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Senior Engineering Design Problem: Paper 473

NON-CHLORINE BLEACHING
OF
SODA-ANTHRAQUINONE PULP

By

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For

Thesis Advisor: Dr. Raja Aravamuthan

* submitted in partial fulfillment of the course
requirements for The Bachelor of Science Degree

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December, 1990

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NON-CHLORINE BLEACHING OF SODA-AQ PULP

Introduction:

The objective of this project is to apply the soda-anthraquinone pulping process and non-chlorine bleaching sequences in the formation of a pulp with market brightness levels. The bleaching sequences applied in this project will be evaluated from pulp brightness and brightness reversion. The non-chlorine bleaching sequences evaluated include the ODEP, ODED, and OPEP.

Problem Statement:

The justification for this project includes the elimination of organic sulfide gases and chlorinated lignin compounds in the production of a bleached pulp of market quality. These two by-products of the Kraft pulping and chlorine bleaching stages, respectively, are associated with environmental concerns that impact air and water quality. Chlorolignins form major part of the organic fraction in spent effluents, and the non-chlorine bleaching method allows for their removal in this stream (1). Dioxins produced through chlorinated bleaching of lignins are mainly considered to be 2,3,7,8-tetrachlorodibenzodioxins (TCDD) and chlorinated dibenzofurans (TCDF) (2).

Literature Review:

Soda-AQ Pulping:

The high yield soda-AQ pulping process was chosen for this project due to its pulp strength characteristics at high yield levels (3). The main attribute of the soda pulping process for this project is the elimination of organic sulfide gases (4).

Soda-AQ pulping was considered over non-AQ soda pulping from the lower color reversion, less carbohydrate degradation, and equivalent strength criteria after full bleaching for soda-AQ pulps (3). High yield soda-AQ pulping minimizes the degradative effects on pulp strength compared to a low yield soda-AQ alternative. This goal is achieved by application of oxygen for extended delignification on the high yield soda-AQ pulp. Soda-AQ pulps have an increased sensitivity to oxygen delignification at yields over 60% (5). In general, high yield soda-AQ/oxygen pulps have been shown to exhibit superior bleached brightness, and higher bleached tensile and burst strengths compared to the low yield pulping alternative (5). High yield soda-AQ/oxygen pulps are also reported to have a better response in short bleaching sequences compared to low yield soda-AQ pulps (6).

Oxygen Delignification:

Brightness gain associated with the oxygen bleaching stage is created by lignin removal, and not lignin bleaching (7). Oxygen delignification was also considered because it can remove approximately one half of the residual lignin in the brown stock without considerable damage in physical properties (8). The extent of delignification is limited by adequate alkali to neutralize the acidic degradation products of the lignin (9). The rate of delignification lowers as alkali is consumed by the carboxylic acids (10). The carbonyl groups common to both lignin and cellulose are functional groups, which act as precursors to the formation of harmful peroxide by-products. The degradation of cellulose during oxygen bleaching is associated with this phenomenon (8). The delignification rate is generally lowered at pH levels below 10. The delignification beyond this rapid reaction stage is typically avoided (9).

Parameters to be considered in the oxygen bleaching stage includes alkali concentration, temperature, pulp consistency and magnesium ion presence as a carbohydrate protector. A very low alkalinity during the oxygen bleaching of high yield soda pulps may also contribute to lignin condensation (5). An increased sodium hydroxide content, oxygen pressure, reaction temperature and/or time of the oxygen bleaching aid in the reduction of high yield

soda pulp's lignin content (10). Recommended maximum temperature range and sodium hydroxide addition for high yield soda pulps are 120 degrees Celsius and 7-9% alkali addition on o.d. pulp (10&11). Oxygen bleaching above these ranges may be detrimental to pulp strength properties (10). The medium consistency oxygen bleaching process is performed in the 10-14% consistency range (12). The delignification of medium consistency compared to low consistency (under 3%) oxygen bleaching is slightly lower. Medium consistency delignification of 40-45% is achievable compared to 50-60% delignification for low consistency methods (12). The benefits of the low consistency alternative compared to medium and high consistency oxygen bleaching includes a greater interfacial area of contact between fibers and oxygen, more efficient delignification, and fewer required bleaching stages (12).

The addition of magnesium compounds can significantly reduce the degradation of cellulose during oxygen delignification. The need for magnesium, in oxygen bleaching, increases in importance at higher degrees of delignification. The addition of a Mg^{++} charge beyond .05-.10 % on o.d. pulp is not justified for economic reasons, and entails the upper limit of normal Mg^{++} addition (8). Magnesium sulfate ($MgSO_4$) is typically applied as the source of Mg^{++} protector in oxygen bleaching. This is due to its solubility in water and

efficient distribution in pulp bleaching solutions.

Hydrogen Peroxide Bleaching:

The hydrogen peroxide stage has the ability to bleach to high brightness levels economically. The by-products of this stage consist simply of organic residues (13).

Peroxide is used in later stages of bleaching for chemical pulps to provide marginal increases in full bleach brightness, and to improve brightness stability (4).

Temperatures applied with peroxide bleaching of chemical pulps typically range from 70 to 80 degrees Celsius to provide brightness increases of 10 to 15 points (15).

The bleaching action of hydrogen peroxide is attributed to the oxidative action of the perhydroxyl ion (HO_2^-). The dissolution of the perhydroxyl ion increases with temperature. Perhydroxyl ion concentration in a process solution is dependent, to a great extent, on the alkalinity of the solution. Peroxide solutions are buffered and stabilized prior to bleaching applications. This can normally be achieved by sodium silicate addition. Sodium silicate is employed in additions up to 6% on pulp where large amounts of alkali may be consumed (13). Sodium silicate is applied in lower concentrations with chemical pulps (13). Buffering and adjusting pH in peroxide bleaching to achieve an initial pH of 10.5 has been seen to provide optimal results for pulp brightness (4).

Neutralization and pH adjustment of the peroxide bleaching stage is typically done by use of sulfur dioxide (13). Hydrogen peroxide is susceptible to catalytic decomposition of metallic ions (Mn^{++} , Cu^{++} , and Fe^{+++}). Pretreatment of pulp with a chelating agent is not normally required to remove trace metal ions when an initial chlorination stage is applied to the pulp (13).

Peroxide, used in combination with other bleaching stages and agents, aids in solubilization and lignin residue removal. The peroxide bleaching stage, when used in the last stage of a bleaching sequence, typically shows the greatest incremental brightness improvement. A major attribute of peroxide bleaching in chemical pulp bleaching is brightness stability. This trait is associated with a final peroxide bleaching stage being applied to chemical pulps (13).

Reaction of peroxide with cellulosic components of the pulp is marginal, but increases with temperature. Excessive peroxide decomposition may take place with extremes in alkalinity of bleach liquor (13). Oxygen may be released through peroxide decomposition and with the alkali present, react with lignin to generate new chromophores. The bleach liquor must be sufficiently alkaline to maintain an adequate concentration of perhydroxyl ions. The pH may fall to a point where bleaching ceases if insufficient alkali is not present (13).

