STUDIES ON PULPING AND BLEACHING OF POPLAR DELTOIDES

A THESIS

Submitted in fulfilment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

in

PULP AND PAPER ENGINEERING

By

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in this thesis entitled, **"Studies on Pulping and Bleaching of Poplar deltoides"** in fulfilment of the requirement for the award of the **Degree of Doctor of Philosophy** and submitted in the Department of Institute of Paper Technology of the University is an authentic record of my own work carried out during the period from August, 1994 to Feb 2000 under the supervision of **Dr. J .S. Upadhyaya, Professor (Pulp and Paper), Institute of Paper Technology.** The thesis has been revised as per suggestions made by one of the examiner and submitted in July 2001

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other University.

Signature of the Candidate

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

1.0 INTRODUCTION:

The demand of paper and paper board is expected to enhance with increasing industrial development and growing literacy rate in our country. Future projection shows that percapita consumption figure would have rise up from 4.3 kg to 5 kg in the next few years. This would call projected annual production of 50 lakhs tons by the turn of century compared to the present demand of 3.7 lakhs tons. The demand for higher production of paper would naturally require more fibrous raw material in future.

There is an acute shortage of forest based raw material in our country. Poplar deltoides is a native of North America and can one of the most promising hardwood raw material for Indian pulp and paper industry. P.deltoides is a fast growing tree, raised in close spacing and harvested on short rotation. The biomass obtained from it is good. At present Eucalyptus is the most promising raw material for pulp and paper industry. Due to high transpiration rate of eucalyptus, farmers prefer to grow Poplar trees. Hence it has been planned worthwhile to carry out the detailed investigation on this particular plant with special reference to pulp and paper making.

2.0 STUDIES ON FIBER MORPHOLOGICAL AND PROXIMATE CHEMICAL ANALYSIS OF P.DELTOIDES

The detailed investigation includes the anatomical, morphological and proximate chemical analysis studies of P.deltoides. It has been analysed for density, fiber length, fiber diameter, cellwall thickness, lumen diameter and various other derived properties. Further it has been analysed for proximate chemical analysis which includes determination of extractives

soluble in cold and hot water, alcohol-benzene (1:2v/v) 1% NaOH solubles, lignin, pentosans, hemicellulose, holocellulose, alpha cellulose, beta cellulose, gamma cellulose, ash, content etc. Proximate chemical analysis of P.deltoides is compared to check its suitability vis-à-vis to Eucalyptus, which is the most promising and trusted raw material for pulp and paper industry.

Results and Discussion:

The results of proximate chemical analysis indicated that the carbohydrate fraction of Poplar is more than that of eucalyptus, which is presently the most promising raw material for pulp and paper making. The Poplar wood has porous structure and lignin content of Poplar has been found to be lower than eucalyptus, which indicates that fewer chemicals will be required for pulping. Hence Poplar can be pulp for higher yield with less chemicals.

3.0 PULPING STUDIES

The wood logs of P.deltoides were chipped in the chipper and screened. The chips of the accepted quality were used for pulping studies. The chips of P.deltoides were delignified by various delignification processes.

(A) Soda and Soda - AQ process

(B) Kraft and Kraft - AQ process

(C) Alkaline sulphite and alkaline sulphite - AQ process

(D) Polysulphide process.

3 A SODA AND SODA AQ DELIGNIFICATION

Since Poplar wood has low density and open structure. It has porous structure, and show good penetration of the cooking liquor and it has been found that it can be conveniently delignified by soda process.

During soda delignification process, the various pulping parameter viz., time, temperature and alkali doses were optimised. At optimum delignification conditions, the effect of AQ was

studied. During soda pulping a cooking temperature of 170°C, cooking time 120 minutes, active alkali dose 16% and liquor to wood ratio of 3:1 may be taken as optimum conditions.The various combinations of AQ and active alkali dosage were used in initial study. These included four levels of AQ dose 0.0, 0.05, 0.1, 0.2 percent on o.d. wood bases each at four active alkali concentration (14,16,18 and 20 percent as Na_2O) All the cooks were made at the same H factor.

Result and Discussion:

It has been observed that Poplar has low density and comparatively more open structure. It show good penetration of cooking liquor and found that it can be conveniently delignified by soda process. During soda pulping a cooking temperature of 170^0C and time at temperature 120 minutes, active alkali dose of 16% and liquor to wood ratio 3:1 were found to be optimum conditions.

Anthraquinone plays an important role in enhancing delignification and stabilization of carbohydrates. The addition of 0.1% AQ (on o.d. wood basis) was found to have beneficially effect on both the aspect of reducing kappa no. along with increase in pulp yield. It has been found that addition of 0.1% AQ increases the yield at the same kappa no. and decrease the kappa no. at the same yield. It has also been found that the use of AQ decreases the alkali consumption at the same yield of kappa no.

3 B KRAFT AND KRAFT - AQ DELIGNIFICATION.

In kraft delignification process the effect of active alkali, sulphidity, time and temperature was studied in order to optimise the pulping conditions. The cooks were made at same H factors. On the basis of experimental results, the effect of alkali change and sulphidity was studied. The experiments were carried out at 165+5°C under a constant reaction time of 1.5 hr at four different active alkali concentration of 14,16, 18 and 20% as Na_2O and at different sulphidity levels of

16,18,20% as Na_2O alongwith three different levels of AQ dose (0.05, 0.1 and 0.2% AQ on O.D. wood basis)

Result and Discussion:

Since Poplar has low lignin content and comparatively more open structure , therefore it has been found that the active alkali dose of 16% and sulphidity 20% and time at maximum temperature 90 minutes has been found to be an optimum condition. The use of higher active alkali decreases yield enhancing carbohydrate degradation. The effect on yield is more pronounced at sulphidity value of 15% and there is little increase in pulp yield by increasing sulphidity level from 20-25% The influence of sulphidity on yield seems to be somewhat higher at low active alkali charges. Thus 20% sulphidity may be considered as an optimum dose. Addition of 0.1% AQ under constant condition leads to a significant reduction in kappa no., an addition of 0.2% AQ shows nearly similar result.AQ effectiveness decreases with increasing sulphidity in kraft pulp. The strength properties of kraft –AQ pulp found to be better than kraft pulp.

3 C: ALKALINE SULPHITE AND ALKALINE SULPHITE-AQ PROCESS

In alkaline sulphite and alkaline sulphite-AQ delignijfication process, the chips were digested with different proportion of alkali and sodium sulphite doses, at different time and temperature using varing doses of AQ to get the optimum condition.

Results and Discussions:

On the basis of experimental result the maximum digestion temperature of 180° C time at temperature 150 minutes. Sodium Sulphite dose of 10% as Na_2O and NaOH 10% as Na_2O was found to be optimum during AS delignification. AS process delignifies at a slower rate than

kraft process. The yield obtained to be similar to kraft pulp but at higher kappa no.Use of 0.1% AQ in AS process increases the rate of delignification and pulp yield. The strength properties were found to be comparable to kraft pulp.

3 D POLYSULPHIDE PULPING

The use of polysulphide (PS), Anthraquinone (AQ) and oxygen delignification are another alternatives for decreasing the kappa number. Under alkaline conditions PS oxidize the aldehyde groups (reducing end) in polysaceharides to carboxylic groups, rendering the polysaccharides in particular glucomannans stable against the peeling reaction resulting in an increased pulp yield due to the retention of hemicellulose.

Results and Discussion :

The polysulphide pulp shows an increase in pulp yield an the properties were found slightly better than the kraft pulp. Use of AQ is still improved pulp yield and properties.

4.0 BLEACHING STUDIES

The bleaching of P. deltiodes pulps have been done using the following methods

(A) Oxygen delignification

(B) Conventional bleaching techniques using CEH and CEHH bleaching sequences

(C) Chlorine di-oxide based bleaching sequences

(D) Elemental chlorine free bleaching sequences

(E) Enzymatic bleaching Conventional bleaching techniques using CEH and CEHH bleaching sequences

4A OXYGEN DELIGNIFICATION OF PULP

The pulp of Poplar deltoides obtained by the various pulping processes were delignified in a .02m^3 electrically heated laboratory digester. In bleaching, oxygen has resulted in significant environmental benefits such as substantial reduction in color. COD and formation of

chloro-organics. During oxygen delignification the lignin content of the pulp is reduced to 40-50% without sacrificing significantly the strength properties of pulp. Oxygen delignification in turn decreases in the bleach chemical demand alongwith decrease in the pollution load to the tune of around 50%.

4B CONVENTIONAL BLEACHING SEQUENCES

The unbleached soda and soda-AQ kraft and kraft-AQ pulps of Poplar deltiodes were bleached using. Conventional CEH and CEHH bleaching sequences. The total chlorine demand applied on pulp is .20 of kappa number. The bleach effluent was analysed for the BOD, COD and other derived characteristics.

4 C BLEACHING OF PULPS USING CHLORINE DI-OXIDE

The use of elemental chlorine free (ECF), Chlorine dioxide substituted bleaching to produce high brightness pulps with low environmental concern is receiving increased attention with respect to the environmental quality of bleach plant effluent. Untreated ECF bleaching effluents have generally been found to exhibit low toxicity. Also the amount of chlorine required for bleaching is being reduced by the application of non elemental free bleaching chemicals like chlorine dioxide(D), oxygen (O), hydrogen-peroxide. Various sequences has been studied and a brightness level of around 90% ISO brightness has been obtained. The bleach effluent is tested for COD and BOD which is found to be very low as compared to conventional bleaching sequence. The following bleaching sequences has been studied CEDED, OCEDED, DEDED, ODEDED, D(EOP)DED, OD(EOP)DED, D(EOP)DP, O D(EOP)DP

4D ELEMENTAL CHLORINE FREE BLEACHING

The common definition of elemental free bleaching (ECF) of pulps means the pulps bleached without molecular chlorine. This definition implies that the pulp bleached with chlorine

dioxide, hypochlorite, oxygen, peroxide etc. comes under the category of ECF bleaching. The demand for elemental chlorine free (ECF) bleached pulps and total chlorine-free (TCF) bleached pulps have really forced the pulp and paper producers to stretch the desired technology to meet these tough demands in terms of environmental pollution load.

The soda, soda AQ, kraft, and kraft-AQ pulps of poplar deltoides with and without oxygen delignification were bleached using DEDED, D(EOP)DP and D(EOP)DED bleaching sequences.

4 E ENZYMATIC TREATMENT OF PULP

Preparation of xylanase

The species of thermophillic fungi exhibiting high xylanse activity with greater stability at high temperature and at near about neutral pH value were used for standardization of bio-bleaching process.

Phanerochaete chrysosporium was isolated from decaying wood samples and tested for hyperxylanase productions. The strain was inoculated and grown at temp. of 40°C. After desired growth the enzyme is harvested and stored at below 5 °C. The maximum activity of the enzyme was observed to be on 17^{th} day of incubation.

Treatment of Pulp.

The soda and soda-AQ, kraft and kraft-AQ pulps of Poplar detoides has been treated with enzyme at different dosages, at different time and temperature. The following bleaching sequences studied are XCEHH, XCEDED, OXCEHH, OXCEDED

Results and Discussions:

The dose of xyanase 10 I.U./gm pulp for 1 hour was found to be the optimum dosage,It has been interesting to note that the xylanase prepared from Phanerochaete chrysosporium has a significant effect of decreasing the kappa number of about 8.10% . It indicates that this enzyme

may have some amount of liginase also.The enzyme treated pulp was bleached with conventional and non conventional ECF and TCF bleaching sequences. It has been found that the enzyme treatment of pulp may save about 25-30% of bleaching chemicals for the same brightness.

4 E TOTAL CHLORINE FREE BLEACHING

Total chlorine free bleaching have been done using enzymatic treatment, oxygen delignification and hydrogen peroxide. The ECF bleaching sequences have been studied are X(EP)P, OX(EP)P X(EOP)P, OX(EOP)P. The brightness of the pulp during these bleaching sequences studied was found to be more than 70% ISO.

5.0 STUDIES ON WET WEB PROPERTIES

Wet web properties of pulps directly effect the paper machine runnability which has direct impact on the final production of the paper. The unbleached pulp of poplar and poplar blends with imported softwood and bamboo were chosen for studies. The wet web strength properties were studied at a freeness level of 350± 10 ml CSF. For the blend pulp, the constituent pulp were separately beaten and blended. These pulps were studied for wet web tensile index, wet web elongation and tensile energy absorption (TEA) using L&W wet web tensile strength tester as per scan C:31:77 method at the dryness values of around 20%.

6.0 BLENDING STUDIES:

The blending studies were conducted as follows:

a) Blending the chips of Poplar with long fibred raw material in different proportions, followed by joint cooking and further processing of pulps.

b) Cook the short fibred and long fibred material separately and blend the pulps before beating in different proportions.

c) Cook the short fibred and long fibred material separately, beat them separately and blend the beater pulps in different portions.

Results and Discussion:

The results of blending studies conducted on blending of Poplar chips with bamboo, soft wood chips were found to be poor in comparison to blending studies with pulps than would be expected. The results of the Poplar pulp blended with bamboo and soft wood pulp should an improvement in strength properties as compared to chip blending prior to cooking. The properties as compared to chip blending prior to cooking. The results of blending of separately beaten pulp of Poplar, and softwood in different proportion indicated the overall improvement in strength properties even in comparison to the pulp blending prior to beating operation.

7. CONCLUSIONS:

#The carbohydrate fraction of Poplar is more as compared to eucalyptus. Therefore it will provide more pulp yield than eucalyptus.

#The lignin content of Poplar is less than eucalyptus, also Poplar has porous structure it require less chemicals and shorter cooking cycles for pulping.

#The density of Poplar is less than that of eucalyptus therefore per digester yield will be less.

#Due to porous structure Poplar can be pulped with non sulphur soda AQ process.

#The unbleached pulp obtained is brighter and has low kappa no. This will require less chemical for bleaching which inturn decreases the pollution load & bleached at low kappa factor.

#Poplar has good response for enzymatic bleaching because the hemicellulose in Poplar has about 23% xylan. Enzymatic treatment can save upto 30% bleaching chemicals.

#The wet web strength properties of poplar were found to be comparable with other raw materials such as eucalyptus and the wet web strength increases linearly on blending with long fibered pulps.

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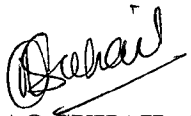

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LIST OF PUBLICATIONS

RE SEARCH PAPERS PUBLISH ED / ACCEPTED/COMMNUCATED

Dutt, Dharam., Suhail A. Rao., Upadhyaya J. S., Tiwary K.N., Upadhyay M. K., *Studies on Alkaline Sulphite and Alkaline Sulphite AQ Delignification of Ipomea Carnea Jacq.* - IPPTA Vol.7 No.3, Sept.1995, p 19 to 29

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5. Kapoor, S.K., Sood, Y. V., Pandey P.C., Rao, S. Akhtar., S. Kumar., D. Yadav., *"Quality Improvement of paper Manufactured From Agricultural Residues."* IPPTA Conventional Issue March 2000, p 37-47

6. Suhail A. Rao,& J.S. Upadhyaya, *"Studies on Kraft and Kraft-AQ Pulping and Elemental Chlorine Free Bleaching of Poplar deltoides."* (Communicated JSIR)

7. Suhail A. Rao,& J.S. Upadhyaya, *"Studies on Soda and Soda-AQ Pulping and Bleaching of Poplar deltoides."* (Communicated JSIR)

8. Suhail A. Rao,& J.S. Upadhyaya, *"Studies on Enzymatic Bleaching of Poplar deltoides Pulps."* (Communicated JSIR)

9. Kapoor, S.K., Sood, Y. V., Pandey P.C., Rao, S. Akhtar., S. Kumar., D. Yadav., *"Studies on Fiber Rising Tendency and Surface properties of Newsprint Manufactured from Secondary Fiber"* (Communicated)

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction:

The Indian pulp and paper industry has made significant strides in the past three decades. The demand of paper and paperboard is expected to enhance with increasing industrial development and growing literacy rate in our country. The percapita consumption figures have rise up from 4.3 kg to 5 kg, by the turn of this century. The present installed capacity of paper, paperboard and newsprint is about 5.4 million tons of paper and 1.06 million tonnes of newsprint (11,176). In the 1998-99 fiscal year the industry utilization was about 86%, given estimated production of 4.25 million tons (11). The estimated demand is projected to rise up to 7-8 million tons by turn of 2010AD. Paper meets the basic needs of modern society by contributing to commnucation education, packaging and hygiene. Indian paper production accounts for about 1.2% of the world production. The total annual consumption of paper including newsprint in India is currently about 5.0 million tons with per capita consumption of approx. 5kg, which is abysmally low compared to Malaysia (145kg), Korea (114kg), China (26kg), Indonesia (14.9kg) and Philippines (12kg). The demand for higher production of paper would naturally require more fibrous raw material in future (64).

India is perhaps the only country in the world to be using all available fibers for papermaking including bamboo, wood, bagasse, rice straw, wheat straw, jute and waste paper. Use of agro-residues currently entails constraints in its collection and transportation and also calls for cost effective, innovative and contemporary solutions. Wood as raw material for papermaking remains the most important input for manufacturing of quality paper, which is the growing need of the modern world.

There is an acute shortage of forest based raw materials in our country. The planning commission has fixed the target capacity of the forest-based raw material for pulp and paper making at 10 million tonnes towards the turn of century. In adequacy and high cost of raw material continue to be the single most inhibiting factor for the growth and development of paper industry. Poplar deltoides is a native of North America and can be one of the most promising hardwood raw materials for Indian Pulp and Paper Industry.

Poplar deltoides is a fast growing tree, raised in close spacing and harvested on short-term rotation. The biomass obtained from it is good. At present Eucalyptus is the most promising raw material for pulp and paper industry, but due to high transpiration rate of eucalyptus, farmers prefer to grow poplar trees rather than eucalyptus plantations. In India, yet no detailed investigations on this particular plant with special reference to pulp and papermaking have been made. Hence it has been planned worth while to carry out the detailed and systematic investigations on this particular plant for pulp and paper-making.

1.2 Status of Paper Industry In India :

Indian sub-continent is the 13th largest paper and paperboard consumer in the world. The demand being 4.7million tons in 1998. According to the long-term scenario presented in business and investment opportunities in pulp and paper industry in the Indian sub-continent, Indian will reach a consumption of 24 million tons of paper and paperboard by 2020 (64). The peak of the rate of growth in consumption of paper and paperboard for India will occur in 2010 – 2020.

The relative structure of consumption is indifferent in P&B grades in India, and it is currently biased towards cultural papers. Newsprint and uncoated printing, writing papers have been already loosing their relative share in the total consumption since the 80's. The higher relative growth of the consumption of board products is a phenomenon, which is forecasted to

continue until 2030, after which the cultural papers will maintain their share or start a slight increase. Because of the lack of wood in India, paper and board sectors continue to invest in non-wood fiber based production, but also increasing extent, in fast growing wood and recycled paper (64).

Indian pulp and paper industry is more than 100 years old practicing the technologies oldest to the modern one. Indian pulp and paper industry adopted technologies developed in Europe and North America for pulping and papermaking. Most of the machinery were imported from reputed copanies of different countries, however few indigenous machinary manufacturers have developed fabrication facilities for equipment required for paper industry. However the continous digesters, high speed paper machine with sophisticated instrumentation and technology are supplied to Indian paper industry by reputated foreign manufacturers.

The pulp and paper Industry is one of the India's key industrial sectors. Unfortunately, it is highly fragmented. According to the Development Council for Pulp, Paper and Allied Industries (Govt. of India) report of 1990 there are about 380 paper mills in India with an installed capacity of about 4 million tons per annum, as registered with the Government of India (175), however it has reported that the present installed capacity is about 5.4 million tons (11). The raw material wise classification of 380 paper mills is given in Table-1.1. In India, out of 380 No. of mills, 21 are large mills, each one having a capacity to produce above 33,000 tonnes of paper per annum and 359 mills are termed as medium and small mills with a capacity to produce less than 33000 tonnes per annum; small mills capacity is below 10,000 TPA (2,182). However presently as many as 135 nos. in total of large, medium and small paper mills are lying closed. The total capacity of the closed units is about 1.02 million tonnes per annum and thus, the effective capacity of 245 running mills is about 2.934 millions tonnes as reported in 1990 data (2,175). Against the effective capacity, the production of paper during 1997-98 was 4.1 million tonnes as

reported by Indian paper manufacturers association (IPMA). The Newsprint Industry in India is about 40 years old and it has an installed capacity of 7,50,000 tonnes per annum during 1997-98 as reported by Indian paper manufacturers association (IPMA). Six mills having togather a capacity of 4,35,000 tonnes per annum are in the public sector and about 19 companies having a capacity of 3,15,000 tonnes per annum are operating in the private sector (11,175).

