.09
	275	3.17	6.21	20.10	8.72

TABLE 10.: Model equations for the calculation of yield and kappa no.

Additive	Equation	R ²
<u>Linear</u>		
DDA	$Y = 73.40 - 0.10(T) - 0.27(S) - 10.19(Ad)$	0.94
AQ	$Y = 71.78 - 0.12(T) - 0.17(S) - 9.23(Ad)$	0.92
DDA	$K = 139.0 - 0.59(T) - 0.53(S) - 50.5(Ad)$	0.90
AQ	$K = 150.8 - 0.57(T) - 0.87(S) - 51.1(Ad)$	0.89
<u>Non-linear</u>		
DDA	$Y = 108.51 + \text{Log} [T^{-2.7} * S^{-5.9} * Ad^{-2.1}]$	0.96
AQ	$Y = 114.35 + \text{Log} [T^{-11.3} * S^{-3.9} * Ad^{-1.8}]$	0.99
DDA	$K = 318.0 + \text{Log} [T^{-52.4} * S^{-13.7} * Ad^{-10.1}]$	0.99
AQ	$K = 360.4 + \text{Log} [T^{-56.0} * S^{-19.6} * Ad^{-9.9}]$	0.98

 Explanation and Range of Variables:

K: Kappa number
 (23.1 to 124.8 for DDA; 29.1 to 122.0 for AQ)

Y: total pulp yield
 (47.2 to 63.0 for DDA; 47.1 to 64.2 for AQ)

S: sulfidity (10 to 30%)

Ad: additive concentration (0.025 to 0.5% on o.d. wood)

T: cooking time
 (30 to 180 min for DDA; 40 to 180 min for AQ)

Other restrictions: Cooking temperature, 170 °C;
 liquor to wood ratio, 7:1; Alkali charge, 20% on o.d. wood

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29. Following TAPPI Standards from "TAPPI standards and suggested methods":

T 236 os-76: Kappa Number of pulp.

T 254 pm-76: CED disperse viscosity of pulp
(Falling Ball Method).

T 217 os-48: Brightness of pulp.

T 248 pm-74: Laboratory beating of pulp (PFI Mill).

T 227 os-58: Freeness of pulp.

T 205 om-81: Forming handsheets for physical
testing of pulp.

T 220 om-83: Physical testing of pulp handsheets.

T 211 om-80: Ash in wood and pulp.

T 222 om-83: Acid-Insoluble Lignin in wood & pulp.

T 410 om-83: Grammage of paper and paperboard.

T 403 os-76: Bursting Strength of paper.

T 414 om-82: Internal Tearing Resistance of paper.

T 494 om-81: Tensile Breaking properties of paper
and paperboard.

T 511 om-83: Folding Endurance of paper (MIT).

APPENDIX A: Definitions

ACTIVE ALKALI: NaOH + Na₂S, expressed as Na₂O.

BEATING: Beating is defined as the mechanical action applied to pulp between two parallel surfaces, under constant loading, moving differentially relative to one another. The PFI Mill achieves this action by having the inner roll and outer casing rotate under constant load, in the same direction, but with differing peripheral speeds.

BLACK LIQUOR: The name applied to liquors recovered from the digesters, up to the point of their incineration in the recovery plant.

BREAKING LENGTH: Breaking length is the calculated limiting length of a strip of uniform width, beyond which, if such a strip were suspended by one end, it would break of its own weight.

BRIGHTNESS: Measures the 'whiteness' of the paper. Technically, it is the percent reflectance of a thick pad of paper to MgO standard at a wavelength of 457 nm.

BURSTING STRENGTH: Bursting strength is defined as the hydrostatic pressure in kilopascals or pounds per square inch required to produce

rupture of the material when the pressure is increased at a controlled constant rate through a rubber diaphragm to a circular area, 30.5 mm diameter. The area of the material under test is initially flat and held rigidly at the circumference but is free to bulge during the test.

FOLDING ENDURANCE: Folding Endurance is the logarithm (to the base 10) of the number of double folds required to break the paper when a strip of paper 15 mm wide is tested under a standard tension of 9.81 N (1 Kg.).

FREENESS: Canadian Standard Freeness is an empirical procedure which gives an arbitrary measure of the rate at which a suspension of three grams of pulp in one liter of water may be drained. The test is carried out under the specified conditions.

GREEN LIQUOR: The name applied to liquor made by dissolving the recovered chemicals in water and weak liquor preparatory to causticizing.

INTERNAL TEARING RESISTANCE: Internal Tearing Resistance determines the average force perpendicular to the plane of the paper required to tear a single sheet of paper through a specified distance after the tear has been

started using an Elmendorf-type tearing tester.

KAPPA NUMBER: The Kappa Number is the volume (in milliliters) of 0.1 N potassium permanganate solution consumed by 1 gm. of moisture free pulp under specified conditions. The results are recorded to 50% consumption of the permanganate added.

KRAFT PULPING: Pulping by use of an aqueous solution of NaOH and Na₂S. It has a better kappa-yield relationship and strength properties than soda pulping.

SULFIDITY: The percentage ratio of Na₂S to active alkali, expressed as Na₂O.

TAPPI: TAPPI is the acronym for the Technical Association of the Pulp and Paper Industry.

TENSILE STRENGTH: Tensile Strength is the maximum tensile stress developed in a test specimen before rupture on a tensile test carried to rupture under prescribed conditions.

WHITE LIQUOR: The pulping liquor in alkaline pulping. This name is applied to liquors made by causticizing green liquors. White liquor is ready to use in the digester.

YIELD (%) : $\frac{\text{Dry weight of pulp out of digester}}{\text{Dry weight of wood into the digester}} \times 100$

APPENDIX B : Chemical Composition of the Douglas-fir Chips
used in the Experiments

The chemical composition of the wood was as follows:

Holocellulose:	68.9 %
Lignin:	29.0 %
Ash:	0.15 %
Extractives:	1.9 %

Holocellulose (with correction for lignin content) was determined by the method of Whistler et al. used for preparation of corn cob holocellulose⁽²⁸⁾. Ash and lignin contents were determined as per TAPPI standards (T211 om-80) and (T222 om-83), respectively.