The limits for peroxide charge in most commercial bleaching operations of chemical pulps range from 1-2% H₂O₂ on pulp, due to economic considerations.

Chlorine Dioxide Bleaching:

The chlorine dioxide stage was chosen for bleaching because it imparts brightness readily to the pulp with insignificant strength losses and low color reversion. Its main function in bleaching is destroying residual lignin by oxidation, while preserving the cellulose and hemicellulose constituents at high and stable brightness levels (4). It does this from its high reactivity, as an oxidizing agent, towards lignin and unsaturated fatty acids in the pulp. Normally in chlorine dioxide bleaching a portion of the lignin is oxidized and chlorinated to water soluble compounds and the remainder becomes dissolved in a hot alkaline extraction stage (14).

The oxidizing power of chlorine dioxide is 2.5 times that of elemental chlorine (4). Parameters to be considered for chlorine dioxide bleaching are pH, temperature, and consistency. The acidity of the chlorine dioxide stage plays an important role in brightening efficiency and cellulose degradation. Higher pH levels accelerates the reaction of chlorine dioxide with water to form chlorate and chloride ions (14). In the presence of pulp the oxidizing equivalent to this reduction of ClO₂ is the

formation of HClO_2 , which is readily taken up by pulp. At higher pH levels this reaction becomes vigorous and cellulose along with the lignin components are attacked (14). Cellulose degradation in chlorine dioxide bleaching is minimal in the pH range of 2 to 7 (14). Cellulose becomes exposed to vigorous attack in the chlorine dioxide stage when the pH exceeds 7. It has been suggested that optimum bleaching occurs when the pH at the end of a chlorine dioxide stage approaches 3.6 (14).

The temperature effects on chlorine dioxide includes higher brightness at higher temperatures, as long as all the ClO_2 is not consumed. At higher temperatures consumption may occur quickly, and color reversion then is entailed in the absence of an oxidizing agent. The recommended optimum temperature for chlorine dioxide bleaching in practice is 70 degrees Celsius (14). This temperature was applied to all chlorine dioxide stages in this experiment. Consistency differences in chlorine dioxide bleaching require times and temperatures to remain unchanged. The consistency used in the chlorine dioxide stage is normally chosen as high as possible for conservation of heat and is typically in the range of 11-12% (14).

Experimental Design and Procedures:

Experimental Soda-AQ Pulping:

A hardwood fiber source (aspen) was chosen for this project due to a high unbleached brightness and lower lignin content, compared to softwood fiber sources. The application of a hardwood with high initial brightness should allow better evaluation of the bleaching responses on the high yield soda-AQ pulp under investigation. The greater lignin content associated with softwoods may restrict the bleaching responses between stages and sequences, in turn affecting brightness evaluations. Hardwood as a fiber source is considered due to the short bleaching sequences involved in this project.

An "ideal" chip size of 20 mm long, in the grain direction, and 4 mm thick should be maintained in pulping. Offsize chips in chemical pulping are considered less than 10 mm or greater than 30 mm long, and less than 2 mm or greater than 5 mm thick (4). Hand classification of wood chips prior to pulping in this project prevents the addition of offsize chips, which may affect pulp processing and quality.

The pulping equipment applied for the high yield soda-AQ pulping process was the laboratory M/K Batch Digester. Conditions for the high yield soda-AQ pulpings were chosen based on similar experiments performed by Allison (5), and Andrews and Yethon (6). The process

conditions applied to the high yield soda-AQ pulping of hardwood chips, for this project, is illustrated in Table 1. Multiple cooks were required to provide enough pulp for bleaching and handsheet testing. Replication of the DED, DEP, and PEP bleaching sequences also created the need for multiple cooks. Cooking conditions under additional batch pulpings remained at those stated in Table 1. After the cooks were completed, the pulp was defibered in the Waring Blender to ensure fiber separation before further processing. After defibering, the pulp was dilution washed with distilled water. Dilution washing below or at 1% consistency and thickening to 10% consistency effectively removes 90% of all dissolved solids. This occurs assuming there is no preferential absorption on the fibers (7). Kappa number of the unbleached soda-AQ pulp source was determined after all the cooks were combined and thoroughly mixed. Procedures followed for Kappa number determinations in this experiment are found in Tappi Standard T 236.

This combination of pulp batches assures a uniform unbleached fiber source prior to oxygen delignification. The unbleached pulp brightness and brightness reversion was determined on the mixed unbleached pulp stock. Procedures followed for brightness determinations are as per Tappi Standard T 452. Handsheets for brightness and reversion testing were made using the British Sheet Mold, following Tappi Standard T 218 procedures. The handsheets were then

air dried and tested under standard conditions listed in Tappi Standard T 402 and T 220, respectively. The evaluation of aging properties of the pulp was done according to Tappi Standard T 260. Brightness reversion was reported as Post Color Number. Yield determination was also made on the defibered and washed pulp.

Table 1: Experimental Soda-AQ Pulping Conditions

Active Alkali (% as Na ₂ O)	13
Cook Temperature (degrees Celsius)	170
Time to Temperature (minutes)	90
Time at Temperature (minutes)	90
Liquor:Wood Ratio	4:1
AQ Addition (% on o.d. wood)	.10
Hardwood Fiber Source	Aspen

Following the unbleached pulp analysis the pulp was oxygen delignified, and finally bleached by the non-chlorine bleaching sequences stated earlier. Evaluation of brightness, brightness reversion, and Kappa number, after the above bleachings, were done following the stated Tappi Standard methods. Bleaching chemicals chosen to replace chlorine in this experimental design include oxygen, chlorine dioxide, and peroxide. Caustic extraction was applied after the first stage chlorine dioxide and

peroxide stages in this experiment. Uniformity in the bleaching sequences were also maintained by applying the same bleaching conditions for all common bleaching stages. Bleaching sequences employed on the high yield soda-AQ pulp were ODED, ODEP, and ODED

Experimental Oxygen Delignification Stage:

Oxygen delignification is considered for this experimental design because of its selective nature compared to extending the soda-AQ pulping stage (15). Low consistency oxygen delignification was used in this experiment. The washed brown stock was diluted with distilled water to 2% consistency prior to oxygen delignification. The M/K Batch Digester was used for the oxygen delignification on the unbleached high yield soda-AQ pulp. Low consistency oxygen delignification at 2% allowed for liquor circulation to take place within the M/K Digester unit. Oxygen was fed and maintained under necessary pressure limits specified in this report.

The M/K Digester allowed oxygen loading to occur through the digester vessel relief lines. A high pressure oxygen tank was used to supply oxygen to the M/K Digester unit. Hydraulic tubing (250 psig rated) and a swivel check valve (350 psig rated) allowed for tank connection to the digester unit relief lines. Required oxygen addition was provided according to the pressure required to contain

sufficient oxygen in the volume above the pulp level,

within the digester. Oxygen pressure has been found to influence the initial rate of delignification, but has little influence on reaction kinetics later in the oxygen bleaching process (16). Initial oxygen pressure in the vessel is listed in Table 2.