The figures pertinent to demand and supply of paper and board vary by sources upto date, statistical data on production and demand is made available by various agencies both in public and private sector like Development Council under Govt. of India, the experts group constituted at the behest of Govt. of India in year 1995 and INFAC-a renowned consultancy firm on health and economy of Industry. The growth rate of writing and printing varieties, as estimated by the industry experts is expected to be 4-6% per annum, while the growth rate of industrial papers is expected to be around 12% per annum. The demand and supply position of paper and paper boards are projected as given in Table-1.2 (11). However indigenous paper supply has to be enhanced to meet the future projected demand of paper and paperboard products. The projected newsprint demand and supply is given in Table-1.3 (11). Indigenous production during 1996-97 and for some part during 1997-98 was restricted because of cheaper availability of imported newsprint in the country due to dumping.

A recent study by expert group consultants by Industries indicates, that short fall in supply for indigenous fibre based on projected demand and possible production may be much larger i.e. 17 millions tonnes for 2000-01, 25 million tonnes for 2005-06 growing to 36 million tonnes by 2010-11 as given in Table-1.4 (2,175). Unless effective measures are initiated for long term supplies of wood based raw materials for the pulp and paper industry; There will be ever increasing gaps between demand and supply of paper, paperboard and newsprint products. Based on 1990 report of Development Council the projected short fall will be nearly 1.6 million tonnes

during 2000AD and 3.1 million tonnes during 2010 (Singhania 1990) as given in Table-1.5 (2). The pulp, paper and board production, imports and exports figures for the year 1997, 1998, 1999 are reported in table 1.6 (131,132). With the emergence of open market economy and consequent post haste dismantling of tariff barriers, the Indian Paper industry today finds itself at cross roads. In the rapidly changing scenario there is a need for restructuring and reshaping of the industry to achieve global competitiveness. However the industry has exhibited its preparedness to build up an edge in quality and cost parameters through technological upgradation to face future challenges. One of the major problems of pulp and paper industry is the forest-based raw material.

It is true that our country is a fiber deficient country. Unless industrial plantation are undertaken on a war footing the prospect of long term fiber availability appears bleak. India will have to depend on large-scale import of pulp and paper products. The imminent fall out would be inhibiting the growth potential of the industry and handling down the economic and ecological advantages of the overseas producers of paper. Unfortunately the national forest policy in its present form is neither conductive to sustainable development of forest based raw material nor supportive to the dependent pulp and paper industry. The policy completely negates the role of forest for economic development through integrated development of forest based industries. This needs to be relooking keeping in view today's globalization environment in which Indian industries are required to operate.

The survival of the pulp and paper industry depends not only on technological advances but also on the source of inexpensive fiber. Over the past natural forests constitute the main fiber supply for pulp and paper industry. The trend may not last for ever for economical reasons as well as the competition from developed countries. The forest product industry would have to develop strategies to ensure a reliable sustainable fiber supply. In this respect forest plantations

of short rotation is gaining more and more attention of the forest industry as one of the strategies. Recognizing the potential of short rotation culture of fast growing species the forest research institute of India Dehradun has started several R&D programs on poplar aiming at improving the indigenous species as well as developing different clones. Several clones of poplars have shown excellent growth performance and resistance to diseases and pests.

1.3 BOTANICAL DESCRIPTION OF POPLAR DELTOIDES :

Populus is a bewildering genus. The genus populus belongs to the family Salicacae, taxonomically the genus populus is divided into five sections. Populus are commonly known as Poplars, Aspens and Cottonwoods distributed chiefly in the North Temperate Zone between 30°N and 45°N. Some species occurring in the sub tropical regions. Populus is a native of North America, the areas of natural poplar forests occurs predominantly in Canada and the United States but now a days poplar have spread over in most of the countries. In India the cultivation of Poplar is not very old due to its fast growth and productivity the cultivation is increasing rapidly.

Two types of Poplars found in India:

(i) Indigenous Poplar

(ii) Exotic Poplar

Indigenous Poplar: Poplars are not new in India, all the five sections of genus populus are indigenously occurring in India. Indigenous poplars have a limited distribution that is only in Himalayas regions. Populus ciliata, populus laurifolia, populus gamblei, populus euphratica, populus alba and P. nigra are indigenous to India and found along water courses in higher hills, valleys and hill sides in Himalayan regions (215). However none of the six Himalayan species are important for timber production.

Exotic Poplars: The genus populus, easily propagated by vegetating means, dieoceious flowing and hybridization between different species and strains, has resulted in the development of a large number of clones or hybrids for planting under edaphic and agroclimatic conditions. Considering the importance of exotic poplar clones for their fast growth and ability to provide substantial production of wood on a short rotation,

A major program of Introduction to select suitable species and their hybrid or clones for varying agro climatic conditions in India was initiated at Forest Research Institutes of India. Poplar deltoides and Poplar euramericana are the two species or hybrids, which have succeeded well in India (215), of which Poplar deltoides is superior. Poplar deltoides has assumed the status of being commercially most useful species of the genus populus in India. At present the primary products of this species are plywood and matchwood, while secondary products include charcoal and fuel wood etc. In India, attempt has to be made to use poplar for pulp and paper industry because of its suitability for the papermaking.

Poplar deltoides is a large tree reaching the height over 25-30 mts., fissured crown, branches angular, leaves triangular ovate 10-18 cm long and broad with dense serrate margin, subtrancate to subcordate at base, acuminate, crenatedentete, glossy green, petiole long and flat. The tree develops tall strength bole abundant foliage makes the crown quite dense. The tree is deciduous; the leafless period varies from 3 to 4 months. Flowing is normally is dry season.

1.4 Hardwood Fiber as a Paper making Raw Material and Environmental Aspects of its Utilization :

The most important raw material of the pulp and paper Industry is pulpwood. Wood is the preferred source of fibers for the paper industry, although non-woods such as bagasse and straws are also the sources of fiber for papermaking. Because of the lack of wood in India paper, and

board continue to invest in non-wood fiber based production, but also increasing extent, in fast growing wood and recycled paper. A characteristic for the Indian market is a fast growing population growth (1.5 – 2% during the present decade). The cultural pluralism has a slight decreasing impact on paper and board consumption. In India, round wood production is 24 million m^3. In India the broad leafed species with a high degree of diversity dominates. In India only few mountainous states in the northern part of the country have notable coniferous forests.

The forest plantations mainly include eucalyptus, teak, acacia, poplar, pine etc. and the projections of annual production are estimated to be about 24 milliom m^3 during the present decade. Plantations are established both by private and public sector. The most salient of the non-wood timber forest product for pulp industry is bamboo, which is widely needed by Indian pulp mills

Woods are still being considered as the best source of fibers because of its availability, convenience in handling, storage and operation. The pulp obtained from wood is of good quality. The different species of wood provides the versatility of the fiber properties. The pressure on forest resources is increasing tremendously, because of continuous demand for timber, pulpwood, plywood and fuel etc.

The paper Industry in India mainly utilizes bamboos and mixed tropical hardwoods. Of the raw material consumed by the paper industry, the share of forest based raw material is 66%. There is an increasing reliance on eucalyptus and other hardwoods in the wake of bamboo scarcity. In the last four decades, forest utilization policies have undergone a radical change. With a reduction in total forest cover in the country, these policy changes have drastically curtailed the raw material availability to the forest based industries.

India's demand for paper and paperboard is estimated to be 4.7 million tonnes and that for newsprint 1.03 million tonnes at the end of this century. Under assumption that 30% of the total paper demand would be met by productions based on waste paper and non-conventional raw materials, nearly 2.38 million tonnes of paper and paper board and 0.7 million tonnes of newsprint would be dependent on forest based raw-materials. Thus there is huge short fall of 4 million tonnes of forest based raw material (37).

India has a landmass of 3.29 million square kilometers and 0.64 million sq. km. of forest cover i.e. nearly 2.5% of world's geographical area, and 1% of the forest area, supporting nearly 990 million peoples (about 16% of the world's population). The recorded forest area in the country is 7,065,210 sq. km. (23.42% of the geographical) area of the country while the satellite data analysis indicates a forest cover of 6,39,600 sq. km. (19.47%). However, only 3,85,756 (11.73%) has good forest cover of over 40% crown density and up and rest is open forest with 10 to 40% density (2,49,311 sq.km.) and there are nearly 60,000 sq. km. of blank area without tree cover. Additionally there is a significant amount of wood lots less than 25 hacters in size. The growing stroch is estimated at 4740.9 million m^3 with an annual increment of 88 million m^3.

In future, the Indian pulp and paper Industry will require more forest based raw materials, and has to strives for providing the increasing demand for pulp and paper products. Some of the ways to meet the increased demand are more intensive forest, more efficient utilization and shorter rotation with increased use of Juvenile wood, and more intensive tree improvement such as selection, genetic engineering, breeding, short rotation and intensive culture systems, incorporate agronomic systems. Poplar deltoides is one of the plant which can be grown in short rotation and the yield excellent pulpwood.

1.5: Objectives of Present Studies:

The demand of paper and paperboard is expected to enhance with increasing industrial development and growing literacy rate in our country. Future projection shows that percapita consumption figure would rise up from 4.3 kg to 5 kg in the next few years. This would call projected annual production of more than 50 lakhs tons compared to the present production of 4.6 million tons. The demand for higher production of paper would naturally require more fibrous raw material in future. There is an acute shortage of forest based raw material in our country. To bridge the gap between demand and supply for the forest based raw materials up to some extent it necessary to grow the fast growing species woods.

Poplar deltoides is a native of North America and can one of the most promising hardwood raw material for Indian pulp and paper industry. P. deltoides is a fast growing tree, raised in close spacing and harvested on short rotation. The biomass obtained from it, is good. At present Eucalyptus is the most promising raw material for pulp and paper industry. Due to high transpiration rate of eucalyptus, farmers prefer to grow Poplar trees. No detailed investigation in India has been made on poplar with reference to pulp and papermaking. Hence it seems worth while to make comprehensive study on poplar with reference of pulp and papermaking as mentioned below:

Proximate Chemical Analysis.

Pulping Studies.

Bleaching Studies.

Blending Studies.

Table 1.1 : Raw material wise classification of Paper Mills in India

Type of raw material	No. of mills	Installed capacity (million tons)	Percentage of capacity
Forest based (wood and bamboo)	28	1.449	37
Agro-based (straws, bagasse etc.)	111	1.240	31
Others waste paper etc.	241	1.265	32
Total	380	3.954	100

Source : Development council for pulp, paper and allied products Govt. of India (1990).

Table 1.2: Yearwise demand Installed capacity and Production of paper and paper boards (11).

Year	Demand *(Lakh tons)*	Installed Capacity *(Lakh tons)*	Growth, %	Production *(Lakh tons)*	Capacity Utilization, %	Import *(Lakh tons)*	Export *(Lakh tons)*
1996 - 97	40.00	45.20	-	40.50	89.60	1.10	1.00
1997 - 98	41.00	45.20	2.44	41.50	91.80	3.00	0.60
1998 - 99	42.10	49.36	2.68	42.50	86.10	2.71	0.75
1999 – 2000	46.00	52.00	9.70	46.50	89.40	2.77	1.05
2000 – 2001 *(Estimated)*	47.26	54.08	2.73	47.95	88.70	2.00	2.00
Average			3.80		89.10		

Source : IPMA (Indian Paper Manufacturers Association), IARPMA

Table 1.3: Yearwise demand Installed capacity and Production of Newsprint (11).

Year	Demand *(Lakh tons)*	Installed Capacity *(Lakh tons)*	Growth, %	Production *(Lakh tons)*	Capacity Utilization, %	Import *(Lakh tons)*
1996 - 97	7.00	7.60	-	3.00	39.50	5.40
1997 - 98	7.50	8.00	24.7	3.74	46.70	5.00
1998 - 99	8.00	8.50	32.1	4.94	58.10	3.95
1999 – 2000	8.50	9.25	(-)6.1	4.64	50.00	3.79
2000 – 2001 *(Estimated)*	9.00	10.65	26.7	5.40 *(Upto Jan 2001)*	50.70	2.60 *(Upto Oct 2001)*
Average			20		49	

Source : IPMA (Indian Paper Manufacturers Association)

Table 1.4 : Demand and supply scenario of cellulosic fiber

Year	Projected demand (lakhs tons)	Compounded growth rate (%)	Total possible production of paper from indigenous fiber (lakhs tons)	Short fall indigenous fiber in paper equivalent Term (Lakhs Tons)	Per capital consumption kg/year
1994 – 95	32.78	5.5	24.08	8.70	3.4
2000 – 2001	49.50	7.8	32.58	16.92	5.0
2005 – 2006	67.00	6.5	41.61	25.39	6.5
2010 – 2011	85.50	5.5	49.10	39.40	-

Table 1.5 : Projected short fall of fibrous raw materials(2).

Year	Demand (million tons)	Production (million tons)	Short fall (million tons)	Import cost (Rs. Million)
2000	4.112	2.560	1.552	19690
2005	5.045	2.762	2.283	29930
2010	6.297	3.154	3.143	42760
2015	7.981	3.325	4.656	64190

Table 1.6: Pulp and paper board production, import and export (131,132):

Paper and paper board	Production '1000 tonnes			Imports '1000 tonnes			Exports '1000 tonnes		
	1997	1998	1999	1997	1998	1999	1997	1998	1999
News print	380	440	450	500	440	270	-	-	-
Printing/ writing	1,110	1,280	1,510	130	60	50	10	55	65
Corrugating materials	685	730	795	25	10	5	-	-	-
of which,									
Virgin fiber liner	105	125	145	25	10	5	-	-	-
Waste based liner	240	250	275	-	-		-	-	-
Waste based fluting	340	355	375	-	-		-	-	-
Other wrapping papers	45	50	60	-	-		-	-	5
Tissues paper	30	35	35	6	5	5	-	-	-
Other papers	90	115	125	15	10	5	10	10	10
Board	660	700	820	24	15	-	10	20	30
Total paper and board	3,000	3,350	3,795	700	540	335	30	85	110
PULP									
Bleached sulfate	760	800	850	125	25	40	-	-	-
Unbleached sulfate	210	220	210	35	10	10	-	-	-
Bleached sulfite	-	-	20	10	-	-	-	-	-
Unbleached sulfite	-	-	-	40	40	40	-	-	-
Semichemical pulp	-	-	-	30	36	40	-	-	-
Mechanical Pulp	-	-	-	-	-	35	-	-	-
Non wood Pulp	930	1,130	1240	-	-	-	-	-	-
Total pulp	1,900	2,150	2,320	250	171	125	000	000	000

CHAPTER 2

STUDIES ON FIBER MORPHOLOGY AND PROXIMATE CHEMICAL ANALYSIS

2.1 Introduction :

Cells are the basic building blocks of the plants. In the early stages of growth, the cell cavities contain protoplasm, but after the complete formation of cell wall, the protoplasm disappears, and the structure is called as wood cells. Wood cells are produced in the vascular cambium from the two types of meristematic cells, fusiform initials and the ray initials. The cells derived from the fusiform initials are upright in the stem, occupies a major part of xylem and plays an important role in the chemical, physical and mechanical properties of the wood. The principal function of xylem tissues are water conduction from roots to shoots and the mechanical support to huge plant body and the physiological role such as the storage of carbohydrates. The secondary xylems formed by cell division in the vascular cambium after onset leaving only the hollow tubular or quill shaped type of structure known as fibre. The xylem of which may be an important source for pulping material. Wood is a natural composite material and chemical complex of cellulose, hemicellulose lignin and extractives.

The principal constituent of a wood fibre is cellulose, which is a polymer and is the structural material out of which the fibre is built. It is a white substance, insoluble in most solvents, and resistant to the molecules in different fiber surfaces, is the principal source of fiber to fiber bonding in paper. Cellulose is the frame work substance comprising 40 to 60% of wood in the form of cellulose microfibrils, whereas hemicellulose are the matrix substances present between cellulose microfibrils, lignin on the other hand, is the incrusting substance solidifying the cell wall, associated with the matrix substances. All the plant fibre cells have a inter cellular layer and the S_1, S_2 and S_3 layers. At first step of the differentiation of the woody cell, the living

protoplasm produces a primary wall and the substance between the primary walls of adjacent cells is called the intercellular layer or the middle lamella. The combined layer with the two adjacent primary walls is called as compound middle lamella. After the enlargement, the cells ceases, and the cell wall layers are formed by the deposition of wall substances into the inside of the primary wall, and these wall layers are called the secondary wall. The secondary wall is composed of a relatively narrow or the outer layer and inner layer and a relatively thick middle layer. The primary wall and the secondary wall contain cellulose, hemicellulose and lignin.

Hemicellulose is second major chemical constituent of a wood fiber. Many hemicellulose are removed by mild chemical action. They are very important in paper making because they promote the development of fibre to fibre bonding. Lignin is the third major chemical, which serves as a binding agent and is a complex material. It is insoluble in water and most common solvents but can be made soluble by chemical action. All chemical pulping processes are based on chemical reactions with solubilization to remove lignin. Lignin thus decreases the paper strength. Extractives are also present in the original wood but are mostly removed by chemical pulping and bleaching processes. Trace amounts of these compounds do survive and may cause problem in pulp and paper making.

Substances such as pectin materials, waxes, starches, resins gums, organic materials, extractives and proteins are also present in the wood. These substances exist in the specific location and are not the component of the fibre. For papermaking, softwoods, bamboo and different hardwoods and bagasse are well known. In the case of softwood, the fibers are thin walled, long and they collapses during sheet formation. The vertical structure of conifers is composed almost entirely of long tapering cells called tracheids. In some species, vertical resin canals are also present. The horizontal system is composed of narrow rays, only one cell in width

but often several cells high. There are two specialized types of ray cells, the ray parenchyma, present in all species, and ray tracheids, present in only certain species.

In bamboo, the fibers make up 60-70% of the total cells. The fibers wall are much thicker and cell cavities are rather narrow with gradually tapering pointed ends, and sparse slit like pits. The bamboo fibers are stiff straight with few cenlings and invariably show compressed buckled areas with obvious knot like marks, which stand out rather prominently in thick wall fibers. The general fiber dimensions are fiber length 1.5-2.0 mm width 20 to 28 μm, average cell wall thickness is 6.6 μm. Bagasse fibers are thick to thin walled usually straight, pointed ends and relatively more numerous slits or ventricular pits than in bamboo. The average dimensions of bagasse fiber are, fiber length 1.5 mm and width 22.5 μm, fiber wall thickness 3.26 μm and lumen diameter 17.9 μm. The morphological factors of the raw material also affects the properties of the paper. The characteristics affecting strength properties are reported in table 2.1(36). Typical morphological characteristics of bamboo and softwood are given in table 2.2.

The chemical analysis of plant material is called as proximate chemical analysis, which provides important information regarding its suitability for pulp and papermaking. These important tests includes, water solubility- provides a measure of tannins, gums, sugars, colouring matters and starches in wood. The one percent sodium hydroxide solubility of wood indicates the degree of fungal decay or degradation by heat and light. As the wood decays or degrades, the percentage of the alkali soluble material increases. It is often desirable to ascertain to what extent a low cellulose value is due to attack by fungi, because in general, the greater the such attack, the lower the pulp yield. The alcohol-benzene solubility of wood is a measure of such substances as wax, fats, resins, gums and phytosterols. The extractive, influence both the pulping process and the quality of the resulting pulp. The extractives may inhibit pulping and creates lot of problem during processing, as deposits on the process equipments in the pulp mill. High content of

extractives means a higher tendency for so-called pitch problem and the homogeneities of paper are affected by resin particles.

The percentage of lignin in the wood is related with the chemical dose and time required for delignification, the higher the lignin content, the higher the chemical dose and longer the cooking cycle required for pulping. The residual lignin present in the pulp influences paper properties and particularly the stiffness, the more the lignin, the higher the stiffness. The typical proximate analysis of softwood and bamboo are reported in table 2.3 and 2.4 (152).