Air was purged from the vessel to ensure only the presence of oxygen in the digester vessel. Purging was done by pressurizing the digester to 100 psig with supply oxygen. The digester was then exhausted through the relief lines to 5 psig purging air within the vessel. Agitation can not be provided in the M/K Batch Digester, and the mechanism of dispersion for oxygen depended on its dissolution into the bleaching solution. The initial oxygen pressure within the digester vessel was reached by regulation of oxygen addition from a supply tank. The temperature in the oxygen bleaching stage was automatically regulated by the M/K Digester controls. The temperature, oxygen pressure, and pulp consistency parameters were maintained at the same levels, in multiple oxygen delignification batches.

Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) was supplied as the Mg^{++} ion for carbohydrate protection in this project. The conditions for oxygen delignification of the high yield soda-AQ pulp are listed in Table 2. Oxygen delignification conditions were selected on the basis of conditions and results

illustrated in Evans (16) and Allison (5).

The delignified pulp was washed using distilled water. Dilution washing was again applied. After oxygen delignification the pulp batches were combined and thoroughly mixed to provide a uniform pulp source for the DED, DEP, and PEP bleaching sequences. Kappa number, pulp brightness, brightness reversion, and yield determinations were performed according to Tappi Standards prior to further bleaching.

Table 2: Experimental Oxygen Delignification Conditions

NaOH Addition (% on pulp)	8.0
Temperature (degrees Celsius)	110
Time (minutes)	30
Consistency (%)	2.0
Mg, as Mg 2+ (% on pulp)	.10
Initial Oxygen Pressure (psi)	100

Experimental Bleaching Stages:

Hydrogen Peroxide:

Sodium silicate additions for peroxide bleaching were selected based on results from experiments performed by Allison (17). When sodium silicate buffers are used, the peroxide bleaching solutions are typically prepared by silicate addition to a dilute $MgSO_4$ solution, followed by

NaOH and H₂O₂ addition (13).

In this experiment preparation was done by sodium silicate and DTPA addition at ambient temperatures prior to peroxide addition. The absence of a chlorination stage in this experiment requires the use of a chelating agent to remove trace metal ions. An organic chelating agent, sodium diethylenetriaminepenta-acetate (DTPA) was applied to remove any trace metals on pulp in this investigation. Allison reported DTPA additions to peroxide bleached soda-AQ pulps resulted in the highest brightness gains (17). Sodium hydroxide addition was not necessary to achieve the desired pH in bleaching for this experiment. Sulfuric acid addition was also not necessary since the pH targets were initially reached after sodium silicate and DTPA additions.

The peroxide charge applied in this bleaching experiment was chosen on the basis of results of brightness gains or various peroxide charges on a poplar pulp obtained by Andrews and Singh (13). (Experimental conditions for peroxide bleaching are listed in Table 3.)

Temperature was maintained during peroxide bleaching using a water bath. Consistency targets were reached by the addition of distilled water to the oxygen delignified pulp. The bleaching was performed on the pulp in encasement in polyethylene bags. Distilled water was used to wash the peroxide bleached pulp.

After bleaching in the first and final peroxide stages, pulp brightness and brightness reversion was determined on British Sheet Mold handsheets. After first and final stage peroxide bleachings the Kappa number and bleached yield was also determined. All the tests were performed according to Tappi Standards.

Table 3: Experimental Peroxide Bleaching Conditions

H2O2 Addition (% on pulp)	2.0
Temperature (degrees Celsius)	70
Time (minutes)	180
Consistency (%)	10
DTPA Addition (% on pulp)	.10
Initial pH	10.5

Chlorine Dioxide:

The pH in the chlorine dioxide stages for this experiment was targeted to the levels listed in Table 4.

Rapson and Strumila suggest optimum chlorine dioxide bleaching occurs when the pH at the end of a bleaching stage approach 3.6 (14). The initial pH of the chlorine dioxide bleaching stage was adjusted to targeted levels by the addition of HCl. Distilled water was used to dilute pulp to the consistency maintained in all chlorine dioxide bleaching stages. Chlorine dioxide bleaching was performed

in the laboratory using the water bath and polyethylene bags. Tests performed on bleached and washed pulp were equivalent to those stated under the peroxide bleaching stages. These tests were made after pulps were processed in the first and final chlorine dioxide bleaching stages.

Table 4: Experimental Chlorine Dioxide Bleaching

Conditions

	first stage	second stage
ClO ₂ Addition (% on pulp)	1.5	0.9
Temperature (degrees Celsius)	70	70
Time (minutes)	180	180
Consistency (%)	10	10
pH	3.5	3.2

The extraction stage following first stage bleaching was a caustic extraction stage. The conditions maintained in the caustic extraction stage are listed in Table 5. This stage was also performed in polyethylene bags immersed in a water bath. The pulp from the extraction stages was washed and then used for the final bleaching stage in each of the three sequences investigated. British Sheet Mold handsheets were not made from extracted pulp, and no brightness or reversion testing was performed on this pulp.

Table 5: Experimental Caustic Extraction Conditions

NaOH Addition (% on pulp)	2.0
Temperature (degree Celsius)	70
Time (minutes)	60
Consistency (%)	10
pH	10.5-11

The pulping and oxygen delignification stages of this experiment required multiple batches to be produced to supply sufficient pulp for subsequent bleaching sequences. Identical conditions were maintained for all the batches and the pulps from different batches were completely mixed to provide a homogeneous material for the subsequent processes. The three bleaching sequences examined in this experiment were replicated three times to provide a statistical base for their comparison.

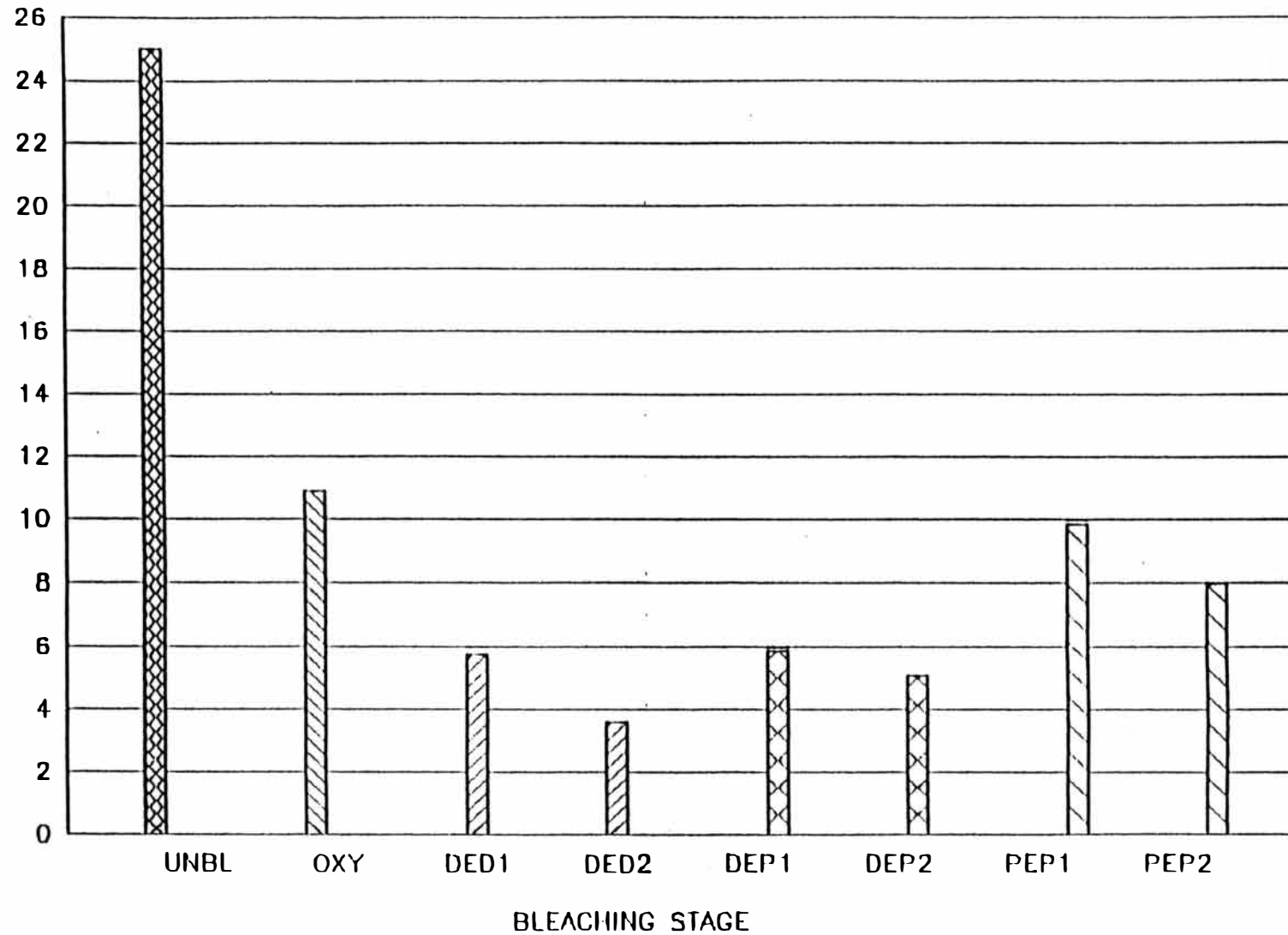
Results and Discussion:

Kappa Number:

The degree of delignification of unbleached and bleached pulps are evaluated by the Kappa number results. The unbleached soda-AQ pulp was found to have a Kappa number of 25. This result is comparable to results seen in Andrews and Yethon for a bleachable grade soda-AQ pulp (6). After oxygen delignification Kappa number was seen to reduce to 10.9. Lignin removal in the oxygen bleaching stage is evident based on this result. Kappa number results for bleached pulps illustrates the least amount of lignin removal for the PEP bleaching sequence, in both the first and second stage of bleaching, compared to DED and DEP bleaching applications. The DEP sequence was found to have a greater Kappa number in comparison to the DED bleaching process. These results can be considered typical due to peroxide acting as a lignin preserving agent compared to chlorine dioxide bleaching, where lignin components are solubilized to a greater degree. Based on the above results the degree of delignification of the DED and DEP bleaching sequences may be considered greater in comparison with the PEP bleaching sequence. Results of the Kappa number determinations in this experiment are graphically illustrated in Figure 1.

FIGURE 1: KAPPA NUMBER RESULTS

BLEACHED AND UNBLEACHED SODA-AQ PULP



Brightness:

Brightness evaluation of non-chlorine bleaching sequences for this experiment was done to determine the response on diffuse brightness. An initial goal of 85% full bleached brightness was set for this experiment to achieve pulps with marketable brightness levels. Figure 2 illustrates the brightness results for unbleached, oxygen delignified, and first and second stage bleaching on all three bleaching sequences examined.

The DED and DEP bleaching sequences were found to have the highest overall brightness response after full bleaching. The DED and DEP bleaching sequences performed are found to be statistically similar in terms of full bleached brightness response. Statistical analysis was performed by the Student T-Test under a 95% confidence level (18). The full bleached brightness of the PEP applications was found to be lower than the DED and DEP sequences in the first and second bleaching stages under a 95 % confidence level. Results for brightness and variance for all bleaching sequences involved are presented in Table 6. Appendix 1 illustrates calculations performed for Student T-Test determinations.

Table 6: Brightness Response to Bleaching

Stage	Brightness	Variance
Unbleached Pulp	20.3	0.25
Oxygen Bleached	38.7	0.24
DED: 1st Stage	52.3	2.18
DED: 2nd Stage	65.7	4.15
DEP: 1st Stage	54.0	1.13
DEP: 2nd Stage	64.9	0.54
PEP: 1st Stage	48.5	0.63
PEP: 2nd Stage	58.8	1.23

Expected overall brightness for all bleaching sequences involved were found to be below the set objective of 85% full bleached brightness. Oxygen delignified pulp brightness reached an initial brightness level of 38.7%. Allison found soda-AQ oxygen delignified pulp to achieve a brightness approximately 10 points greater than that resulting from this experiment (5). This reduced brightness for oxygen delignified pulp may account for the lower than expected overall bleached brightness for this experiment. Improvement in oxygen bleached brightness would be expected with the application of a static mixer improving contact between the pulp and oxygen loaded in the bleaching vessel. Oxygen bleaching in this experiment contained no static mixer application. Dissolution of oxygen into the bleaching liquor was the mechanism involved for contact of pulp with

the applied oxygen contained in the M/K Digester unit. An increase in retention time for oxygen bleaching in the digester unit may be a solution to improving the oxygen bleached brightness response. Temperature, alkali addition, and Mg ion addition with the oxygen stage were applied near or at recommended maximum conditions which are mentioned earlier in this report. Alteration of temperature or alkali addition parameters could lead to degradative effects on pulp if added beyond these recommended limits.

Hydrogen peroxide bleached pulp brightness was found to be below expectations based on results seen from Andrews and Singh (13). Probable reasoning for this lower peroxide bleached brightness response include DTPA applications at high consistency. Andrews and Singh suggest pretreatment of DTPA at .3-.5% consistency and subsequent thickening of the pulp prior to sodium silicate and hydrogen peroxide addition (13). This application is normally applied to softwood pulps, but may have had a positive impact if applied to this experiment to remove trace metal ions. Chelating agent pretreatment is suggested to be beneficial for high consistency peroxide bleaching applications from improved DTPA distribution throughout the pulp. DTPA addition at 10% consistency may have restricted the chelating agent from achieving sufficient distribution.