In the chemical pulping, the cellulose is the main component and variation in pulp yield and economy in pulp production therefore, directly reflect the variation in cellulose content of the wood. Cellulose is long chain polymer while the hemicellulose has a much lower molecular weight than the cellulose and has low degree of crystallinity. The hemicellulose dissolves to a large extent during chemical pulping, however, a substantial quantity of hemicellulose is always associated with the pulp. It also has a great influence on the swelling behaviour of the fibre. The ash content gives an estimation of the content of mineral salts and other inorganic matter while silica content reflects the burning and sedimentation operations in the chemical recovery process. In the present investigation the studies on the morphological and chemical composition of poplar deltoides has been done to assess its potential as one of the fastest growing hardwood plants for pulp and papermaking.

2.2 Morphological and Anatomical Studies:

The term hardwoods refer to the broad-leafed trees, which are all deciduous. Botanically they belong to the dicotyledon class of angiosperms. The principal vertical structure of hardwoods is composed of relatively long fibrous cells of small diameter. The larger diameter cells are called vessels. In a cross-section of wood, the vessel appears as numerous rounded pores, which in some species of hardwoods, are visible to the naked eye. Consequently, the

hardwoods are also called as porous woods. In all hardwoods pores are big enough to be observed with a hand lens on cross-section, because the diameter of these pores, as well as there grouping and distribution in the annual rings, are very characteristics in each genus. Another noticeable feature in a cross section is parenchyma, although not all hardwoods have it. When parenchyma is abundant, it often give rise to definite patterns on the cross-section. In many hardwoods, the thicker feature that is readily detectable is the system of rays. They appears as a series of radiating lines on transverse surface, while on freshly split radial surfaces they are visible as a series of streads. Hardwood rays are much more variable in width and in height, than those of softwoods. Most of the hardwoods can be identified with a hand lens on the basis of their pronounced rays, distribution of pores, parenchyma and colours.

Vessel Features:

Hardwood has some distinguished vessel features. They are short, large diameter cells through which sap is transported. They are diffused porous, the pores are fairly uniform in size or vary gradually, reduced in size from early wood to late wood. The size and number of vessel elements vary strongly from species to species. Vessels have open ends and a grate like connecting tissues called scalariform plates. The perforation plates are simple, the end walls of vessel elements with a single large opening devoid of bars. In hardwoods, the spiral thickening of the vessels is absent. No evidence of spring like helix over any portion of vessel element and the inter vessel pits are alternate. Pits are present in diagonal rows across a vessel element (77).

Parenchyma Arrangements:

In the case of the hardwoods, parenchyma is present marginally. Marginal parenchyma confined to boundary of growth rings. It appears as a fine lines around the growth rings. The fine lines of the parenchyma delimit the growth ring.

Rays: Rays are homocellular, all rays are only one cell wide and they are exclusively uniseriate. Rays are composed entirely of procumbent (usual case) or upright cells (77).

Experimental Methodology:

The specific gravity was determined by oven dry/green volume method. For the anatomical studies 20 μm thick cross-section were prepared, the sections were stained with fast green and safranin so as to differentiate. The sections were used to determine vessel frequency, tangential and radial diameters of vessels and proportion of tissues i.e. percentage of vessels, fibre and rays. Twenty counts each were taken for vessel frequency and vessels diameters. For the measurement of cell size, the chips of poplar deltoides were subjected to chemical and physical maceration to separate the individual cellular elements from each other without damage. It involved the use of a hot aqueous sodium chlorite solution acidified by acetic acid. It remove most of the lignin and other cementing materials without appreciable degradation of cellulosic material. The microscope slides of cellular materials were prepared according to BIS Method 5285. Microscope slides were projected at the magnification of 40× in the compound microscope and fibre length were measured, while the fibre width and cell wall thickness and vessel length were obtained by measuring the projected images at a magnification of 160×. Vessel area was also determined by the formula: vessel area = vessel frequency × vessel diameter. The results are reported in table 2.5.

Results and Discussion:

The results of anatomy and morphology of poplar deltoides are reported in the table-2.2. These results indicates that the fibre length of poplar is comparable to that of eucalyptus but are approximately half of bamboo. The fiber diameter of poplar is almost two times more than those of eucalyptus and bamboo. Higher fiber diameter is expected to give better bulk. The density of poplar is lower than that of eucalyptus, hence per digester pulp yield of poplar will be slightly

lower in comparison to eucalyptus. Lower density indicate the porous wood, which facilitates the penetration of the cooking liquor during pulping and utilizing lower chemicals along with shorter cooking cycle.

The anatomical structure alongwith specific gravity influences the paper properties. The presence of higher percentage of vessels, which occupy surface area of the papers, creates problems during offset lithographic printing. Vessels have open ends and a grate like connecting tissues called scalariform plates. Vessel elements are not suitable as paper making material unless they have been broken down. Fiber characteristics also influence the various properties of pulp and paper. Similarly tissue proportions of vessel, ray, parenchyma and fiber percentage also give an indication of the composition and its influence on paper quality. The fiber characteristics are collectively represented by Runkel ratio and fiber shape factor.

Proximate Chemical Analysis

Experimental Methodology:

The chips of poplar deltoides were air dried and disintegrated in a Weverk laboratory disintegrator. The –40 + 80 BSS mesh wood fractions (meals) were collected for chemical analysis. The proximate chemical analysis includes cold and hot water solubles, one- percent sodium hydroxide solubles, alcohol benzene solubles (1:2 v/v), lignin, pentosans, holocellulose alpha cellulose, ash, and silica etc. All these tests have been performed as per TAPPI standard method to check the suitability of poplar deltoides for pulp and papermaking. The results have been reported in table-2.6

Results and Discussion:

The results of the proximate chemical analysis of poplar deltoides and eucalyptus have been reported in table- 2.6. These results have been compared with the results of the proximate

chemical analysis of eucalyptus, which is at present the most promising raw material for pulp and papermaking. These results clearly revealed that the water solubles of poplar deltoides, eucalyptus and bamboo are 4.5, 7.8 and 6.8% respectively. Poplar deltoides has less water solubles in comparison to the water solubles of eucalyptus and bamboo. The alcohol-benzene solubles of poplar, eucalyptus and bamboo are 2.8, 1.4 and 1.9% respectively. All the soluble materials come under the category of extractives and are totally undesirable for pulp and papermaking and affect the pulp yield and further processing of the raw material. These results indicate that poplar deltoides have lesser quantities of extractives and will create less pitch problems and improve pulp yield and homogeneity of the paper. The one- percent sodium hydroxide solubles of poplar, eucalyptus and bamboo are 19.6, 16.2 and 20.6 percent respectively. The alkali solubles are slightly more, compared to that of eucalyptus. The lignin content of poplar and eucalyptus are 21.8 and 25.9% respectively. Poplar has lower lignin content, compared to eucalyptus; which is the most promising raw material for pulp and paper making. The low lignin content in Poplar deltoides indicates that poplar deltoides will require comparatively less cooking chemicals and shorter cooking cycle compared to that required for eucalyptus. The shorter cooking cycles helps in improving the productivity as well as in preserving the strength properties of the pulp.

The total carbohydrate fraction (holocellulose) of poplar, eucalyptus and bamboo are 69.4, 65.2 and 58.5% respectively. Poplar has substantially little higher total carbohydrate fraction compared to eucalyptus. The alpha cellulose content of poplar, eucalyptus and bamboo are 47.4, 43.8 and 41.1 respectively. The pentosan content of poplar, eucalyptus and bamboo are 17.3, 16.0 and 17.8% respectively. The pentosan content of poplar is little higher compared to eucalyptus. The ash content of poplar, eucalyptus and bamboo are 0.63, 0.58 and 1.2%

respectively, thereby indicating less damaging effect on processability of the wood and will require less cleaning of the equipments.

Conclusion:

The fibre length of poplar is comparable to that of eucalyptus, but the fibre diameter is two times more hence poplar is expected to have a lower bulk in comparison to eucalyptus. The poplar has lower packing density, thereby producing less pulp yield per digester, compared to eucalyptus. The results of proximate chemical analysis shows that poplar has lower lignin content and higher total carbohydrate content compared to eucalyptus. Therefore it requires less cooking chemicals with shorter cooking cycle. Poplar is a fast growing tree and fast growing trees have low tension wood content, as compared to other hardwoods, and have good papermaking properties. However Poplar deltoides have different clones and anatomical variation differ slightly. The topographic conditions also differ the anatomical variation (20,204). Poplar has higher fiber percentage and lower vessel percentage. The fiber length is comparable to other hardwood pulps.

It has been widely reported in the literature that significant variation in physical and chemical composition exists among hybrid poplar clones. Several researchers (20,204) have demonstrated that genetic make up can influence fiber characteristics and the specific gravity of the tree. The quality of the pulp is also influenced by these properties (197). The investigation by these researchers found a larger variation of alpha cellulose content from 40-51%, which would result in pulp yield difference. The environmental factor, cultural practices, the age of the tree further influences the fiber and pulping properties of hybrid poplar trees (50) as shown in table 2.7. The plantation trees, because of their short rotation time, may contain a significant amount of juvenile wood. The juvenile wood might affect papermaking properties and could have an impact on the optimum harvesting. Cisnereos et al.(26) reported that the fiber length increases

with the age of the tree while the specific gravity shows a gradual decline and the fiber coarseness show no clear correlation with tree age. Similar results have been obtained in another study (50). Boeyce (20) also found that the length of the fiber increases with the number of rings from the piths and with the diameter of the tree.

Table 2.1 Strength characteristics for morphological factors. (36)

Particulars	Tensile strength	Bursting strength	Tearing strength	Sheet density	Folding strength
Fiber length	0 to +	0 to +	++	0 to +	0 to -
Cellwall thickness early(spring) wood fraction(ribbon structure) rising	+	+	0 to -	++	++
Cellwall thickness late(autumn) wood fraction(ribbon structure) rising	-	-	0 to +	--	- -
Fiber length to width (L/D) ratio rising	- to -	- to -	+	+	
Curling of fiber rising				+	-

0 Shows no effect
+ Shows positive effect
++ Shows decisive positive effect
- Shows negative effect
-- Shows decisive negative effect

Table 2.2: Typical morphological characteristics of Bamboo and softwood (152).

Particulars	Bamboo	Softwood
Density cm^3/g	0.483	-
Fiber length,L(mm)	1.7	3-3.5
Fibre width,D(μ)	23.6	25-40
Lumen width,d (μ)	9.5	23-43
Cell wall thickness,W(μ)	7.0	4-7
Flexibity coefficent (d/D 100)	40.56	-
Ratio of length to width L/D	72	80-100
Ratio of twice cellwall thickness to fibre width (2W/D)	0.593	-
Wall fraction, (2W/D 100)	59.3	-
Runkel ratio, (2W/d)	1.47	-
Ratio of cellwall thickness to lumen width (W/d)	0.74	-

Table 2.3: Proximate Chemical Analysis of Softwoods (152).

Particulars	Pinus longifolia	Pinus spinulosa	Spurce	Fir spectablia
Cold water solubles ,%	1.62	3.1	-	3.2
Hot water solubles ,%	3.36	5.2	5.9	6.8
1% NaOH solubles ,%	13.2	12.6	14.6	18.3
Alcoh- benz solu ,% (1/2 v/v)	2.15	2.4	3.1	6.1
Lignin ,%	28.5	28.6	28.7	29.2
Pentosans ,%	7.2	12.3	11.9	12.3
Holocellulose ,%	61.5	68.4	71.7	67.4
Ash ,%	0.25	0.3	0.32	0.4

Table 2.4: Proximate Chemical Analysis of Bamboo (152)

Particulars	Bambusa Tulda	Giant bamboo	Dendroclamus strictus
Cold water solubles ,%	3.01	7.2	3.3
Hot water solubles ,%	5.57	10.49	6.12
1% NaOH solubles ,%	20.82	27.76	-
Alcoh- benz solu ,% (1/2 v/v)	1.9	4.62	3.1
Lignin ,%	23.7	27	27.9
Pentosans ,%	17.8	-	15.6
Holocellulose ,%	58.5	54.93	59.9
Ash ,%	1.2	2.3	2.1

Table 2.5: Mean values of anatomical parameters of Poplar deltoides and Eucalyptus

S.No.	Particulars	Poplar deltoides	Eucalyptus
1.	Specific gravity cm^3/g	0.437	0.580
2.	Fiber length, L (mm)	0.984	0.938
3.	Fiber Lumen diameter, d (μm)	17.6	8.0
4.	Fiber diameter, D (μm)	25.6	14.75
5.	Cell wall thickness, W(μm)	4.1	6.8
6.	Vessel length, (μm)	470	-
7.	Vessel, %	28.4	30.4
8.	Fiber %	61.9	57.1
9.	Ray, %	10.7	12.0
10.	Paranchyma, %	-	18.2
11.	Vessel frequency	63.4	-
12.	Vessel diameter(tangential),μm	68.7	-
13.	Vessel diameter(radial),μm	110	-

Table 2.6:Results of Proximate Chemical Analysis of Poplar Deltoides and Eucalyptus.

S.No.	Particulars	Poplar deltoides, (±0.1)	Eucalyptus (±0.1)
1.	Cold water solubles,%	3.8	2.9
2.	Hot water solubles,%	4.5	7.8
3.	1% NaOH solubles,%	19.6	16.2
4.	Alcohol benzene solubles ,% (1/2 v/v)	2.8	1.4
5.	Lignin ,%	21.8	25.9
6.	Pentosans ,%	17.3	16.0
7.	Holocellulose ,%	69.4	65.2
8.	Alphacellulose ,%	47.4	43.8
9.	Ash ,%	0.63	0.58

Table 2.7 Chemical composition of Poplar clones (50).

Clone	Extractives Content,%	Kalson lignin,%	Holo-celluose,	Alpha-celluose,%	Hemi-celluose,%
1	1.7	20.3	73.8	40.3	32.5
2	ND	24.0	76.1	51.7	20.1
3	ND	26.4	78.8	52.5	24.4
4	1.4	20.5	81	45.8	35.3
5	3.1	16.6	85.7	51.2	34

CHAPTER 3

PULPING PROCESS

The primary aim of pulping is to separate fibers and to produce a fibber surface suitable for bonding in the papermaking process. Plant fibres are made up of cellulose, hemicellulose (short chain of branched & unbranched sugars, including galactose, mannose and xylose), and lignin which gives the inherent strength properties to plants). The ratio of these constituents and the chemical nature of the lignin and hemicelluloses will vary with different plant types and species. Many processes have been developed over the years to convert wood or nonwood-based raw materials into separate fibres suitable for use in paper and board making. The range of pulping methods available for this conversion process can be divided into three processes.

- Mechanical
- Semichemical/chemimechanical
- Chemical

These differ principally by the nature of the process used and the yield of pulp obtained. Typically, chemical processes give pulp yields in the range of 40%-55%, where as mechanical processes give yields in excess of 80%-85%. This yield difference highlights the fact that the chemical process effectively separates the cellulose from the lignin present, whereas the mechanical process converts all the constituents present. The choice of process will depend primarily on the nature of the material to be pulped and the grade of paper or paper product being made from it, chemical processes.

Mechanical Pulping Processes:

The oldest mechanical pulping process is the stone ground wood process. In this process, pulp is produced by pressing wood logs against an abrasive rotating stone surface. The slurry of

fibres and fibre fragments is screened to remove shives and other over sized particles and is subsequently thickened by removal of water from a pulp stock suitable for papermaking.

Another process known as refines mechanical pulping (RMP) process involved grinding chips between the rotating discs of an equipment called refiner. RMP usually retains long fibres then SGW and yield stronger paper. The heart of RMP process is disc refiner. Another process known as thermochemical pulping (TMP) is a modification of EMP. It involves steaming the raw material for a short period of time prior to refining. The steaming softness the chips results the pulp produced wither longer fibres and less shives than RMP. Mechanical pulps form highly opaque sheets having excellent printing characteristics, however paper is weak and discolors readily on exposure of light over a period of time. Most of mechanical pulp is used in newsprint, etc.

Semichemical Process :

The principal semichemical pulping process is the neutral semichemical process (NSSC) which involves a chemical pretreatment followed by refining. The major distinction between this and the chemically pretreated mechanical processes, such as CMP, is in the concentration of the chemicals used and the conditions under which the pretreatment stage takes place. The chemical treatment involves typically the use of up to 15% of sodium sulphite by mass of material, and approximately 4%-5% of sodium carbonate by mass.

Chemical Pulping Processes :

Soda Process:

The soda process is based on sodium hydroxide and has been widely used in the processing of nonwood fibres. Chemical recovery is straightforward and the virtual absence of reduced sulphur compounds in the recovery process means there are few air emission problems with the process. Major developments have centred around improving the yield from the process with additives such as anthraquinone.

Kraft Process :

The kraft is predominant process used for the pulping of wood. In the kraft process, chips are cooked at high temperatures and pressures in the presence of NaOH and Na_2S. The cooking time depends on the intended use of the pulp. The chips are cooked with NaOH and Na_2S to dissolve and soften their lignin and then separating the resulting wood pulp from spent cooking chemicals and dissolved wood. One of the main advantages of the kraft process is the existence of an efficient chemical recovery system. Without chemical recovery system, the kraft process would not be economical, and it would adversely affect the environment. A characteristic of the process is the sulphur-based air emissions, which have been the subject of research to reduce or eliminate them. This has only met with partial success to date. The process is well established for wood-based raw materials but is considered unnecessarily severe for most nonwood raw materials where the lignin is less strongly bonded to the cellulose.

Sulphite Process:

The sulphite process was one of the earliest chemical processes and has developed into an array of variations used on wood and nonwood materials. It has become less favoured in recent times as an economic process, and the recovery of the pulping chemicals has not been perfected.

Organosolv Process :

A number of organosolv processes have been developed in which an organic solvent or mixture of organic chemicals are used as the pulping chemicals. In such processes recovery of all the components of the raw material, i.e. cellulose, lignin and hemicelluloses, is possible for subsequent use. The solvent recovery is also straightforward. Although there have been a number of systems proposed in recent years, only the ALCELL process developed by Repap Technologoies in Canada and using an alcohol-based system has been developed to a full-scale commercial operation.

CHAPTER 3A

SODA AND SODA-AQ PULPING PROCESSES

3.1A Introduction :

Soda process is particularly applicable to low lignin fibrous raw materials like agricultural residues where the advantages of sulfidity are of lower magnitude. Soda process have some basic draw backs viz. low pulp yield, relatively lower strength properties, longer cooking time, high temperature and caustic charges, but on the other hand paper manufactured from soda pulps bear high bulk, opacity, absorbency and printability. Soda pulps are therefore best suited to paper grades where pulp strength requirements are not demanding. Soda pulps are weak and strengthened by blending with longer and stronger fibres.

The chemical reactions that occurs between wood components and alkali used for delignification are extremely complicated. In the splitting of lignin molecule by hydrolysis, formation of additional hydroxyl groups occurs during delignification, possibly from the hydrolysis of methoxyl groups from the furan or pyran ring or from the breaking of linkages between lignin and carbohydrates. At optimum pulping temperature, aqueous alkali hydrolyses many β-O-4 linkages of native lignin, cleaving the polymer chains and the decomposed products so formed are soluble in the alkali and thus can be removed from the fibers (154).

Kraft process is the dominant pulping process today, the greatest disadvantage of kraft pulping is the release of malodorous reduced sulphur compounds to the atmosphere. To ease the odor problem, kraft mill must install and operate expensive systems to control these non-condensable gases. The soda pulping process with or without anthraquinone (AQ), does not release any such reduced sulphur compounds to the atmosphere. However, the soda process is carried out at higher H-factor (cooking time and temperature) and higher chemical charge than

properties of the pulp. Soda pulp has lower tear resistance (142,169). The cause of lower strength properties is due to the reduced fiber strength rather than to a decrease in the bonding ability of the fiber has been shown by Mckenzie (121). Use of AQ improves the yield (80,109,112), strength properties as well as helps in over coming the tear problem of soda pulps. However, the strength properties of soda-AQ pulp are slightly lower but comparable to kraft pulp (118,119).

3.2A EXPERIMENTAL METHODOLOGY

3.2.1A Raw Material and its Preparation:

The Poplar deltoides wood was procured from the local region of Saharanpur District. The wood was chipped in the chipper and the chips passing through a 32 mm screens were utilized for pulping studies.

3.2.2A Optimum Conditions of Pulping:

All the cooks were made in laboratory CCL digester. The cooking were made in six stainless steel bombs of about 2.5 liters capacity, containing 300 gms o.d. chips of poplar deltoides, by maintaining the wood to liquor ratio of 1:3. The following time schedule for heating was maintained during the experiments.

Time from room temp. to 105 °C : 45 minutes.