Increasing the oxygen retention time, and low consistency pretreatment of DTPA on peroxide bleached pulps

might have allowed the brightness goal of this experiment to be reached. The application of a peroxide bleaching stage after the DED bleaching sequence may also be a method that would elevate the brightness of bleached pulp to higher levels when using non-chlorine bleaching methods. This was not done in this experiment, but may be of interest for further investigations involving non-chlorine bleaching.

Brightness Reversion:

Reversion of the bleached soda-AQ pulps was performed by application of the Fad-o-meter. The Fad-o-meter allows for maintenance of temperature and relative humidity conditions specified in Tappi T 260. A carbon arc lamp source within the Fad-o-meter chamber provides a light source to aid in accelerating the reversion of paper samples. This accelerated reversion occurs from exposure of paper to ultraviolet wavelengths created by the carbon arc lamp. Wavelengths of light beyond the ultraviolet range present from the lamp source may have influenced the samples tested, in terms of bleaching the samples with high lignin contents. It was seen in this experiment that the unbleached and oxygen bleached pulp samples exposed to the Fad-o-meter conditions had an increase in brightness. This brightness increase may also be a result of residual bleaching and delignification chemicals in the pulp samples

FIGURE 2: INITIAL BRIGHTNESS RESULTS

UNBLEACHED AND BLEACHED SODA-AQ PULPS

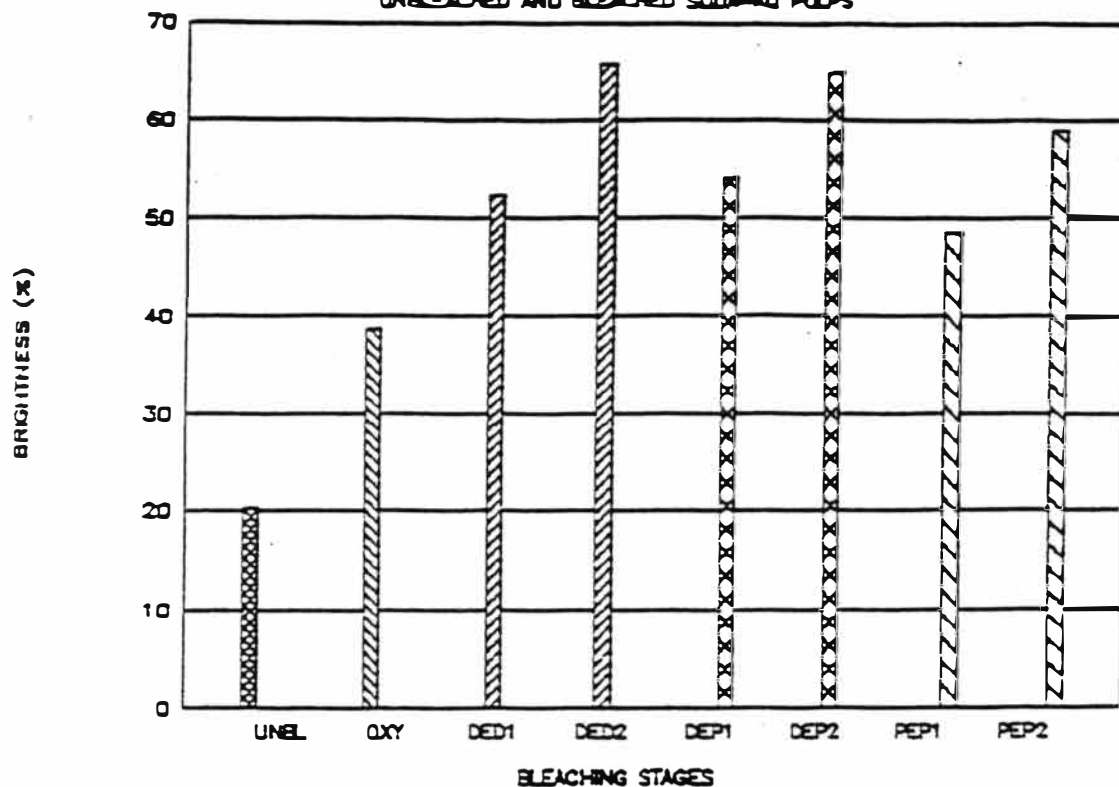
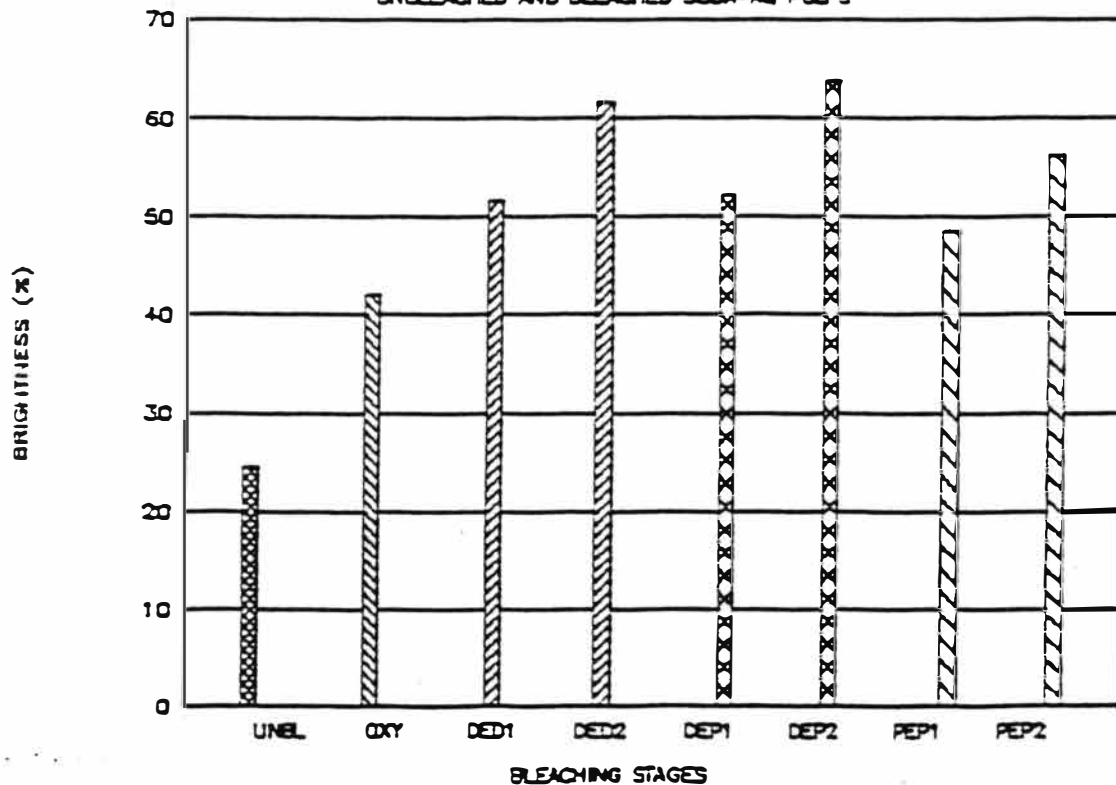


FIGURE 3: BRIGHTNESS AFTER REVERSION

UNBLEACHED AND BLEACHED SODA-AQ PULPS



tested. Pulp samples exposed in the Fad-o-meter after DED, DEP, and PEP bleaching did not have the reversion response seen with the unbleached and oxygen delignified samples.