Time from 105 °C to max. temp. 170 °C : 45 minutes

During soda delignification process, the various pulping parameters viz. Time, temperature and alkali doses were optimised. The various combinations of AQ dose (0.0, 0.05, 0.1, 0.2% on o.d. wood) at different active alkali (14, 16, 18 and 20%, as Na_2O) have been studied. All these cooks were made at same 'H' factor (time and temperature). At the end of the cook, the pulp was washed thoroughly, screened in laboratory Weverk screen. The total pulp yield, screening rejects and screened pulp yield were determined by screening on a standard laboratory screen with 0.15mm slot and then drying . Errors caused by fiber losses during

screening were avoided as far as possible. The lower the amount of rejects, the more uniform is the pulping. The response variables such as kappa number, CED viscosity, black liquor pH, residual alkali were determined using standard method. The kappa number and 0.5% CED viscosity were determined by Tappi standard T – 236 and T – 230 respectively. The white liquor titration was done according to T-624 and the black liquor titration according to T-625.

3.3A Results and Discussion:

The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions of temperature, pressure, time at temperature with constant active alkali charge. As the pulping experiments are extremum type, no two sets can be identical therefore average of the four / five set of data are shown only. The maximum and minimum deviation of statistically mean value is not shown or the all four sets of data are not shown, merely to reduce the large volume of data.

In the present investigation, data found from the laboratory experiments for a specific set of input parameters such as time, temperature, bath ratio, alkali dose etc. all the data are not reproduce the brevity of rather average data of the set is depicted in tables. However it is observed that there is marginal difference in the set of data which is permitted in this type of experiments. The variation in the responding variables were found to be well within the experimental error.

For the statistic modelling the responding parameters during pulping namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content of the pulp at different active alkali were regressed with the time at temperature as independent variables. The responding variables of pulp evaluation such as tear index, tensile index and burst index were regressed with different freeness as independent variable. In most of the cases the quadratic

model ($y = ax^2 + bx + c$, where a, b and c are parameters to be estimated) were obtained. Where y is the responding variable and x is the time at temperature, which is found to fit well to the data. The quadratic model reflects the behavoir of various pulping conditions and pulp evalution.

3.3.1A Influence of Time and Temperature:

In a series of experiments, the soda pulping of Poplar deltoides were studied at different time (60 min. to 180 min.) and temperature (ranging from 150 °C to 180 °C). The results of these experiments are reported in table 3.1A. The residual lignin content associated with the pulp (on o.d. wood basis) was determined and these were plotted versus cooking time at temperature of reaction, as shown in fig.3.1A. The steeper slope is related to the bulk delignification (rapid solubilisation of bulk of the lignin) and the more gentle curve correspond to the slow solubilisation of the residual lignin (residual delignification) and have different velocity constants. The data fitted statistically smooth curves having concavity upwards with R square values ranging from 0.97 to 1 for all the four curves at 150-180^{0}C respectively. The R square values indicate the closeness of the fit of the data. The bulk delignification corresponds to the removal of easily assessable lignin present in the middle lamella and the residual delignification corresponds to the removal of lignin present in primary wall, secondary wall, and the central inter connecting cavity of the fiber. Bulk delignification is generally associated with alkali catalyzed cleavage of β-aryl ether bonds in non-phenolic units and cleavage of aryl alkyl ether bonds. These reactions have first order kinetics with respect to alkali concentration (81,109,112). Mortha (120) studied the alkaline pulping kinetics of hybrid poplar and calculated for the values of the rate constant K for different pulping temperatures as shows in table-3.4A for both soda and kraft pulping.

Fig.3.2A and 3.3A show the effect of time at temperature over kappa number and yield at 16% active alkali at different temperature respectively. The regression co-efficient between

kappa number, total pulp yield at 16% active alkali at different temperature was around 0.89-0.98, which indicates strong dependence of these parameters of pulping conditions. At a particular time, the kappa number decreases on increasing the temperature. This shows that the rate of delignification increases on increasing the temperature. The increase in temperature decreases the cooking cycle for obtaining a particular kappa number. Thus from the results of these experiments, a temperature of 170 ^{0}C may be taken as optimum for soda delignification. Moreover the degradation of cellulose is enhanced at temperature beyond 170 °C. From the figures 3.2A and 3.3A we may also conclude that the rate of delignification in soda pulping is slower, takes longer time for the bulk delignification. During soda delignification, almost 75% lignin is removed in first 90 minutes of the delignification and in latter cooking period only 10-15% lignin is removed. Thus from a series of experiment, the optimum cooking period of 120 minutes at 170 °C has been taken as optimum for soda delignification.

3.3.2A Effect of Active Alkali Charge:

Active alkali is the most important variable affecting the pulp yield and the degree of delignification. The influence of active alkali charge during bulk delignification was investigated at 170 °C using 14,16,18,20% active alkali doses (as Na_2O). Active alkali is the most important variable affecting pulp yield and degree of delignification. The results are reported in Table-3.2A and 3.3A and illustrated in fig. 3.4A and 3.5A. The regression co-efficient between kappa number, ligin content at 16% active alkali at different temperature was around 0.94 -0.99, which indicates strong dependence of these parameters of pulping conditions. The data fitted statistically smooth curves having cocavity upwards and indicate the closeness of the fit of data. The steeper slope is related to bulk delignification and more gentle slope corresponds to residual delignification and have different velocity constants. It indicate that when the concentration of active alkali decreased, the cooking time to reach transition from bulk to residual delignification

transition point, lower pulp lignin contents were obtained at higher alkali doses than at lower alkali doses. Figure 3.4A clearly indicates that the magnitude of decrease in pulp lignin content is directly proportional to the active alkali doses.

Time at temperature versus kappa number and pulp yield versus AQ dose at different active alkali are plotted in fig.3.5A and 3.6A. These figures indicate that both the kappa number and pulp yield decreased linearly on increasing active alkali doses. The pulp yield also decreased linearly as a result of an increase in active alkali dose up to a limit of 16%, and afterwards the magnitude of decrease in pulp yield was higher. Therefore 16% active alkali dose may be considered as optimum dose during soda delignification of Poplar deltoides.

The results of the effect of active alkali charge and AQ are reported in table 3.5A. The effect of AQ on pulp yield and kappa number at different alkali charges are is shown in figure 3.6A and 3.7A. The R square values (0.73-1) indicate the closeness of the fit of the data showing the dependence of these conditions.The experiments for soda-AQ pulping were carried out at 170 °C at constant time of 120 minutes at four different AQ doses (0, 0.05, 0.1 and 0.2%). These results clearly indicate that, in case of soda pulping as the active alkali increases from 14% to 20% (as Na_2O) the unscreened pulp yield was found to decreased from 59.0% to 48.6% respectively while the corresponding drop in kappa number was found to be 32.2 to 15.1. On increasing the active alkali concentration, the degradation of carbohydrates material also increases which results in severe pulp yield loss. Moreover with an increase in alkali dose, the selectivity of lignin dissolution decreases and increases the cellulose degradation; therefore higher alkali doses must be avoided in order to check the severe cellulose degradation Therefore, 16% active alkali may be considered as optimum dose with a pulp yield of 57.1% at a kappa number of 21.8

3.3.3A Effect of wood to liquor ratio:

The effect of wood to liquor ratio has been studied at 18% active alkali charge (as Na_2O) at 170 °C for the soda delignification of poplar deltoides. The results are reported in table 3.6A. In these experiments, the wood to liquor ratio of 1:2.5, 1:3, and 1:3.5 have been studied at different time i.e. 60, 90, 120, 150 minutes. In the case of bath ratio 1:2.5, the screened yield was found to be lower with lesser kappa number compared to the results of the bath ratio 1:3 and 1:3.5. The rejects were found to be higher which may be due to the lesser accessibility of liquor to penetrate the chips.The lower kappa number showed that the higher concentration of alkali has enhanced delignification. In the case of bath ratio 1:3.5, the screened yield has been found to be more with higher kappa number and this is due to decrease in concentration of alkali at higher bath ratio, which reduces the rate of delignification; thus increasing the time at temperature to achieve the target kappa number. The results of the bath ratio of 1:3 shows the lesser reject and better screened yield with moderate kappa number. Thus the bath ratio of 1:3 have been selected for the pulping experiments.

3.3.4A Influence of AQ dose:

As discussed earlier AQ has a pronounced effect on both the pulp yield and the rate of delignification (fig. 3.6A and 3.7A), figure 3.8A shows of effect of AQ on screened yield. The regression co-efficient between total pulp yield, kappa number, screened yield at different active alkali at same time and temperature was around 0.58 - 1, which indicates strong dependence of these parameters of pulping conditions. When AQ is added, the delignification is accelerated and the carbohydrates are protected against peeling by oxidation of the reducing end groups (1). Thus the use of AQ results in markedly higher pulp yield at targeted kappa number. The results of soda-AQ pulping are reported in table- 3.5A. The addition of .05% and 0.1% AQ under constant pulping conditions leads to a significant reduction in kappa number. The addition of 0.2% AQ

showed nearly similar results as that with 0.1% AQ. The soda-AQ process (14% active alkali, 0.1% AQ) and soda process (16% active alkali) has screened yield of 56.7 and 55.1% with a kappa number 24.8 and 14.2 respectively. Soda-AQ process requires less alkali and improves yield and the kappa number was found to be closely similar. Therefore based on experimental data, it can be concluded that the AQ is beneficial in reducing the active alkali charge to the tune of 2% at the targeted pulp yield or kappa number.

3.5A: Spent Liquor Characteristics.

The spent liquor obtained by soda pulping of poplar deltoides was analysed for residual alkali, total solids, organics, inorganics and calorific values, as per TAPPI standard methods (192) and results are reported in table-3.7A.

These results indicate that the addition of anthraquinone (0.1%) during soda pulping has a beneficial influence on chemical consumption and pulp yield at the same kappa number (table-3.5A). The soda-AQ process (16% active alkali 0.1% AQ) requires less alkali (2%) and improves the pulp yield at closely similar kappa number as compared to soda pulping at 18% active alkali. Soda-AQ black liquor has higher calorific value as compared to soda process. 16% soda with 0.1% AQ spent liquor has higher organic content (70.4%) thereby giving a higher calorific value (3647 cal/g) as compared to soda black liquor with 69.2% organics having a calorific value of 3382 cal/gm. The higher organics of the soda-AQ liquor are due to the higher extent of degree of delignification achieved/higher lignin content in spent liquor.

3.6A: Pulp Evaluation:

The unbleached soda pulp prepared at the optimum pulping conditions was beaten in PFI mill at 2000, 3000, 4000 revolutions according to Tappi method 248cm-85. The hand sheets of 60 gsm were made on British sheet forming machine according to Tappi method T-205. These sheets were conditioned at a temperature of 27±1 °C and 65±2% relative humidity and evaluated for various physical strength properties. The results of the pulp evaluation of soda and soda-AQ process are reported in table-3.8A and 3.9A.

3.7A: Results and Discussion:

The results of soda unbleached pulp evaluation are reported in table-3.8A. These results indicated that the initial drainage time was found to be nearly similar to that of eucalyptus which is the most promising raw material for pulp and paper making, but the initial freeness of poplar pulp was found to be slightly higher in terms of CSF. This may be due to the thick cell wall of the fibre. The initial CSF of unbeaten pulp was found to be around 700 CSF. The hand sheets formed from the unbeaten pulp found to be bulky having apparent density around 0.60 g/cm^3.

The plots of pulp freeness versus tear, tensile and burst index at different active alkali (14-20%) of poplar deltoides unbleached pulp has been shown in fig.3.9A, 3.10A and 3.11A. The regression co-efficient between tear, tensile and burst index at different freeness 0.85 -0.99 (not reported in figures), which indicates strong dependence of these parameters. These figures clearly indicate that all the strength properties showed an improving trend upto an alkali dose of 16% at a freeness level of around 300 CSF and beyond that (below 300 CSF) there is no enhancement of strength properties, i.e. tensile slightly improves while the tear and burst suffers. It has been observed that the tear has found to be lower in the cases of the soda pulps as compared to kraft pulps. Lower tear indicates the degradation of cellulosic material during soda pulping, another reason for lower tear may be the lower apparent density (higher bulk) of the

hand sheets. The tear has also found to increase with an increase in degree of delignification. The soda pulping process decreases the fibre strength due to the degradation of carbohydrate chains.

The figures 3.9A, 3.10A and 3.11A clearly indicates that the physical strength properties like burst and tensile are having directly proportional relationship with the freeness, while the tear first increases and then sharply declines.

In the case of the soda-AQ pulp the strength properties was found to be better due to the stabilization of carbohydrate and enhanced delignification. The results of the strength properties of 16% Soda-AQ pulp has been reported in Table-3.9A and figure 3.12A, 3.13A 3.14A. The soda-AQ pulps shows an improvement in tear index values, however the other properties also improves marginally. These figures clearly indicate that the various physical strength properties of soda-AQ pulp improved in comparison to soda pulp.

3.8A: Conclusion:

During the studies of soda and soda-AQ delignification of poplar deltoides, it has been found that poplar chips can be easily pulped with soda process due to its porous structure along with low density. Soda process is a sulfur free process and suited for the higher bulk, opacity and absorbency of the product. The use of 0.1% AQ, enhance delignification and the pulp yield. The strength properties were also found to be improved with the use of AQ.

As far as strength properties are concerned soda pulp have little inferior properties. The tear index was found be lower as compared to the kraft process. The use of AQ with soda process was found to have significant improvement in the tear index along with other strength properties similar to that of conventional kraft. The advantage of soda-AQ process over the conventional kraft pulping is that it produces none of the malodorous sulfur compounds associated with the

kraft process and is therefore, environmentally more acceptable. The absence of sulphide in cooking liquors requires no reducing zone in recovery furnace. However, soda-AQ liquors may be regenerated directly by autocausticizing (27). Based on experimental data, it can be concluded that the overall characteristics of soda-AQ pulps were found to be quite comparable with that of kraft pulps with no maladorous problems.

Table 3.1A: Effect of Time (60 min to 180 min) and temperature (150^0 to 180^0C) at 16%Active alkali (as Na_2O) during Soda delignification of Poplar deltiodes.

Temperature (^{0}C)	Time at Temp. (min.)	Screened pulp yield, (%) (± 0.8)	Screen rejects, (%)	Total pulp yield (%)	Kappa Number	Lignin , (%) (± 0.1)
150	60	-	-	78.2 ± 2.0	81.0 ± 3.8	12.1
	90	-	-	70.0 ± 2.0	65.4 ± 3.0	9.8
	120	43.8	19.3± 2.5	63.1 ± 2.0	54.0 ± 2.0	8.1
	150	48.5	13.3± 2.0	61.8 ± 1.5	47.8 ± 2.0	7.2
	180	50.4	9.4± 1.5	59.8 ± 1.2	44.3 ± 2.0	6.6
160	60	-	-	72.3 ± 2.0	54.6 ± 1.5	8.2
	90	52.9	12.2± 1.2	65.1 ± 1.5	41.8 ± 1.5	6.3
	120	53.7	5.5± 1.0	59.2 ± 1.2	31.2 ± 1.5	4.7
	150	52.7	4.6± 1.0	57.3 ± 1.0	28.3 ± 1.5	4.2
	180	53.1	2.1± 0.5	55.2 ± 1.0	26.9 ± 1.0	4.0
170	60	50.3	12.9± 1.5	63.2 ± 1.5	37.0 ± 1.5	5.5
	90	58.0	4.7± 1.0	62.7 ± 1.5	30.6 ± 1.5	4.6
	120	55.1	2.1± 0.5	57.2 ± 1.0	24.1 ± 1.0	3.6
	150	54.7	1.6± 0.3	56.3 ± 1.0	22.3 ± 1.0	3.3
	180	51.5	1.0± 0.2	52.5 ± 0.8	21.2 ± 0.9	3.2
180	60	54.3	5.0± 1.0	59.3 ± 1.5	32.0 ± 1.5	4.8
	90	55.0	2.4± 0.5	57.0 ± 1.0	26.6 ± 1.2	4.0
	120	52.8	1.7± 0.4	54.5 ± 1.0	22.9 ± 1.0	3.4
	150	51.7	1.0± 0.2	52.7 ± 0.8	20.3 ± 1.0	3.0
	180	46.8	0.9± 0.2	47.7 ± 0.5	19.6 ± 0.7	2.9

**The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions and reported as average mean. They are normally found not to be equidistant from the mean values. The maximum and minimum deviation in terms of actual values are within the range stipulated in the table. The variation in the above response variables were found to be well within allowable experimental error.*

Table 3.2A: Effect of active alkali charge (12 to 20 %, as Na_2O) at 170 ^0C during soda delignification of poplar deltoides.

Active alkali,(%)	Time at temp. (min.)	Screened pulp yield, (%)(±0.8)	Screening rejects, (%)	Total pulp yield (%)	Kappa Number	Lignin , (%) (± 0.1)
12	60	36.1	29.9± 2.5	66.2 ± 1.8	57.3 ± 2.0	8.6
	90	42.3	22.0± 2.5	64.3 ± 1.8	49.4 ± 2.0	7.4
	120	46.1	17.2± 1.6	63.2 ± 1.5	44.7 ± 1.8	6.7
	150	48.2	12.6± 1.5	60.8 ± 1.4	41.2 ± 1.5	6.2
	180	50.2	9.6± 1.2	59.8 ± 1.2	38.4 ± 1.5	5.8
14	60	47.2	14.6± 1.2	61.8 ± 1.5	41.2 ± 1.5	6.2
	90	52.1	8.2± 1.0	60.3 ± 1.5	36.6 ± 1.5	5.5
	120	55.2	3.8± 0.5	59.0 ± 1.2	32.2 ± 1.4	4.9
	150	54.8	3.4± .05	58.2 ± 1.0	31.0 ± 1.2	4.6
	180	53.6	22.6± .05	56.2 ± 1.0	28.1 ± 1.1	4.2
16	60	50.3	12.9± 1.5	63.2 ± 1.5	37.0 ± 1.5	5.6
	90	58.0	4.7± 0.8	62.7 ± 1.5	30.6 ± 1.5	4.6
	120	55.1	2.1± 0.3	57.2 ± 1.0	24.1 ± 1.0	3.6
	150	54.7	1.6± 0.3	56.3 ± 1.0	22.3 ± 1.0	3.3
	180	51.5	1.0± 0.2	52.5 ± 0.8	21.2 ± 0.9	3.2
18	60	50.4	5.4± 1.0	55.8 ± 1.0	32.2 ± 1.2	4.8
	90	52.9	1.3± 0.2	54.2 ± 1.0	25.2 ± 1.0	3.8
	120	51.7	1.1± 0.2	52.8 ± 0.8	18.8 ± 0.8	2.8
	150	50.3	1.1± 0.2	51.4 ± 0.7	17.8 ± 0.7	2.7
	180	48.9	1.0± 0.2	49.9 ± 0.7	16.2 ± 0.7	2.4
20	60	53.1	1.4± 0.2	54.8 ± 1.0	23.2 ± 1.0	3.5
	90	50.7	1.2± 0.2	51.3 ± 0.7	18.0 ± 0.8	2.7
	120	47.4	1.6± 0.2	48.5 ± 0.7	15.1 ± 0.6	2.2
	150	46.0	0.6± 0.2	46.4 ± 0.7	13.5 ± 0.5	2.1
	180	43.8	0.6± 0.2	44.6 ± 0.7	13.0 ± 0.5	2.0

**The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions and reported as average mean. They are normally found not to be equidistant from the mean values. The maximum and minimum deviation in terms of actual values are within the range stipulated in the table. The variation in the above response variables were found to be well within allowable experimental error.*

Table 3.3A: Results of soda pulping of poplar deltoides at a different active alkali (12% to 20% , as Na_2O) , using following conditions .

Maximum Temperature: 170 °C

Time at Maximum Temperature : 120 minutes.

Wood to liquor ratio : 1:3

Particulars \ Active alkali,% as Na_2O	12	14	16	18	20
Screened pulp yield ,% (± 0.8)	46.1	55.2	55.1	51.3	47.4
Rejects ,%	17.2±1.6	3.8±0.5	2.1±0.3	1.1±0.2	0.6±0.2
Total pulp yield,%	62.3 ± 1.5	59.0± 1.2	57.2± 1.0	52.4± 0.8	48.0± 0.7
Kappa Number	44.7 ±1.5	32.2±1.5	24.1±1.0	18.2±0.8	15.1±0.6
Black liquor,pH (± 0.1)	9.8	10.2	10.3	11.0	11.2
Residual Alkali, NaOH, gpl	2.4	6.1	8.7	11.4	13.0
Intrinsic viscosity, cm^3/g (±10)	600	570	530	500	450

Table 3.4A Bulk delignification rate constants at various pulping temperatures (120).