All brightness reversion samples were treated to the conditions found within the Fad-o-meter for periods of 4 and 8 hours. The results for reversion stated in this report are for 8 hour exposure times. A very small response to brightness reversion was associated with the 4 hour exposure times and is not considered for this evaluation. Brightness reversion after 8 hour exposure times for unbleached and bleached pulp samples are illustrated in Figure 3. Reversion results for the three bleaching sequences examined in this experiment are presented as a Post Color Number in Figure 4. It is evident from these results that the DED and PEP bleaching sequences had a greater reversion characteristic after full bleaching in comparison to the DEP bleaching application. Excellent brightness stability for peroxide in chemical pulp bleaching, when used in the last bleaching stage, may provide explanation for the DEP pulps lower reverting characteristic. The greater reversion response for the PEP bleaching sequence compared to the DEP sequence is explainable by the higher Kappa number for PEP bleaching. A higher lignin content in this pulp would create a situation for greater reversion to take place. Table 6 lists the brightness and variance results for the unbleached and

bleached pulps examined for reversion response in this experiment. The final reverted brightness results for the DED, DEP, and PEP bleaching sequences were found to all be significantly different. This statistical difference was observed by applying the Student T-Test, at a 95% confidence level, on the final reverted brightness for each bleaching sequence investigated in this project. Calculations applied in determining the confidence level of the Student T-Test between bleaching sequences is illustrated in Appendix 1.

Table 6: Brightness Revesion Response

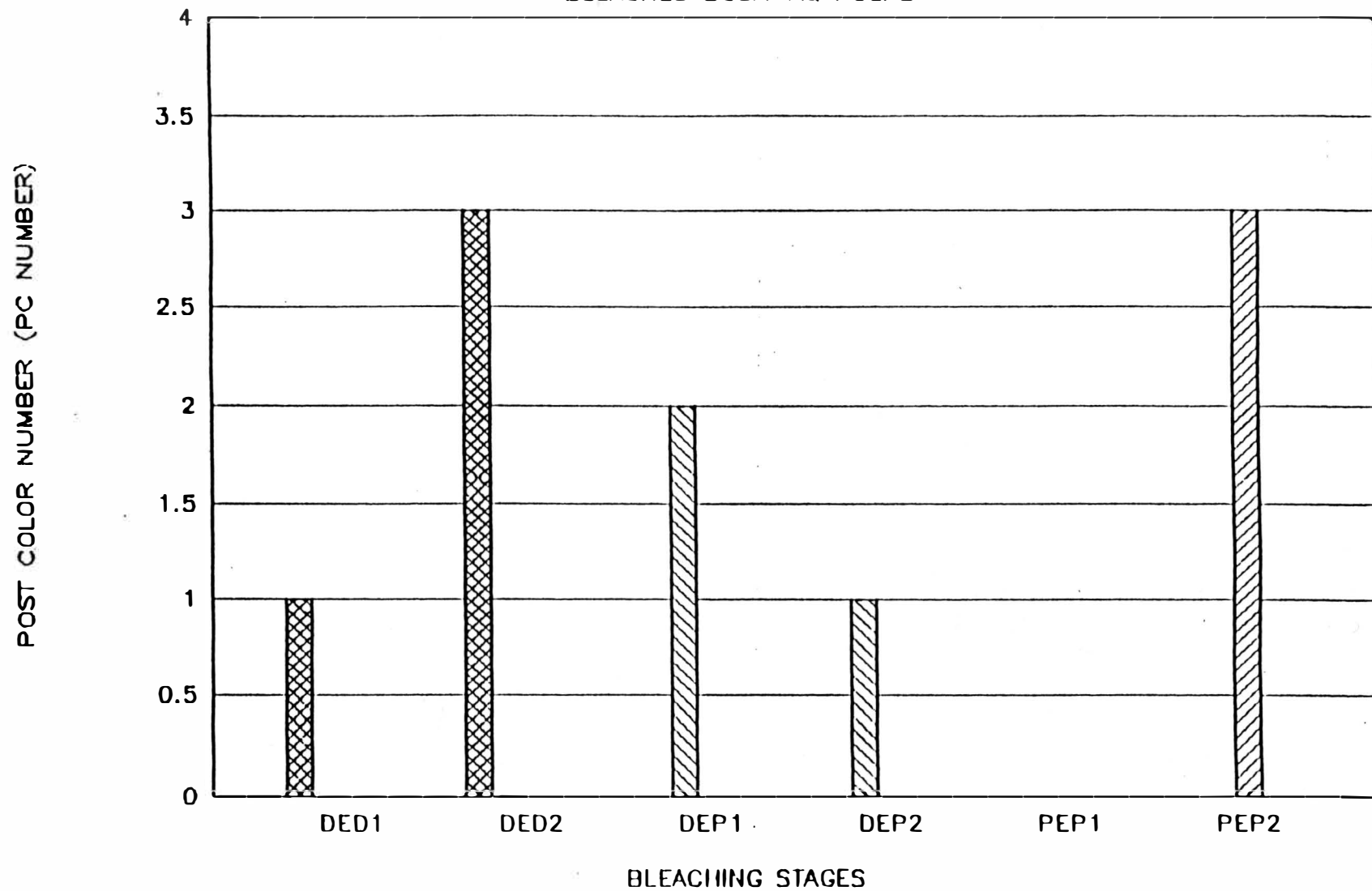
Stage	Reverted Brightness	Variance
Unbleached Pulp	24.6	1.04
Oxygen Bleached	42.1	0.95
DED: 1st Stage	51.6	1.44
DED: 2nd Stage	61.6	2.05
DEP: 1st Stage	52.2	1.09
DEP: 2nd Stage	63.7	0.82
PEP: 1st Stage	48.5	1.12
PEP: 2nd Stage	56.2	1.15

Yield:

The yield for unbleached pulp was determined to be 53.7% based on total o.d. wood. This yield for pulping conditions applied in this experiment is comparable to pulp