Type of pulping	Temperature,°C	Rate constant,1/min
Soda	160	6.59×10^{-3}
	170	2.0×10^{-2}
	180	6.1×10^{-2}
Kraft	140	5.4×10^{-3}
	150	1.6×10^{-2}
	160	3.4×10^{-2}
	170	1.2×10^{-1}

Table 3.5A: Effect of AQ doses (0.05 to 0.2 %) during soda delignification of Poplar deltoides at different active alkali charge (12 to 20 %, as Na_2O) using following conditions .

Maximum Temperature: 170°C
Time at Maximum Temperature: 120 minutes.
Wood to liquior ratio : 1:3

Active alkali , % (as Na_2O)	AQ doses, %	Screened pulp yield ,% (± 0.7%)	Screening rejects ,%	Total pulp yield, %	Kappa Number	Black liquor, pH (±0.1)	Res alk Na g (±
12	0.0	46.0	16.2± 1.5	61.2± 1.8	44.7± 1.8	9.8	2
	0.05	47.8	15.0± 1.5	62.8± 1.8	38.8± 1.5	9.8	2
	0.1	48.6	15.0± 1.5	63.6± 1.8	35.2± 1.5	9.8	2
	0.2	49.1	14.9± 1.5	64.0± 1.8	33.1± 1.5	9.8	2
14	0.0	55.2	3.8± 0.5	59.0± 1.0	32.2± 1.2	10.2	6
	0.05	55.8	3.3± 0.5	59.1± 1.0	27.6± 1.0	10.2	6
	0.1	56.7	3.2± 0.5	59.9± 1.0	24.8± 1.0	10.3	6
	0.2	56.9	3.2± 0.5	60.1± 1.1	24.6± 1.0	10.3	6
16	0.0	55.1	2.1± 0.4	57.2± 1.0	24.1± 1.0	10.3	8
	0.05	56.2	1.7± 0.4	57.9± 1.0	23.0± 1.0	10.3	8
	0.1	57.1	1.5± 0.3	58.6± 1.0	21.8± 0.8	10.4	8
	0.2	57.3	1.4± 0.3	58.7± 1.0	21.8± 0.8	10.5	9
18	0.0	51.3	1.1± 0.3	52.4± 0.7	18.2± 0.8	11.0	11
	0.05	52.3	1.0± 0.3	53.3± 0.7	17.6± 0.8	11.0	11
	0.1	53.0	0.9± 0.2	53.9± 0.7	17.2± 0.8	11.1	11
	0.2	53.2	0.9± 0.2	54.1± 0.7	17.2± 0.8	11.1	11
20	0.0	47.4	1.0± 0.1	48.6± 0.5	15.1± 0.5	11.2	13
	0.05	47.6	0.9± 0.1	48.5± 0.5	14.7± 0.5	11.2	13
	0.1	48.0	0.8± 0.1	48.8± 0.5	14.5± 0.5	11.3	13
	0.2	48.0	0.8± 0.1	48.8± 0.5	14.5± 0.5	11.3	13

**The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions and reported as average mean. They are normally found not to be equidistant from the mean values. The maximum and minimum deviation in terms of actual values are within the range stipulated in the table. The variation in the above response variables were found to be well within allowable experimental error.*

Table 3.6A: Effect of wood to liquor ratio at 18 % active alkali charge at 170 °C for 120 minutes during soda delignification of Poplar deltoides

Wood to liquor ratio	Time at temp. (minutes)	Screened pulp yield ,% (±0.8)	Screening rejects ,%	Total pulp yield %	Kappa Number	Residual alkali, NaOH, gpl (±0.2)
1:2.5	60	49.2	8.2± 1.5	57.4± 1.8	26.2±1.3	13.4
	90	48.0	7.0± 1.0	55.0± 1.0	22.1±0.8	13.1
	120	46.2	6.5± 1.0	52.7± 1.0	14.7±0.5	12.7
	150	45.1	6.0± 10	51.1± 0.8	13.2±0.5	12.0
1:3.0	60	54.4	1.4± 0.2	55.8± 0.8	29.3±1.2	12.7
	90	52.9	1.3± 0.2	54.2± 0.8	24.2±1.0	12.0
	120	51.3	1.1± 0.2	52.4± 0.5	18.2±0.8	11.2
	150	50.3	1.1± 0.1	51.4± 0.5	16.9±0.7	10.5
1:3.5	60	59.6	6.7± 0.7	64.3± 1.2	34.1±1.5	11.5
	90	57.8	3.8± 0.5	61.6± 1.0	27.4±1.2	10.8
	120	55.1	2.5± 0.3	57.6± 0.8	25.7±1.2	10.1
	150	53.9	1.7± 0.3	55.6.± 0.8	21.1±1.0	9.5

Table 3.7A: Characteristics of soda and soda AQ spent liquor of Poplar deltoides at optimum conditions .

Particulars	Soda(16% Active alkali)	Soda AQ (16% Active alkali, 0.1% AQ)
Black liquor pH (±0.1)	11.0	10.6
Residual alkali, gpl (±0.2)	11.4	8.8
Organics,% (±0.5)	69.2	70.4
Calorific value,cal/gm (±10)	3382	3647
Inorganic ,% (±0.5)	30.8	29.6

Table 3.8A: Pulp evaluation data of unbleached soda pulp of Poplar deltoides at different alkali doses (14 to 20% as Na_2O) using following conditions.

Maximum Temperature: 170^0C

Time at Maximum Temperature : 120 minutes. Wood to liquor ratio : 1:3

Active alkali, % as (Na_2O)	PFI revolutions	Freeness CSF (ml)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.02)	Tensile Index (N.m/g) (±1.2)	Tear Index ($mN.m^2/g$) (±0.3)	Burst Inc (kPa.m2 (±0.2)
14	0	710	4.0	0.59	14.8	1.5	0.5
	2000	560	5.3	0.62	35.2	2.8	2.4
	4000	330	7.2	0.74	55.3	4.7	3.6
	6000	200	13.6	0.78	54.2	3.8	3.3
16	0	700	4.0	0.63	15.4	1.7	0.6
	2000	540	5.3	0.67	38.1	3.4	2.7
	4000	320	7.4	0.79	59.7	5.7	4.0
	6000	190	13.7	0.81	58.2	4.9	3.5
18	0	690	4.2	0.63	15.9	1.7	0.6
	2000	540	5.5	0.69	39.2	3.3	2.4
	4000	310	8.3	0.75	59.7	5.5	3.9
	6000	190	16.4	0.82	58.8	4.3	3.6
20	0	680	4.4	0.65	15.3	1.7	0.7
	2000	520	6.2	0.70	37.2	3.3	2.2
	4000	300	9.0	0.77	56.7	5.1	3.6
	6000	180	16.4	0.84	56.0	4.0	3.4

Table 3.9A: Pulp evaluation data of unbleached soda-AQ pulp of Poplar deltoides at following conditions

Active alkali, % (as Na_2O) : 16 AQ doses ,% : 0.1

Maximum Temperature : 170^0C Time at Max. Temperature: 120 minutes.

Wood to liquor ratio : 1:3

PFI revolutions	Freeness CSF (ml)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.02)	Tensile Index (N.m/g) (±1.2)	Tear Index ($mN.m^2/g$) (±0.3)	Burst Index ($kPa.m^2/g$) (±0.2)
0	690	4.1	0.60	16.0	1.7	0.70
1000	580	4.8	0.62	30.4	3.0	1.9
2000	530	5.3	0.65	41.2	3.6	2.6
3000	410	6.1	0.72	56.3	4.8	3.7
4000	310	7.8	0.74	66.7	6.0	4.2
5000	230	12.1	0.78	70.0	5.8	4.2
6000	180	15.6	0.82	70.5	4.9	4.0

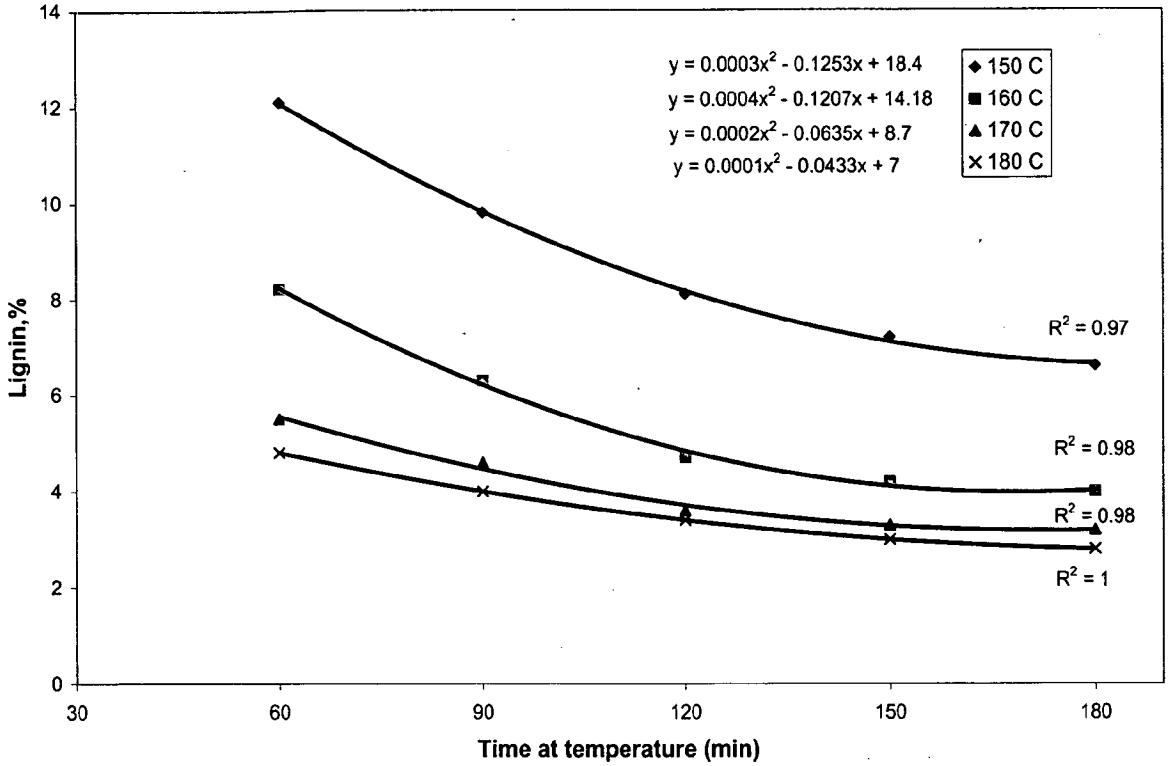


Fig 3.1A: Plots of lignin vs time at different temperature during soda delignification of Poplar deltoides.

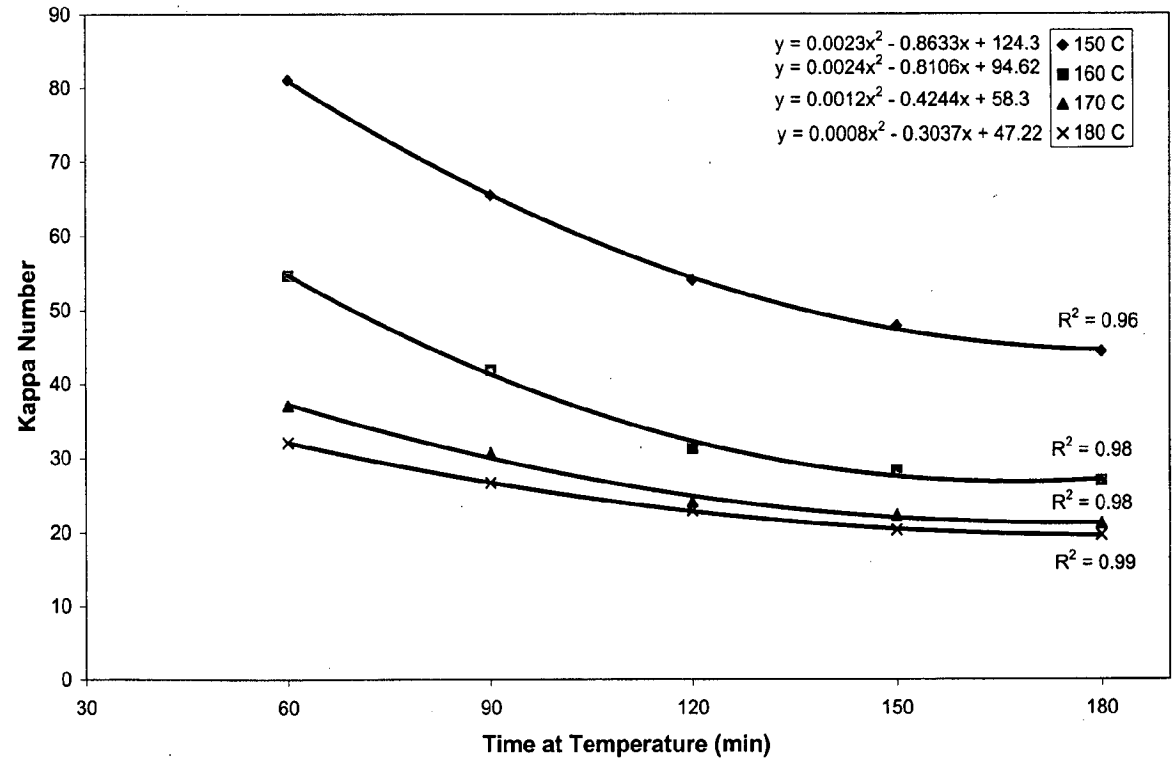


Fig 3.2A: Plots of kappa number vs time at different temperature during soda delignification of Poplar deltoides.

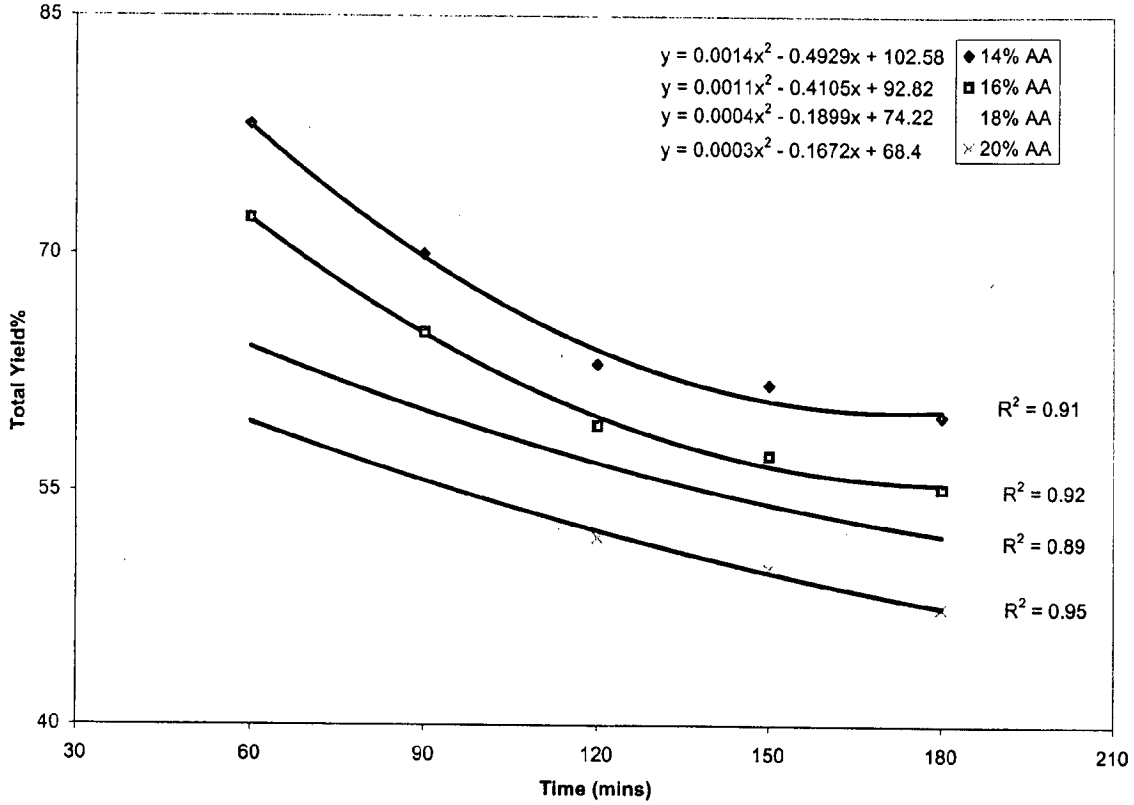


Fig 3.3A Plots of Total yield Vs Time at temperature at different active alkali doses during Soda delignification of Poplar deltiodes

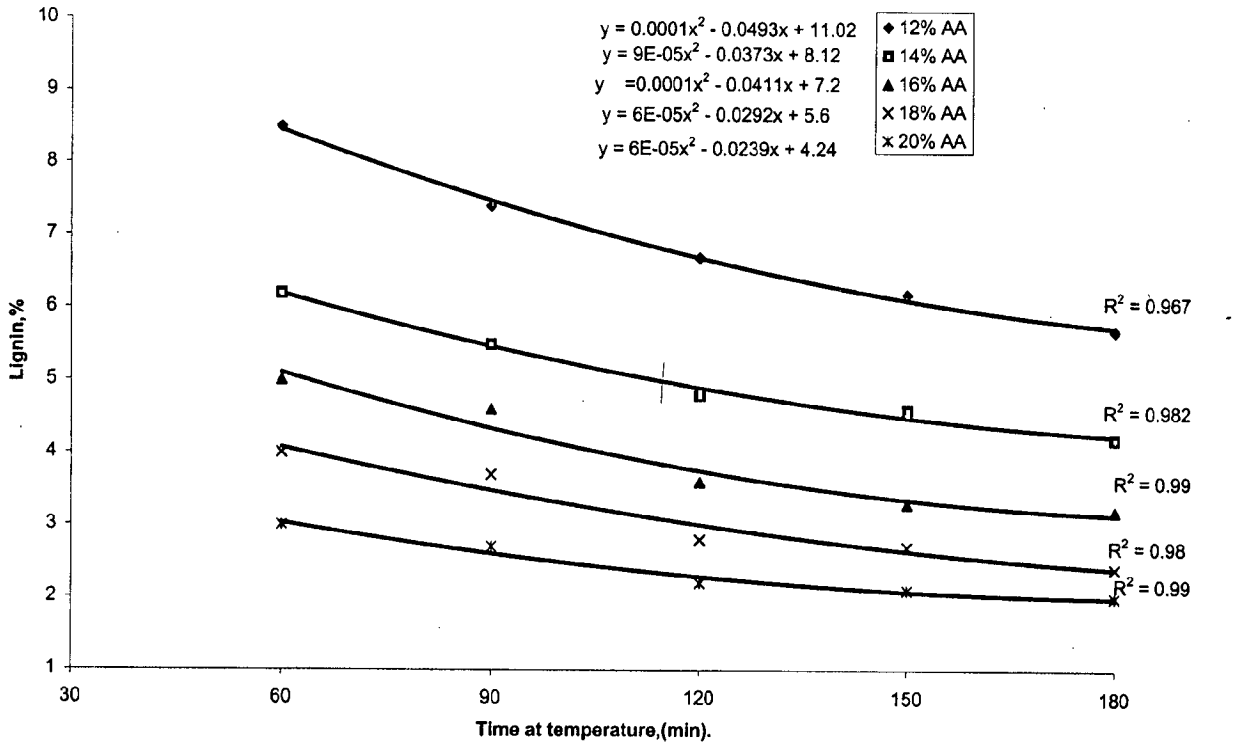


Fig 3.4A Plots of Lignin content Vs Time at temperature at different active alkali doses during Soda delignification of Poplar deltiodes

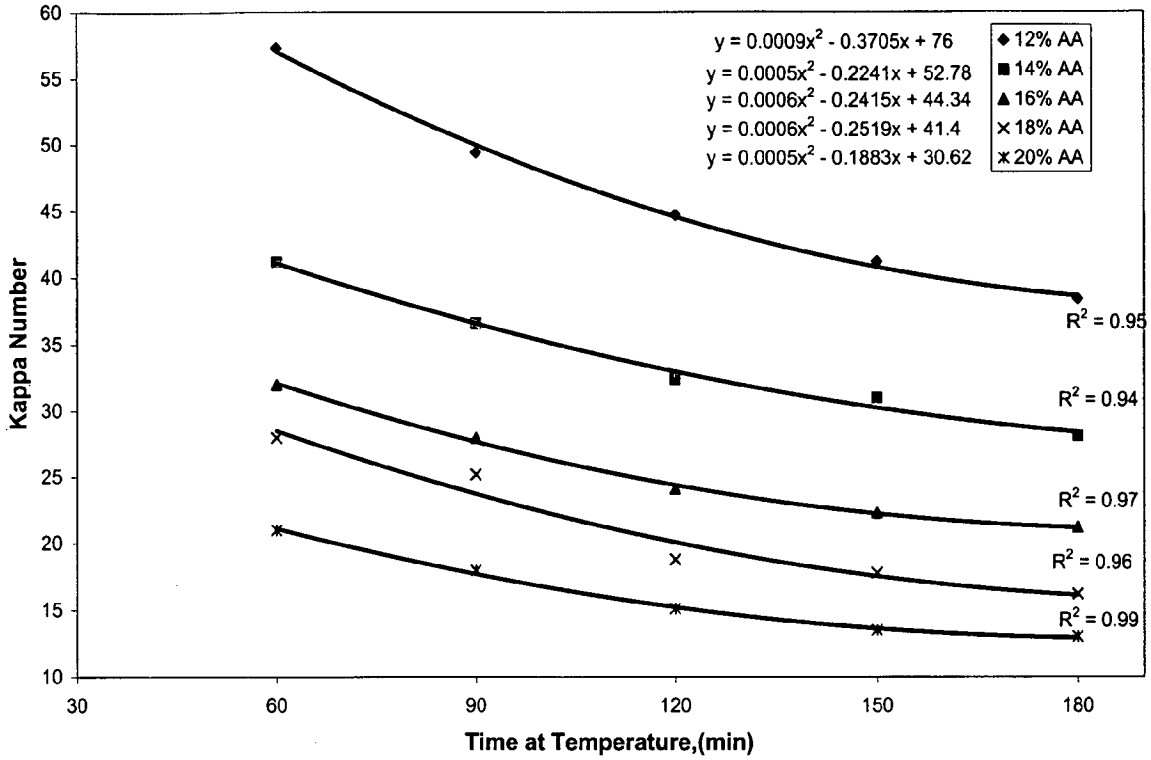


Fig 3.5A Plots of Kappa no. Vs Time at different active alkali during Soda delignification of P. deltiodes

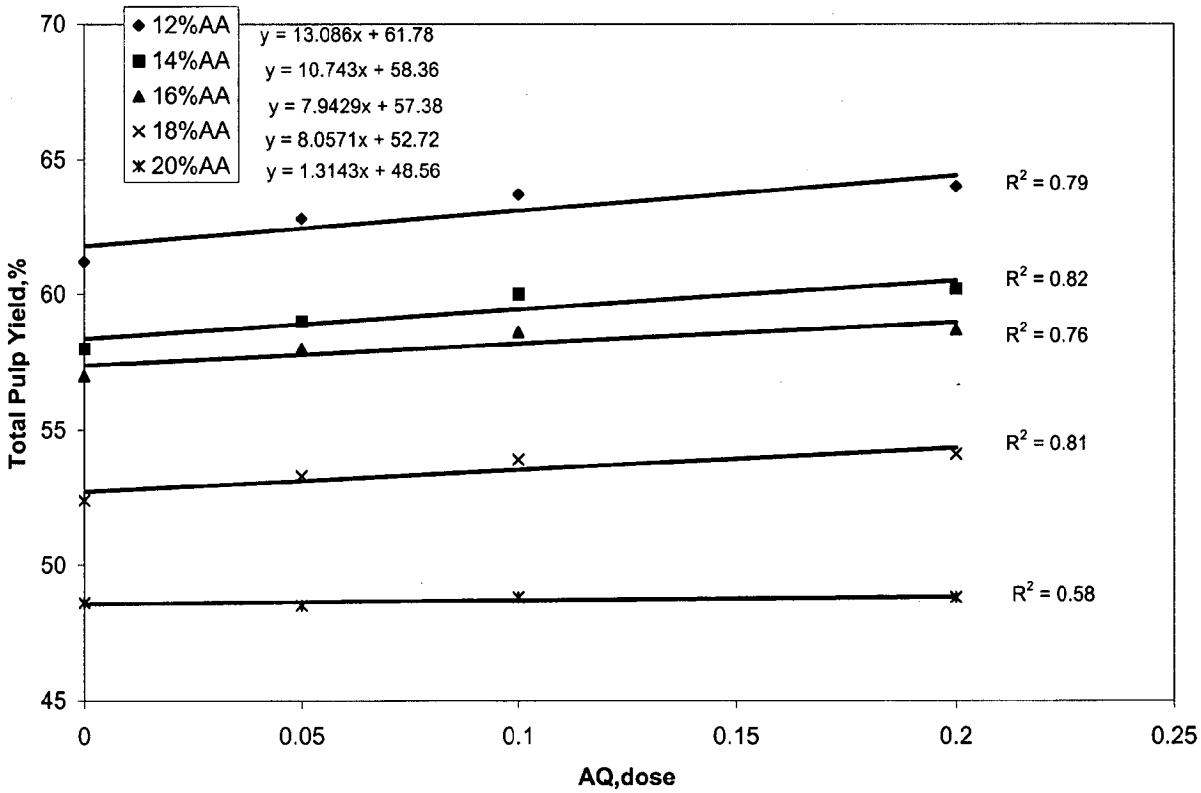


Fig 3.6A: Plots of total pulp yield vs AQ dose at different active alkali during soda pulping of Poplar deltoides.

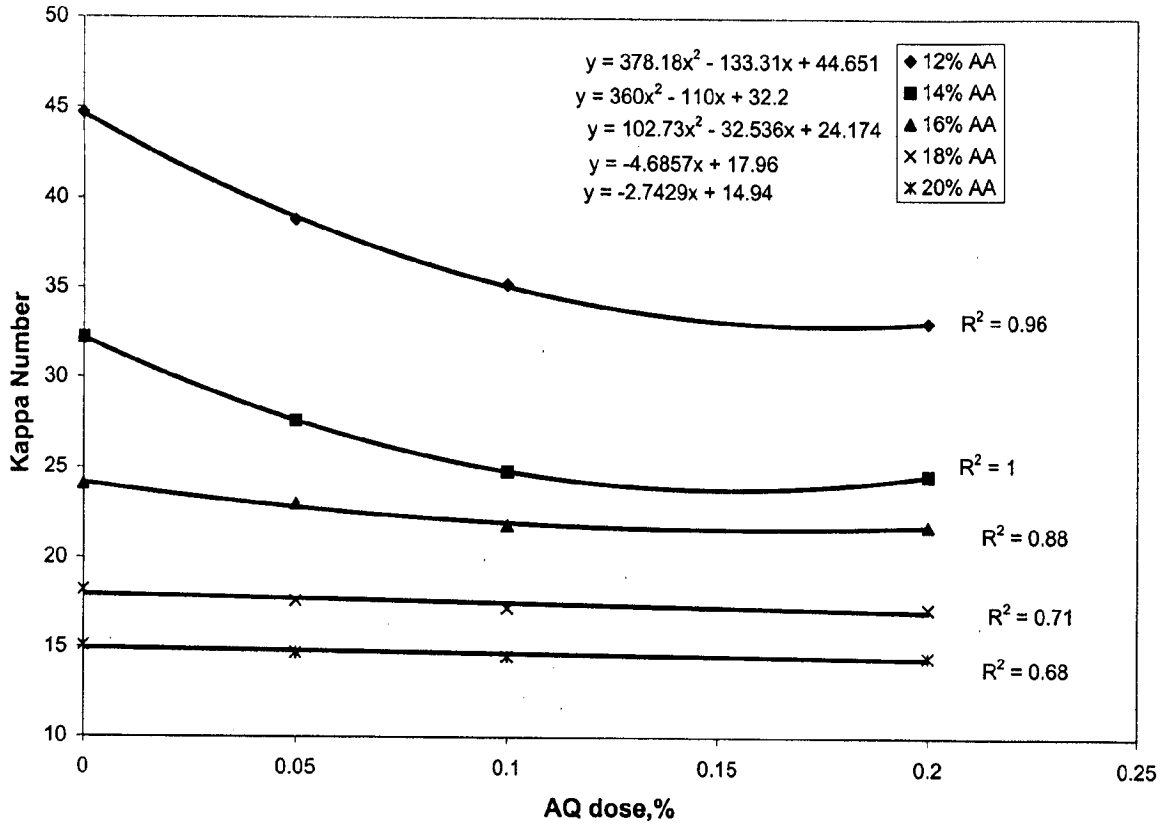


Fig 3.7A Effect of AQ at different active alkali Vs Kappa number on Soda delignification of Poplar deltiodes

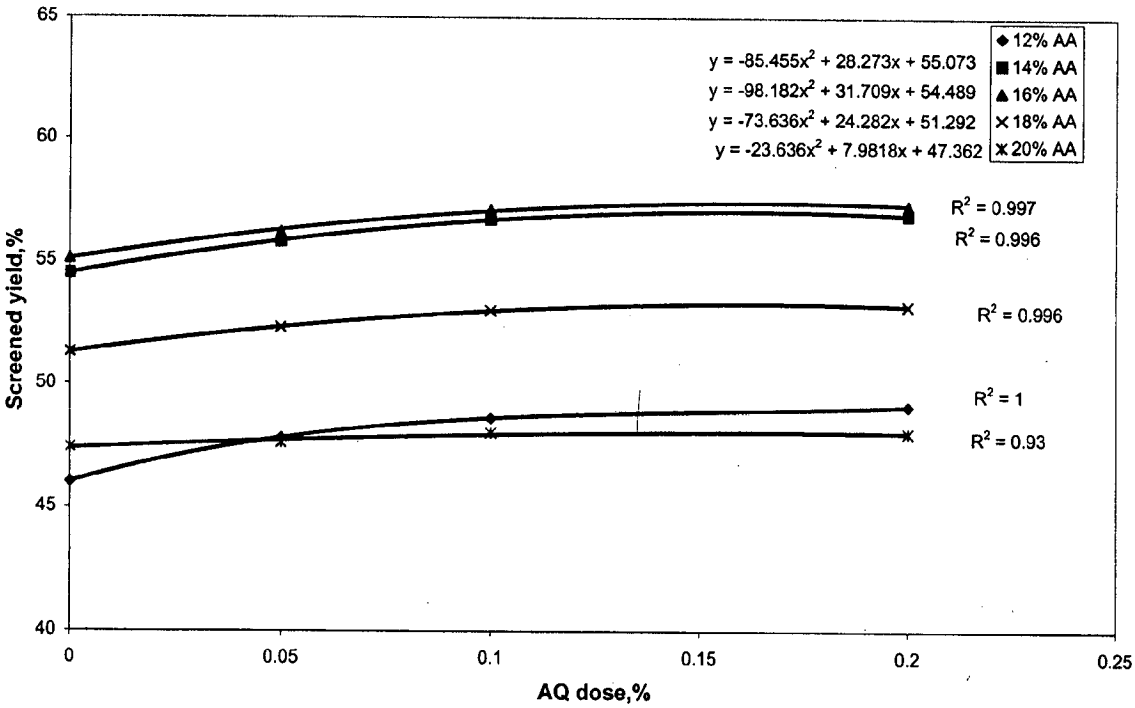


Fig 3.8A Effect of AQ at different active alkali Vs screened yield during Soda delignification of Poplar deltiodes

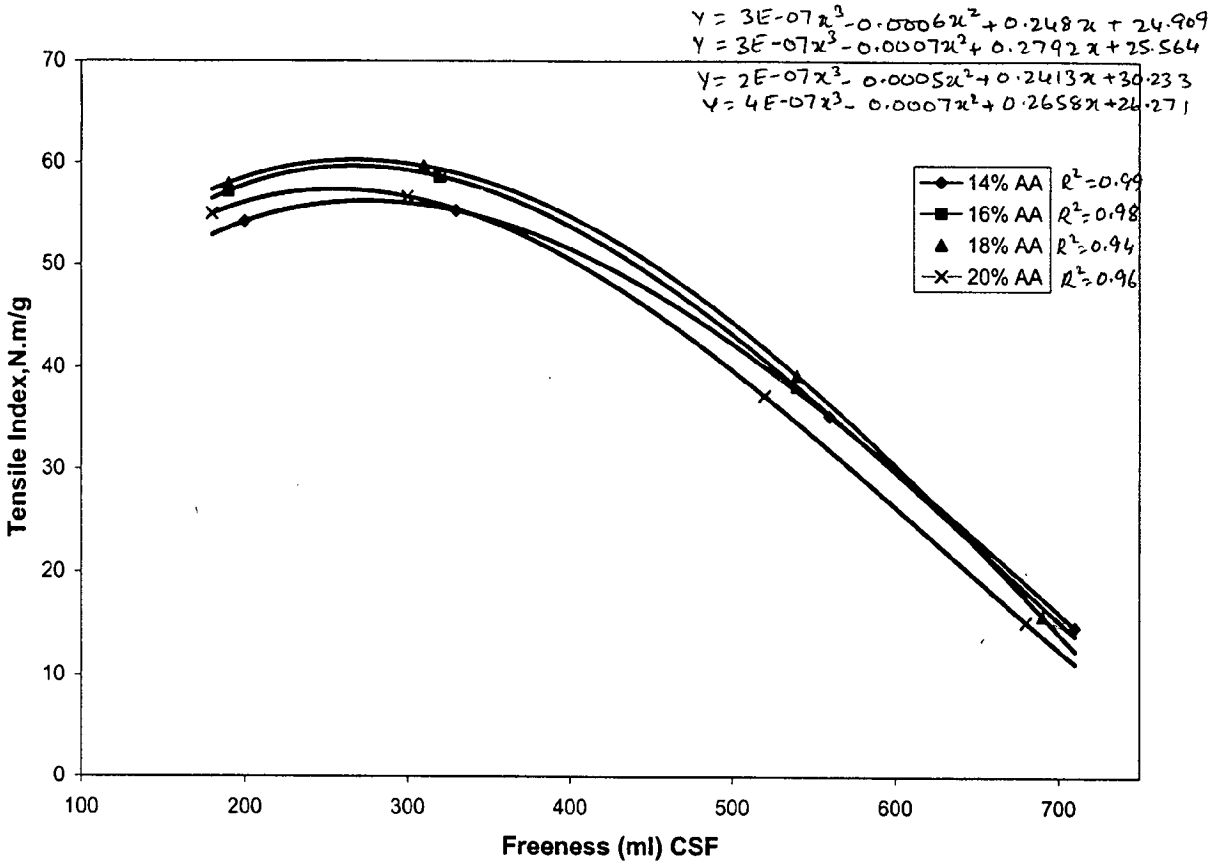


Fig 3.9A: Plots of tensile vs freeness (CSF) at different active alkali during soda pulping of Poplar deltoides.

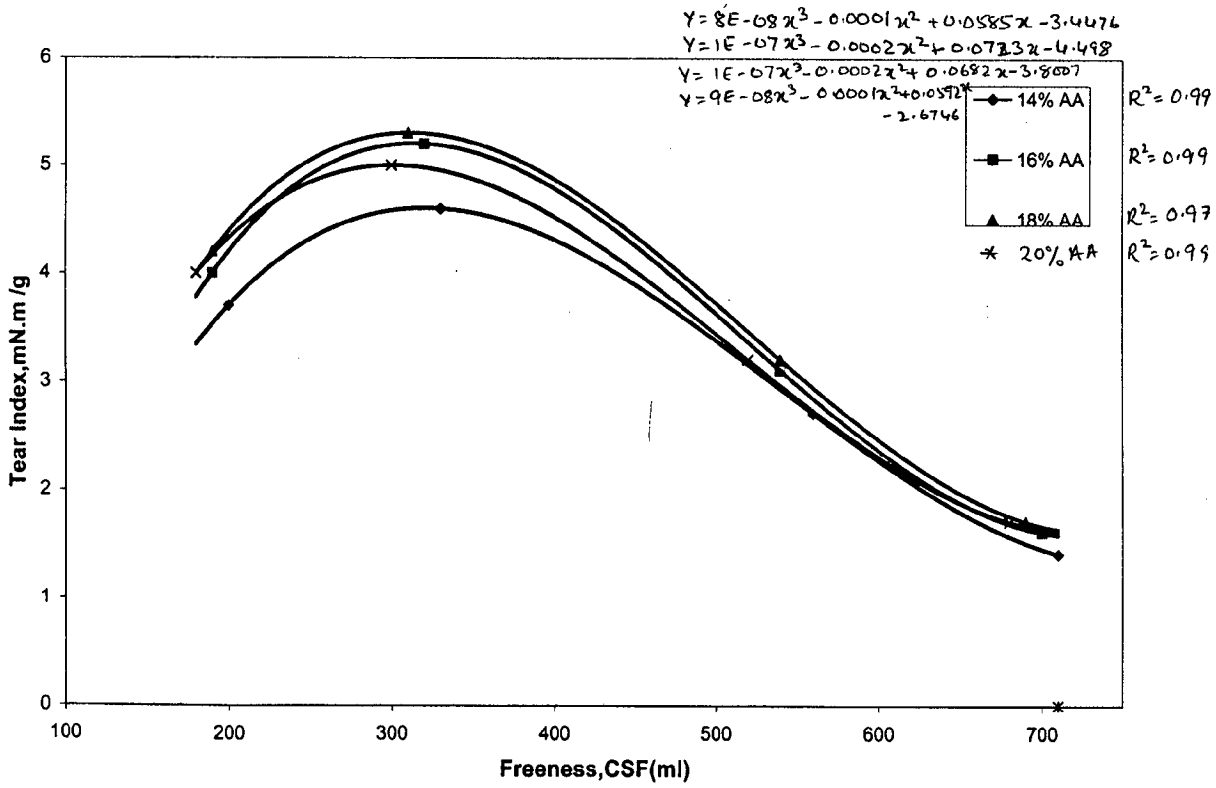


Fig 3.10A: Plots of tear vs freeness at different active alkali during soda pulping of Poplar deltoides.

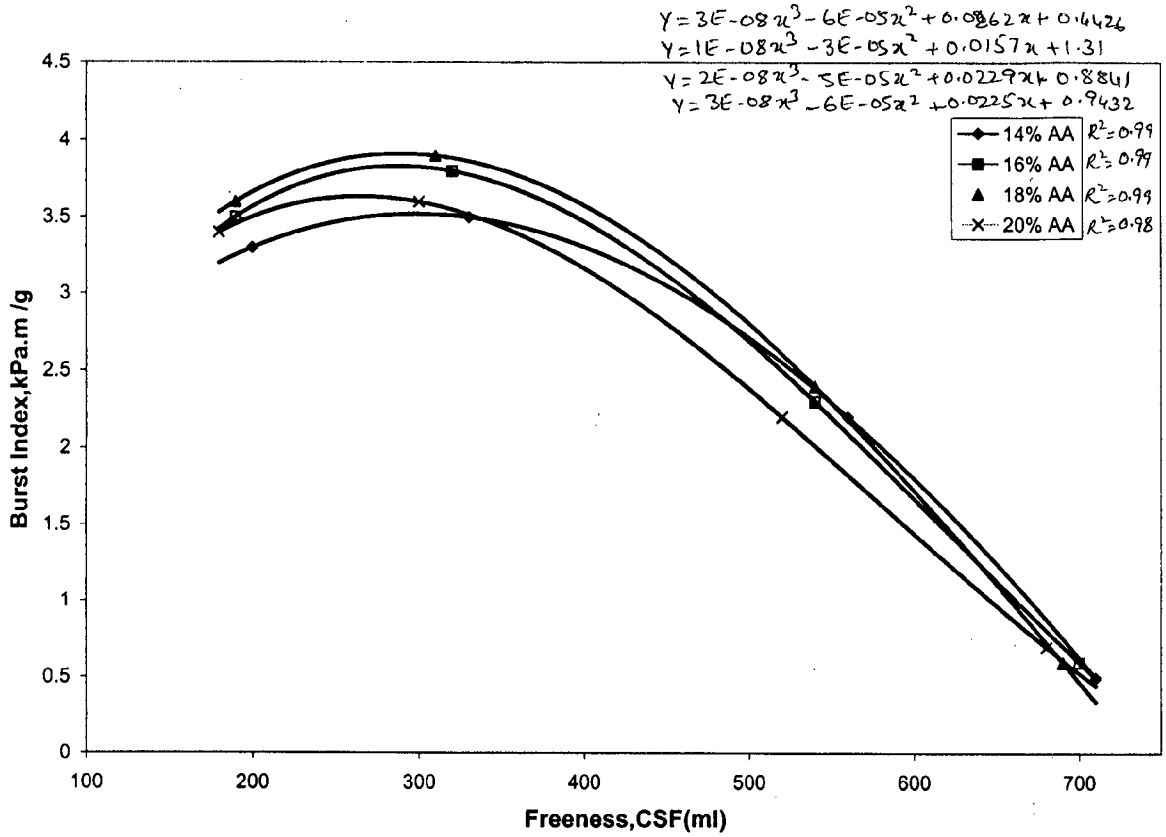


Fig 3.11A: Plots of burst Index vs freeness at different active alkali doses of soda pulping of Poplar deltoides.