FIGURE 4: POST COLOR NUMBER RESULTS

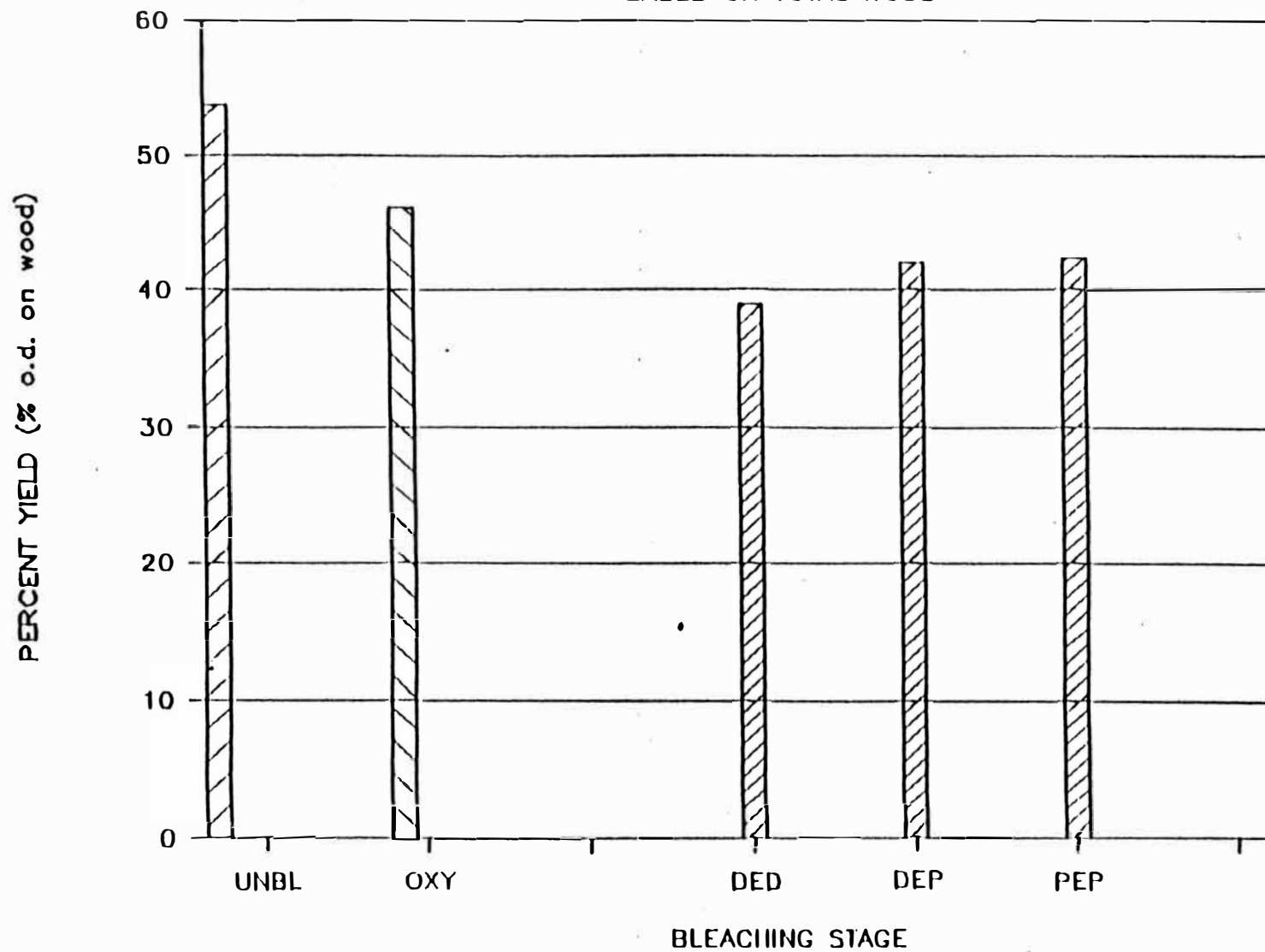
BLEACHED SODA-AQ PULPS



yield obtained by Andrews and Yethon (6) and Allison (5). Oxygen delignification created a yield of 86% on o.d. pulp. The effect on total wood yield is illustrated in Figure 5. Final bleached yield on total wood for the DED, DEP, and PEP bleaching sequences are illustrated in Figure 5 also. Bleaching sequences applying peroxide bleaching were found to exhibit a higher yield in comparison to the DED bleaching application. The PEP bleaching stages exhibited the highest overall yield, with only a slight advantage over the DEP final yield results.

FIGURE 5: FINAL YIELD RESULTS

BASED ON TOTAL WOOD



CONCLUSION

In conclusion, the DED bleaching sequence was found to have the lowest Kappa number compared to the DEP and PEP bleaching sequences. This result is considered to be caused by greater lignin solubilization from chlorine dioxide compared to hydrogen peroxide bleaching stages.

The full bleached brightness of the DED and DEP bleaching sequences were found to be higher in comparison to the PEP bleaching sequence. These two sequences were also found to have similar full bleached brightness results after statistical analysis. All bleaching sequences in this experiment did not reach the set goal of 85% full bleached brightness. The DED and DEP bleaching sequences were found to be under this goal by 15 brightness points.

The DEP bleaching sequence was found to have better brightness stability than the PEP and DED bleaching sequences. This conclusion is based on a lower Post Color number and higher final bleached brightness after reversion for the DEP bleaching sequence. This result is attributed to the final hydrogen peroxide stage, which when applied to chemical pulps provides excellent brightness stability.

Final yields on the bleached soda-AQ pulp in this experiment were found to be slightly greater for the PEP and DEP bleaching sequences. The PEP and DEP final yields were found to have a 5% advantage compared to the DED bleaching sequence.

In conclusion, the DED and DEP bleaching sequences provide the highest full bleached pulp brightness. The addition of a hydrogen peroxide stage to the DED bleaching sequence in this experiment may provide a means for achieving the set objective of an 85% full bleached brightness, while creating excellent brightness stability. This statement is made based on the high permanence from the DEP bleaching sequence in this experiment.

The application of non-chlorine bleaching sequences to a soda-AQ pulp source provides a means of reducing impacts on the environment by eliminating the release of organic sulfide gases and chlorolignins in the production of bleached pulps. This benefit provides great incentive for future investigations of non-chlorine bleaching applications to a soda-AQ pulp.

RECOMENDATIONS

Based on results from this experiment it is recommended that an additional hydrogen peroxide stage be applied to the DED bleaching sequence. This additional stage may provide the brightness response necessary in achieving an 85% or greater final bleached pulp brightness. This final hydrogen peroxide stage should also create high brightness stability on the full bleached soda-AQ pulp.

An increase in the delignification time during the oxygen stage of this experiment may also be necessary to allow for greater dissolution of oxygen in the circulated bleaching liquor. This recommendation is made because brightness after oxygen delignification for this experiment was found to be lower than similar experiments performed on soda-AQ pulps by other researchers. All other conditions for the oxygen delignification stage in this experiment were at or below recommended maximums to prevent excessive degradation to the pulp.

Pretreatment of the hydrogen peroxide bleached pulps with DTPA at .3-.5% consistency and subsequent thickening to the 10% consistency target is also recommended. This allows trace metal ions to be extracted from the pulp prior to bleaching chemical addition, and also allows DTPA to be dispersed to a greater extent within the pulp samples. This pretreatment should create a higher bleached brightness after peroxide bleaching than seen in this experiment.

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APPENDIX I

Student T-Test Calculation:

$$t_x = \frac{\bar{X}_1 - \bar{X}_2}{\sigma_c \sqrt{N_1 + N_2 / N_1 * N_2}}$$

$$\text{where, } \sigma_c = \frac{(N_1 - 1) * \sigma_1^2 + (N_2 - 1) * \sigma_2^2}{(N_1 + N_2) - 2}$$

$$\sigma_1 \text{ and } \sigma_2 = S * \sqrt{N / (N - 1)}$$

\bar{X} = sample mean

S = standard deviation

= population standard deviation

N = number of samples in population

t = tabulated T-Test value

t_x = calculated T-Test value for samples

* if $t_x > t$

for the 95% confidence level in Appendix Table at $(N_1 + N_2 - 2)$ degrees of freedom then: Reject null hypothesis that $\bar{X}_1 = \bar{X}_2$ and both samples are statistically different.

t-distribution

	20%	50%	50%	20%	20%	10%	5%	2.5%
df	0.80	0.40	0.20	0.10	0.05	0.02	0.01	0.001
1	3.325	1.378	1.078	0.814	12.708	31.821	63.657	638.619
2	2.920	1.061	0.886	0.720	4.303	6.965	9.925	31.598
3	2.777	0.978	0.833	0.683	3.182	4.541	5.841	12.941
4	2.707	0.941	0.813	0.663	2.778	3.747	4.804	8.610
5	2.687	0.920	0.803	0.653	2.571	3.385	4.032	5.859
6	2.668	0.900	0.793	0.643	2.447	3.143	3.707	5.208
7	2.650	0.889	0.783	0.633	2.365	2.998	3.499	4.608
8	2.642	0.880	0.773	0.623	2.306	2.898	3.355	4.041
9	2.635	0.873	0.763	0.613	2.262	2.821	3.250	3.781
10	2.629	0.867	0.753	0.603	2.228	2.764	3.169	3.587
11	2.624	0.861	0.743	0.593	2.201	2.718	3.108	3.437
12	2.619	0.856	0.733	0.583	2.179	2.681	3.056	3.318
13	2.615	0.851	0.723	0.573	2.160	2.650	3.012	3.221
14	2.611	0.846	0.713	0.563	2.145	2.624	2.977	3.140
15	2.607	0.842	0.703	0.553	2.131	2.602	2.947	3.073
16	2.603	0.838	0.693	0.543	2.119	2.583	2.921	3.015
17	2.600	0.834	0.683	0.533	2.110	2.567	2.898	2.968
18	2.597	0.830	0.673	0.523	2.101	2.552	2.878	2.922
19	2.594	0.826	0.663	0.513	2.093	2.539	2.861	2.883
20	2.591	0.822	0.653	0.503	2.086	2.528	2.845	2.848
21	2.588	0.818	0.643	0.493	2.080	2.518	2.831	2.819
22	2.585	0.814	0.633	0.483	2.074	2.508	2.819	2.792
23	2.582	0.810	0.623	0.473	2.068	2.500	2.808	2.767
24	2.579	0.806	0.613	0.463	2.064	2.492	2.797	2.745
25	2.576	0.802	0.603	0.453	2.060	2.485	2.787	2.725
26	2.573	0.798	0.593	0.443	2.056	2.479	2.779	2.707
27	2.570	0.794	0.583	0.433	2.052	2.473	2.771	2.689
28	2.567	0.790	0.573	0.423	2.048	2.467	2.763	2.674
29	2.564	0.786	0.563	0.413	2.044	2.462	2.756	2.659
30	2.561	0.782	0.553	0.403	2.042	2.457	2.750	2.646
40	2.558	0.778	0.543	0.393	2.037	2.453	2.744	2.631
50	2.555	0.774	0.533	0.383	2.033	2.449	2.740	2.618
100	2.551	0.769	0.523	0.373	2.029	2.445	2.736	2.605
120	2.549	0.767	0.513	0.363	2.027	2.443	2.734	2.601
∞	2.548	0.766	0.510	0.360	2.026	2.442	2.733	2.599

Appendix II

t distribution

DF	Null hypothesis rejected							
	20%	60%	80%	90%	95%	98%	99%	99.9%
	Probability							
	0.80	0.40	0.20	0.10	0.05	0.02	0.01	0.001
1	0.325	1.376	3.078	6.314	12.706	31.821	63.657	636.619
2	0.289	1.061	1.886	2.920	4.303	6.965	9.925	31.598
3	0.277	0.978	1.638	2.353	3.182	4.541	5.841	12.941
4	0.271	0.941	1.533	2.132	2.776	3.747	4.604	8.610
5	0.267	0.920	1.476	2.015	2.571	3.365	4.032	6.859
6	0.265	0.906	1.440	1.943	2.447	3.143	3.707	5.959
7	0.263	0.896	1.415	1.895	2.365	2.998	3.499	5.405
8	0.262	0.889	1.397	1.860	2.306	2.896	3.355	5.041
9	0.261	0.883	1.383	1.833	2.262	2.821	3.250	4.781
10	0.260	0.879	1.372	1.812	2.228	2.764	3.169	4.587
11	0.260	0.876	1.363	1.796	2.201	2.718	3.106	4.437
12	0.259	0.873	1.356	1.782	2.179	2.681	3.055	4.318
13	0.259	0.870	1.350	1.771	2.160	2.650	3.012	4.221
14	0.258	0.868	1.345	1.761	2.145	2.624	2.977	4.140
15	0.258	0.866	1.341	1.753	2.131	2.602	2.947	4.073
16	0.258	0.865	1.337	1.746	2.120	2.583	2.921	4.015
17	0.257	0.863	1.333	1.740	2.110	2.567	2.898	3.965
18	0.257	0.862	1.330	1.734	2.101	2.552	2.878	3.922
19	0.257	0.861	1.328	1.729	2.093	2.539	2.861	3.883
20	0.257	0.860	1.325	1.725	2.086	2.528	2.845	3.850
21	0.257	0.859	1.323	1.721	2.080	2.518	2.831	3.819
22	0.256	0.858	1.321	1.717	2.074	2.508	2.819	3.792
23	0.256	0.858	1.319	1.714	2.069	2.500	2.806	3.767
24	0.256	0.857	1.318	1.711	2.064	2.492	2.797	3.745
25	0.256	0.856	1.316	1.708	2.060	2.485	2.787	3.725
26	0.256	0.856	1.315	1.706	2.056	2.479	2.779	3.707
27	0.256	0.855	1.314	1.703	2.052	2.473	2.771	3.690
28	0.256	0.855	1.313	1.701	2.048	2.467	2.763	3.674
29	0.256	0.854	1.311	1.699	2.045	2.462	2.756	3.659
30	0.256	0.854	1.310	1.697	2.042	2.457	2.750	3.646
40	0.255	0.851	1.303	1.684	2.021	2.423	2.704	3.551
60	0.254	0.848	1.296	1.671	2.000	2.390	2.660	3.460 ✓
120	0.254	0.845	1.289	1.658	1.980	2.358	2.617	3.373
∞	0.253	0.842	1.282	1.645	1.960	2.326	2.576	3.291