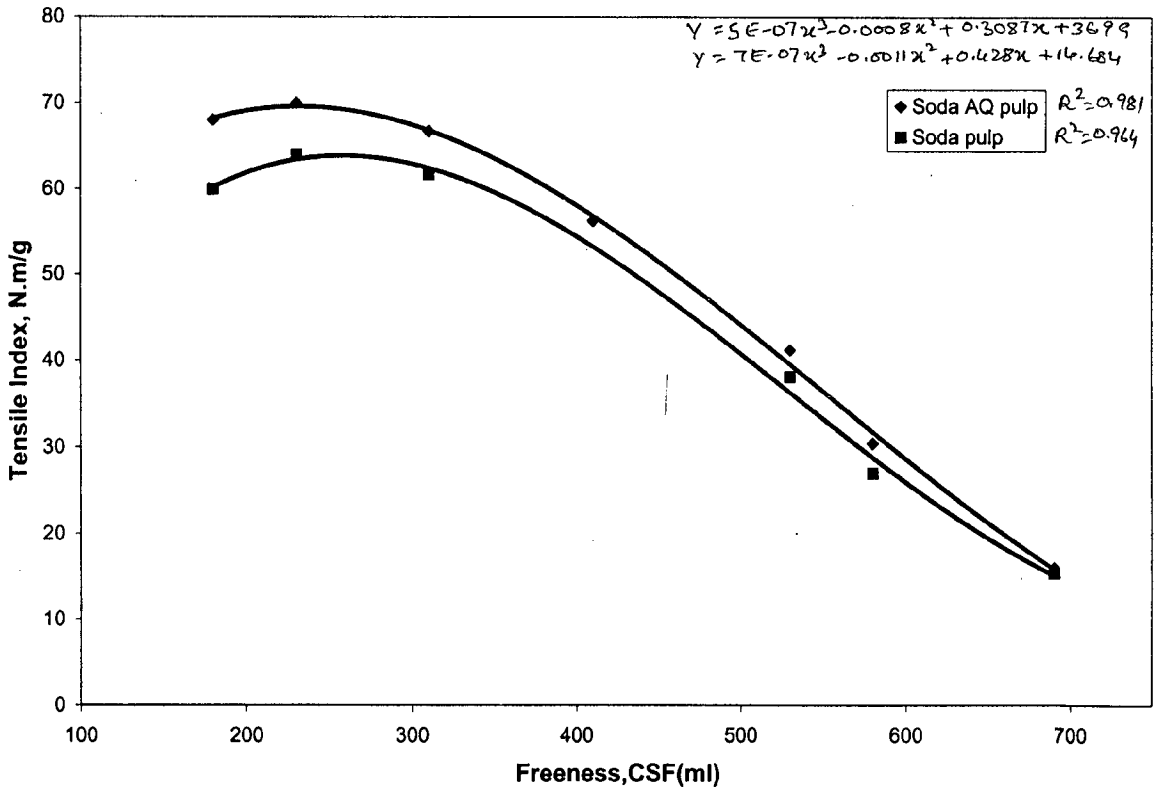


Fig 3.12A: Plots of tensile Index vs freeness of soda and soda-AQ pulps of Poplar at optimum conditions

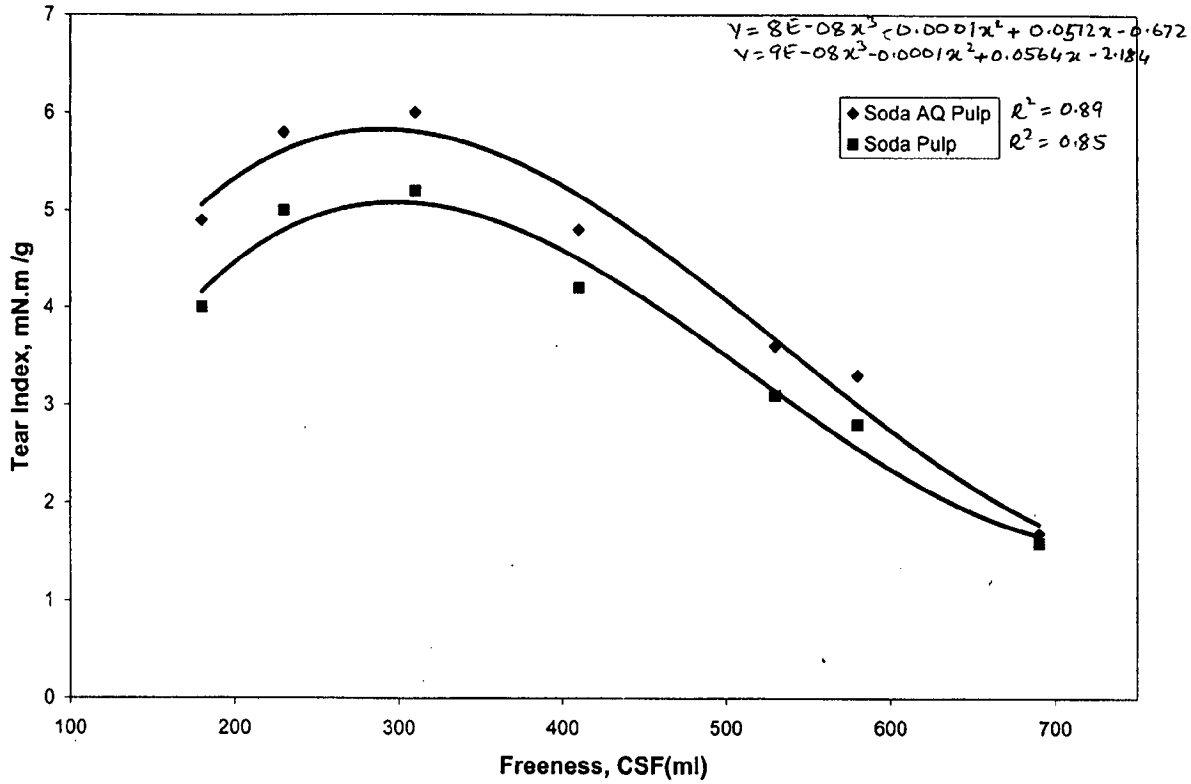


Fig 3.13A Plots of tear Index vs freeness of 16% soda and soda-AQ pulps of Poplar deltoides.

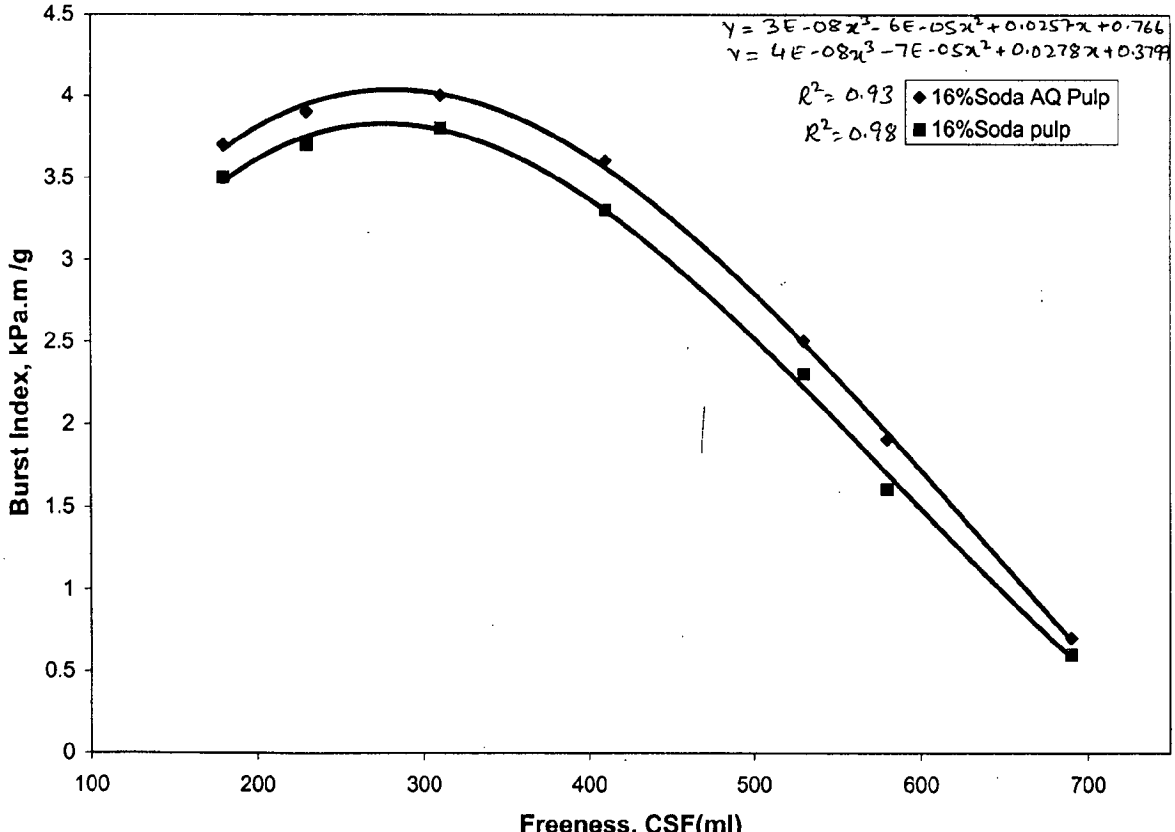


Fig. 3.14A Plots of burst Index vs freeness of 16% soda and sod-AQ pulps of Poplar deltoides.

3.1B: Introduction:

Kraft pulping process is a process for the delignification of wood with a mixture of sodium hydroxide and sodium sulphide. The kraft cooking liquor (white liquor) contains several sodium compounds, of which NaOH and Na_2S are the active ingredients during delignification reactions. The sodium chemicals are expressed in terms of equivalent Na_2O. Na_2SO_4 is found in small amounts due to incomplete reduction in recovery furnace. White liquor reacts with and dissolves much of the lignin in wood during the course of kraft pulping. The reactions are conducted at maximum temperature of 160-175 ^{0}C. The sodium compounds are ionized in aqueous solution. Hydroxide ion (OH^-) reacts with lignin polysaccharides and extractives while hydrosulphide ion (SH^-) participates only in reaction with lignin.

Aqueous NaOH alone (soda process) has certain limitations with regards to the transportation of cooking liquor within the chip mass, based on hardness/density of wood; normally it is not suitable for pulping of hardwoods with higher density. The addition of Na_2S results in faster pulping and better selectivity for delignification over polysaccharide degradation (154,173). The anions (OH^- and SH^-) suffer different fates, from the start, hydroxide ion is consumed rapidly in degradation reactions with readily soluble hemicellulose and their substituents. Only when the temperature reaches around 140^{0}C, OH^- becomes an important participant in reactions with lignin. The OH^- and SH^- ions are the key species in bulk delignification phase. Hydroxide ion continues to react with lignin in the residual phase, but SH^- does not.

Hydroxide ions reacts with polysaccharides in a variety of ways from the start to the finish of kraft pulping. Once the maximum pulping temperature is reached, the bulk phase proceeds at a constant rate and can continue until about 90% of the lignin is dissolved from the wood (154,173).In conventional kraft pulping the activation energy (bulk phase) is about 134 KJ/mole. The pulping process takes place in three-phase system.

(i) The solid phase, consisting of the wood chips.

(ii) The liquid phase, where moisture is inside and the cooking liquor is outside the chips, actually these are two separate liquid phases.

(iii) The gas phase which is made up of gases located in the lumens of fibers, such a system includes not only actual chemical reactions, but also several physical phenomena such as sub-division of the solid phase, flow of fluids, diffusion processes, and flow of heat etc.

The addition of sulphide ion accelerates the rate of delignification, with less damage to the cellulose and hemicellulose. The generally accepted theory postulates that the sulphide brings about an episulphide in the propane chains connecting the phenolic groups in lignin molecule. Further reaction brings about a breaking of the lignins molecule in smaller segments, whose sodium salts are soluble in the cooking liquor. The Na_2S has a further advantage in that it hydrolyses to NaSH and NaOH. As NaOH is consumed in the reaction, more NaOH is available by this hydrolysis thus avoiding excessively high concentrations of NaOH in the liquor supplied to cook. During kraft process many types of hardwood can be delignified more extensively then softwoods without serious losses of carbohydrates; that can be explained by the fact that 4-O-methyl glucuronoxylan, is the preponderant type of hemicellulose present in the hardwoods which is comparatively more resistant to alkaline peeling reactions during kraft pulping (154).

In 1977, Holton first reported that anthraquinone (AQ) reduces the kappa number obtained under identical pulping conditions in both kraft and soda pulping (68,69). At that time,

there was very little interest in low kappa pulping; therefore this reduction in kappa was utilized to achieve other objective such as reducing sulfur emission (14,15,16). Later on growing concern over the use of chlorine for pulp bleaching and production of organochlorine compounds in bleach plant effluents has prompted the pulp and paper industry to investigate ways of reducing the use of chlorinated bleaching chemicals. One approach is to extend delignification during pulping with extended delignification processes such as modified continuous cooking, EMCC, RDH and super batch (146) or with post pulping extended delignification processes such as oxygen delignification (21,22). Anthraquinone (AQ) is one of the important non-capital methods available to lower the brown stock kappa number of the pulp.

The use of pulping additive such as AQ results in lower kappa number without loss in yield or increase in yield at the same kappa number (69,158) AQ in alkaline pulping enhances both delignification and carbohydrate stabilization (51). Addition of a small amount of AQ (0.05 - 0.1%) to cooking liquor accelerates the fragmentation of lignin via cleavage of phenolic β-aryl ether bonds of lignin and reduces the carbohydrate degradation through stabilization of reducing end groups to corresponding aldonic acids (80). AQ-induced oxidation of the lignin structure may also occur and contribute to its breakdown. Evidenced for AQ oxidation of lignin α – hydroxyls to carbonyls in non-phenolic phenyl propane lignin was published in 1995 (112). Data presented in this paper suggested that α –carbonyl structures appears to form very rapid in both soda-AQ and kraft-AQ cooks, but they are produced to only a minor degree in soda and kraft processes. The author suggested that AHQ added to the α –carbon and assisted in the splitting of the β -ether bond by the formation of the oxirane functional group. This is contrary to the most held theory that AHQ is only effective with α–phenolic β–aryl ether structures through intermediate quinomethide structure. AQ added to the pulping liquor oxidizes the reducing end group of the polysaccharide chains and get itself reduced to AHQ. The AHQ thus formed attacks

the phenolic β-aryl ether structures in lignin resulting in their splitting with regeneration of AQ (109). AQ accelerates the delignification (reduces cooking time/H-factor) as well as reduces carbohydrate degradation via the AQ-AHQ redox cycle. AQ has been used as an additive to lower the sulfidity and/or active alkali in kraft pulping (16,69,133,194). Stabilization of carbohydrate results in higher pulp yield and lower black liquor solids.

The use of anthraquinone as an additive for kraft pulping to increase pulping efficiency and pulp yield is now very well documented (68,118). Its effectiveness however, considerably depends upon the species of the wood used (194). There have been several recent reports in the literature on the use of AQ to extend cooking, both in laboratory and in mill trials (52,124,157,212). As suggested by earlier worker(14,15,16), it is believed that no yield penalty was incurred in the production of low kappa pulps. Earlier works has shown that the low kappa AQ pulps are obtained with no yield penalty (178), in some cases low kappa AQ pulps can be obtained at a slightly higher yield than conventional kraft pulps. Consequently, there is no additional load on the recovery system when low kappa pulps are produced with AQ (22,178).

3.2B: Experimental Methodology:

The screened chips of Poplar deltoides were prepared, as mentioned on page 37.

3.3B:Optimum Conditions of Pulping:

All the cooks were made in laboratory CCL digester having six stainless steel bombs of about 2.5 liters capacity, containing 300 gms o.d. chips of poplar deltoides at wood to liquor ratio of 1:3. The following time schedule for heating was maintained.

Time from room temperature to 105 ^{0}C : 45 minutes.

Time from 105 ^{0}C to maximum temperature of cooking : 45 minutes.

The kraft and kraft-AQ delignification process has been studied at various process parameters viz., time, temperature, alkali doses and different AQ doses. At the end of the cook, the pulp was washed thoroughly and screened in laboratory Weverk screen. The screened pulp yield, screening rejects, total pulp yield and kappa number were calculated. The residual alkali and black liquor pH were also determined as per TAPPI standard methods (192).

3.4B: Results and Discussion:

The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions of temperature, pressure, time at temperature with constant active alkali charge. As the pulping experiments are extremum type, no two sets can be identical therefore average of the four / five set of data are shown only. The maximum and minimum deviation of statistically mean value is not shown or the all four sets of data are not shown, merely to reduce the large volume of data.

In the present investigation, data found from the laboratory experiments for a specific set of input parameters such as time, temperature, alkali dose etc. all the data are not reproduce the brevity of rather average data of the set is depicted in tables. However it is observed that there is marginal difference in the set of data which is permitted in this type of experiments. The variation in the responding variables were found to be well within the experimental error.

For the statistic modelling the responding parameters during pulping namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content of the pulp at different active alkali were regressed with the time at temperature as independent variables. The responding variables of pulp evaluation such as tear index, tensile index and burst index were regressed with different freeness as independent variable. In most of the cases the quadratic model ($y = ax^2 + bx + c$, where a, b and c are parameters to be estimated) were obtained. Where

y is the responding variable and x is the time at temperature, which is found to fit well to the data. The quadratic model reflects the behavoir of various pulping conditions and pulp evalution.

3.4.1B: Effect of Time and Temperature:

To study the effect of time and temperature, kraft pulping of poplar deltoides was conducted at 20% sulphidity and 16% active alkali as Na_2O and at different time (60 to 150 minutes) and temperatures ranging from 145 to 175 ^{0}C was studied. The results of these experiments have been reported in table 3.1B. The kappa numbers and residual lignin contents associated with the pulp were determined. These were plotted against the cooking time of reaction as shown fig. 3.1B. The data fitted statistically smooth curves having cocavity upward with R square values ranging from 0.93 to 0.96 for all the four curves at 150-180^{0}C respectively. The R square values indicate the closeness of the fit of the data. The curves with steeper slope correspond to bulk delignification while the curves with gentle slopes correspond to low solubilization of the residual lignin (residual delignification). These plots also clearly indicated that as the temperatures were increased from 145 to 175 ^{0}C, the cooking time to reach transition from bulk to residual delignification,and the lignin content of the pulp corresponding to transition, both decreases, time and temperature are inter dependent variable, increase in the pulping temperature reduces the digestion time and an increase in digestion time allowed a corresponding decrease in temperature. Bulk delignification is generally associated with alkali catalyzed cleavage of β-aryl ether bonds in non-phenolic units and cleavage of aryl alkyl ether bonds. These reactions have first order kinetics with respect to alkali concentration (169). Mortha studied the alkaline pulping kinetics of hybrid poplar and calculated the values of the rate constant K for different pulping temperatures for both soda and kraft pulping, the results obtained by Mortha are shows on page 49 in table-3.4A (120).

The effect of time on kappa number and pulp yield at different temperature have been studied at 16% active alkaline concentration and 20% sulphidity is shown in figure 3.2B and 3.3B. Figure 3.2B indicate that kappa number decreases with time. The regression co-efficient between kappa number, total pulp yield at 16% active alkali at different temperature was around 0.87-0.99, which indicates strong dependence of these parameters of pulping conditions.

Although the delignification rate is higher at the initial stages of the cook and the rate decreases with the progress of the cooking reaction. In kraft pulping at 165 ^{0}C nearly 75% of delignification occurs during first 60 minutes of the cook, whereas further 30 minutes of pulping reaction results in about 10-15% increase in delignification. Over a given period, kappa number decreases as temperature increases. The pulp yield decreases with an increase in temperature, because the velocity constant increases the delignification and the cellulose degradation. In the case of kraft-AQ pulping, the effect of time and temperature on kappa number and pulp yield have been studied at 16% active alkali, 20% sulphidity using 0.1% AQ. The results have been reported in table 3.2B. These results clearly indicate that the addition of AQ accelerate the delignification and protects the carbohydrate degradation, thus decreases the kappa number at a given yield and/or increases pulp yield at a given kappa number. This indicates that the use of 0.1% AQ reduces the cooking time and/or temperature at a given kappa number.

3.4.2B: Effect of Active Alkali Charge:

Active alkali is the most important variable affecting the pulp yield and the degree of delignification. To study the effect of active alkali charge, the experiments were carried out at a temperature of a 165 ^{0}C under the constant reaction time (at temperature) of 1.5 hrs. and at different alkali concentrations (12, 14, 16, 18,20% active alkali, as Na_2O) at a constant sulfidity level of 20%. The results of the effect of active alkali charge on pulp yield and kappa number are reported in table 3.3B. At 12% AA, the screened pulp yield was found to be 45.0%, which

increased to 55.8% at 14% active alkali and decreased to 53.6%, 47.2%, 41.1% at 16%, 18%, 20% active alkali (as Na_2O) respectively, while the kappa number dropped from 39.4 to 13.0. These results indicate that at higher alkali concentration, the degradation of the carbohydrate material increased which results in the lower pulp yield alongwith poor viscosity of the pulps. At higher active alkali, the selectivity of lignin dissolution decreases and cellulose degradation increases, therefore, higher active alkali doses, should be avoided, in order to check the carbohydrate degradation. Based on experimental results it can be concluded that a 16% active alkali dose along with 20% sulphidity may be considered as optimum dose of alkali for kraft delignification of poplar deltoides. The higher rate of delignification for hybrid poplar have been studied by Mortha (120). The fact was explained by the lower specific gravity minimizes the diffusion limitations of lignin out of the wood chips which increases the rate of delignifications. Moreover the higher rate of delignification also depends on the nature and structure of lignin. Nimz (134) reported that β-O-4 linkages in guaiacyl units are hydrolyzed at a slower rate than syringyl units. Chang and Sarkanen (27) have reported a straight line correlation between delignification rate and the ratio of syringyl to guaiacyl propane units. Since the syringyl content of typical hardwood vary from 20-60% (46), therefore the higher rate of delignification is most likely due to higher syringyl contents in the lignin of poplar.

To know the effect of AQ, the delignification studies have been conducted at a constant temperature of 165 ^{0}C, 20% sulphidity under constant reaction time of 1.5 hour, using a bath ratio of 1:3 at five different active alkali doses of 12, 14, 16, 18, 20% (as Na_2O) with four different AQ doses (0,0.05, 0.1, 0.2%). The results of these experiments are reported in table – 3.4B. These results indicate that the addition of 0.05% and 0.1% AQ under constant pulping conditions lead to a significant reduction in kappa number along with a slight increase in pulp yield. Addition of 0.2% AQ showed nearly similar results as with 0.1AQ. Thus 0.1% AQ may be

considered as an optimum dose. It is also clear from these results that the effect of AQ is more pronounced at lower alkali doses.

The pulp viscosity and kappa number relationship is shown in figure 3.8B. The addition of 0.05% and 1% AQ results in higher viscosity as compared to conventional kraft pulp. The increase in viscosity of kraft and kraft-AQ pulps is due to the stabilization of reducing end groups in polysaccharides (68,69). For a given kappa no. the kraft and kraft-AQ pulps obtained from 16% active alkali charge, the kraft pulp shows slightly lower viscosity than kraft AQ pulp, due to higher degradation of carbohydrate materials.

3.4.3B: Influence of Sulphidity:

To study the effect of sulphidity during kraft pulping of poplar deltoides, the cooking were done at 165 ^{0}C, 16% active alkali charge, bath ratio 1:3, for different time (ranging from 30 minutes to 150 minutes) with varying levels of sulphidity viz., 10, 15, 20, and 25%. . The results of these experiments are reported in table 3.5B and plotted in figure 3.4B to 3.5B. The R square values ranges from 0.95-0.99, which indicate the closeness of the fit of the data. These curves follow the same pattern as in the case of influence of time and temperature. The steeper slope of the curves represents the rapid solubilisation of bulk of the lignin and the other part of the curve represent slower delignification. These curves also indicate that the lignin content is having a indirectly proportional relationship with sulphidity. Practically, there is no variation in the amount of lignin content beyond 20% sulphidity level, therefore, a sulphidity level of 20% may be considered as optimum level of sulfidity during kraft pulping.

In the case of kraft-AQ pulping, the effect of sulphidity was studied at two levels of sulphidity viz. 15% and 20% at different active alkali doses viz., 12, 14, 16, 18, 20% at 165 ^{0}C and at different AQ doses and the results of these experiments are reported in table 3.4B. The

effect of AQ on kappa number and pulp yield at different active alkali doses is shown in figure 3.6B and 3.7B. From these results it could be seen that the AQ have significant effect in reducing the kappa number and increasing the pulp yield. At lower sulfidity level, the AQ has more pronounced effect as compared to high sulfidity levels. No additional significant reduction in kappa number was observed at higher sulfidity. One of the possible reasons of this phenomenon may be that at high sulphdity level, the wood was so nicely delignified that no further additional decrease in kappa number with addition of AQ was observed. Thus at higher sulfidity, the effectiveness of AQ diminishes in reducing kappa no.

One of the potential benefits of AQ during kraft pulping conducted at low sulphidity level seems to be the extended delignification with reduction in environmental pollution load.

3.4.4B: Effect of Anthraquinone:

Anthraquinone (AQ) has a pronounced effect on both the pulp yield and the rate of delignifications which have been shown in Fig.3.6B and 3.7B . The R square values ranges from 0.68-0.99, which indicate the closeness of the fit of the data. The regression co-efficient between total pulp yield, kappa number, screened yield at different active alkali at same time and temperature indicates strong dependence of these parameters of pulping conditions. When AQ is added, delignification is accelerated and the carbohydrates are protected against peeling by oxidation of the reducing end group (68,69). Although, the reduction in kappa number and increase in pulp yield is in directly proportion with the addition of AQ, but the magnitude of decrease in kappa number and increase in pulp yield was found to be significant up to AQ dose of 0.1%,and beyond this level the effect was insignificant in both the cases .Thus an AQ dose of 0.1% may be considered as an optimum dose of AQ during kraft pulping.

A major factor in determining the profitability of kraft-AQ pulping is the magnitude of increase in pulp yield, as the pulp yield increase at a given kappa number. As this extra pulp is

obtained at no extra cost apart from the cost of AQ. The yield gained was found to increase around 1.5 to 2.5% using 0.1% AQ at different active alkali concentration (fig.3.7B).

The additional delignification in the presence of AQ appears to be dependent of residual lignin content rather than on any particular cooking variables. Addition of 0.05 and 0.1% AQ under constant pulping conditions lead to a significant reduction in kappa number (Fig.3.6B). At lower alkali concentration, the effect of AQ on kappa no. is more pronounced (Fig.3.6B and 3.7B). Addition of AQ beyond 0.1% results almost no gain in reducing the kappa number as well as in increasing the pulp yield but produces more toxic effluent.

3.5B: Spent Liquor Characteristics:

The spent liquor obtained at the optimum conditions of kraft and kraft-AQ pulping was analysed for residual alkali, total solids, organics, inorganics and calorific values, as per Tappi standard methods. The results are reported in table 3.6B. These results indicate that the addition of AQ (0.1%) during kraft pulping has a beneficial influence on reducing the chemical consumption and corresponding increase in pulp yield at the same kappa no. (table-3.3B and 3.4B). The kraft-AQ process (16% active alkali and with 0.1% AQ) requires almost 2% less active alkali improve pulp yield at closely similar kappa number as compared to kraft pulping conducted at 16% active alkali. Kraft-AQ black liquor has higher calorific value as compared to kraft liquor. The organic content of kraft-AQ was found to be slightly higher than kraft liquor, thereby giving a corresponding higher calorific value of 3990 cal/g as compared to 3760 cal/g for kraft liquor.

3.6B: Pulp Evaluation:

Beating of the pulp to different freeness levels was carried out in PFI mill according to Tappi method 248cm-85 and hand sheets of 60 gsm were prepared according to Tappi method T-205. The hand sheets were evaluated for strength characteristics according to Tappi 220 on-88 method after condioning at 27± 1°C and relative humidity 65±2%.

The strength properties of kraft-AQ was found to be marginally better than conventional kraft pulps. The use of AQ in kraft does not have a much significant effect on strength properties. However, because of the increase in hemicellulose contents, care must be taken to ensure that tear strength does not suffer.

The results of the unbleached kraft pulp evaluation are reported in table 3.7B. The pulp of poplar deltoides could be easily beaten. The handsheets formed have the apparent density of around 0.60 to 0.83 gm/cm^3. Apparent density is a measure of fiber arrangement and packing density and arrangements in the sheet of paper, which in turn determines the physical and strength properties of paper. Apparent density is also related to the morphological configuration of collapse and straightness. In the selection of fiber types for different paper and pulp grades, the apparent density is used as the base against which, other hand sheet properties are compared. Apparent density is best predicted by the width/thickness ratio and length of fiber. Apparent density is a valuable indicator of fiber potential in interfiber bonding. The result of pulp evaluation shows that tensile index increases as the apparent density of the sheet increases. The tensile index values are of limited meaning unless compared to other properties, inparticular to fiber packing density (101). The tensile index increases with increasing apparent density and also be indirectly influenced by fiber properties, other than width/thickness which determines the sheet structural organization. Tensile index depends upon the extent of the fiber to fiber bonding in the sheet matrix, which depends upon the degree of fribillation during beating processes.

Bulky sheets with low density would yield low fiber bonding capacity resulting in decreased tensile strength. The sheets with low density shows inferior strength properties.

In the case of tear index, tear index increases with refining of the pulp and decreases at prolonged refining of the pulp. Tear index is mainly influenced by the fiber length in combination with the width/thickness ratio and fiber to fiber bonding.

Refining the pulp increases the density of the sheets, which helps to obtain the handsheets with good strength properties comparable to other hard wood pulps. Figures 3.9B, 3.10B, 3.11B shows the plots of pulp freeness versus tear, tensile and burst index values of poplar deltoides kraft unbleached pulps. The regression co-efficient between tear, tensile and burst index at different freeness 0.82 -0.99 (not reported in figures), which indicates strong dependence of these parameters. These figures clearly indicate that the burst, tear and tensile index values increases with an increase in active alkali doses upto 16% and upto a freeness level of 300 CSF; and beyond that all these properties showed a continuously declining trend. All the strength properties values at 18% active alkali show a slight decrease and it may be due to the degradation of carbohydrate materials during the course of pulping.

The results of unbleached kraft-AQ pulp at 16% active alkali, 20% sulfidity with 0.1% AQ are reported in table 3.8B. The kraft-AQ pulp of poplar deltoides shows a slight improvement in strength properties. These results have been plotted in figure 3.12B to 3.14B. These results shows that AQ also improves the strength properties. Kraft-AQ pulps shows better tear and tensile with comparable burst values.

3.7B Comparison of Kraft pulping of Poplar with Eucalyptus:

Since, in India eucalyptus is the most promising fibrous raw material for pulp and papermaking, therefore the pulping characteristics of poplar has been compared with that of eucalyptus. As discussed in Chapter-2, the fiber length of poplar is comparable to that of

eucalyptus. The fibre diameter of poplar is almost two times more than that of eucalyptus. The low density alongwith higher fiber diameter of poplar is expected to give higher bulk. The results of proximate chemical analyses indicated the presence of lower lignin and higher cellulose content in poplar. Therefore, it requires lower cooking chemicals during pulping and produce higher pulp yield as compared to eucalyptus.

The pulping studies of eucalyptus was also carried out in CCL digester having 6 bombs each having a capacity of 2.5 liters. The pulping studies was done under following pulping conditions.

Time from room temperature to 105 ^{0}C	=	45 minutes
Time from 105 ^{0}C to 165 ^{0}C	=	45 minutes
Time at temperature	=	90 minutes
Wood to liquor ratio	=	1:3

The pulping studies were carried out at different active alkali doses (16 to 20% as Na2 O) sulphidity 20% and the results of pulp evaluation are given in table 3.9B. The chips of eucalyptus and poplar were cooked at different alkali doses (ranging from 14 to18%) to get optimum yield. The unbleached pulp yield of poplar at 16% active alkali is 53.6 with kappa no. 15.6 as compared to a pulp yield of 45.2% with kappa no. 24.0 in case of eucalyptus, while the same kappa number of eucalyptus pulp may be obtained at an active alkali dose of more than 20%. The unbleached pulp yield of poplar was found to be 5.6% higher, compared to eucalyptus at the same kappa number. The reason for the pulp yield differences could be due to the type of lignin in the wood and alpha cellulose content of the wood. It has been demonstrated that kraft pulp yield is in directly proportional to the α-cellulose of the wood (19). Although the eucalyptus and poplar pulps can normally be refined to the same tensile index, apparent density and other

strength properties. However these properties depends upon the fiber morphology of the raw material and such differences are normally retained with extended refining. The pulps of both of these wood species were beaten to different freeness levels. At optimum freeness level of around 320 CSF, the physical strength properties of poplar pulp shows better tear, comparable tensile and slightly lower burst. The unbleached pulp of poplar was found to be brighter than eucalyptus pulp.

3.7B Conclusion:

On the basis of experimental results poplar deltoides can be conveniently pulped by kraft process utilizing lower active alkali as compared to other hardwoods due to its lower density and porous structure. The pulp yield obtained during kraft pulping of poplar deltoides is markedly higher compared to other hardwoods such as eucalyptus. The reason for the higher pulp yield could be due to the higher alpha cellulose content of the wood. The pulp yield is directly proportional to the alpha cellulose content of the wood (110). Poplar utilize lower active alkali, may be due to the lignin structure which may be easily degradable by alkali. The kappa no. obtained by the kraft pulping at optimum dose of alkali is quite low around (15-16) without major loss in pulp yield, which is an additional advantage in reducing the environmental pollution load during bleaching.

Use of small amount of anthraquinone (AQ) accelerates kraft delignification. Addition of 0.1% AQ on o.d. wood basis increased the pulp yield between 1.5-2.5% in comparision to than conventional kraft pulp. This extra pulp is obtained at no extra cost apart from the cost of AQ. Use of AQ decrease kappa no. that is lower lignin content of pulp at the same yield, which in turn decrease the bleach chemical demand; thereby decreasing the effluent load as compared to

the conventional kraft process. Low sulfidity pulping with AQ significantly reduce sulfur compounds emission because of lower concentration of hydrosulfide ions which consequently reduces the formation of oragano sulfur compounds during pulping. The pulp produced with low sulfidity pulping with AQ have the comparable strength properties to conventional kraft pulp. The strength properties of kraft and kraft AQ pulps of poplar deltoides as compared to eucalyptus was found to be quite comparable with slightly better tear, comparable tensile and slightly lower burst values.

Table 3.1B: Effect of time (30 min to 150 min)and temperature (145° to 175°C) at 16%active alkali (as Na_2O) and 20% sulphidity during Kraft delignification of Poplar deltoides.

Temperature, (°C)	Time at temperature, (min.)	Screened pulp yield ,% (±0.8)	Screen Rejects, %	Total pulp yield, %	Kappa Number	Lignin ,% (±0.1)
145	30	46.4	19.9±2.0	66.7±2.0	59.6±2.4	8.9
	60	47.8	14.8±2.0	62.6±2.0	51.3±2.0	7.7
	90	50.8	9.8±1.2	60.6±1.8	46.1±2.0	6.9
	120	51.9	7.2±1.2	59.1±1.2	39.2±2.0	5.9
	150	51.3	5.8±1.0	57.1±1.2	37.5±1.5	5.6
155	30	51.8	10.8±2.0	64.6±2.2	47.3±2.0	7.0
	60	54.2	6.9±1.1	61.1±2.0	37.0±1.5	5.5
	90	54.9	3.3±1.0	58.2±1.5	29.7±1.5	4.5
	120	54.6	2.1±0.5	56.7±1.2	23.1±1.0	3.5
	150	52.8	1.9±0.5	54.7±1.2	21.4±1.0	3.2
165	30	53.7	7.6±1.2	60.3±2.0	31.2±1.5	4.8
	60	56.7	3.4±0.8	60.1±1.5	26.3±1.4	3.9
	90	53.4	1.6±0.5	55.0±1.0	17.6±0.5	2.6
	120	51.4	1.1±0.2	52.5±1.0	15.8±0.5	2.4
	150	48.9	0.9±0.1	49.8±0.8	15.2±0.5	2.3
175	30	55.0	3.9±0.5	58.9±1.6	23.8±1.0	3.6
	60	51.5	2.8±0.5	54.3±1.0	17.3±0.5	2.6
	90	47.0	1.0±0.3	48.0±0.8	13.6±0.5	2.0
	120	43.2	0.9±0.1	43.1±0.5	13.0±0.5	1.9
	150	41.2	0.8±0.1	41.0±0.5	12.6±0.5	1.8

**The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions and reported as average mean. They are normally found not to be equidistant from the mean values. The maximum and minimum deviation in terms of actual values are within the range stipulated in the table. The variation in the above response variables were found to be well within allowable experimental error.*

Table 3.2B: Effect of time (30 min to 150 min) and temperature (145^0 to 175^0C) at 16% active alkali (as Na_2O) and 20% sulphidity during Kraft -AQ delignification of Poplar deltoides.

Temperature (°C)	Time at temp. (min.)	Screened pulp yield ,% (±0.8)	Screening rejects,%	Total pulp yield, %	Kappa Number	Lignin ,% (±0.1)
145	30	47.3	19.0±2.0	66.3±1.6	57.2±2.4	8.6
	60	48.6	13.9±2.0	62.5±1.6	49.1±2.0	7.4
	90	51.6	9.5±1.2	61.1±1.6	42.7±1.8	6.4
	120	52.2	7.2±1.1	59.4±1.6	35.4±1.8	5.3
	150	52.3	5.5±1.0	57.8±1.6	32.1±1.8	4.8
155	30	52.7	9.8±1.7	62.5±1.6	43.3±1.7	6.5
	60	55.2	6.5±1.4	61.7±1.6	32.2±1.5	4.8
	90	56.1	3.0±0.8	59.1±1.6	26.4±1.0	4.0
	120	55.8	2.1±0.5	57.9±1.2	21.2±1.0	3.2
	150	53.1	1.6±0.5	54.7±1.2	20.8±0.8	3.1
165	30	53.9	7.1±1.1	61.0±1.6	28.2±1.5	4.4
	60	57.5	3.2±0.5	60.7±1.6	24.0±1.0	3.6
	90	54.7	1.3±0.2	56.0±1.2	17.6±0.5	2.6
	120	52.0	0.9±0.2	52.9±1.0	15.2±0.5	2.3
	150	49.2	0.7±0.2	49.9±0.8	14.6±0.5	2.2
175	30	55.6	3.9±1.1	59.5±1.6	21.5±0.8	3.2
	60	52.0	2.6±0.5	54.6±1.0	15.7±0.5	2.4
	90	45.7	0.8±0.2	46.5±0.8	13.0±0.5	2.0
	120	45.0	0.7±0.2	45.7±0.7	12.5±0.5	1.9
	150	41.5	0.7±0.2	42.2±0.6	12.3±0.5	1.8

**The experimental results for all the response parameters are based on four sets of experiments are reported as average mean. They are normally found not to be equidistant from the mean values.. The variation in the above response variables were found to be well within allowable experimental error.*

Table 3.3B: Results of Kraft pulping of poplar deltoides at a different active alkali (12% to 20% , as Na_2O) , using following conditions .

Maximum Temperature: 165°C

Time at Maximum Temperature : 90 minutes.

Wood to liquor ratio : 1:3

Active alkali,% as Na_2O / Particulars	12	14	16	18	20
Screened pulp yield ,% (±0.8)	45.0	55.8	53.6	47.2	41.1
Rejects ,%	14.7±1.2	3.6±0.4	1.4±0.2	1.3±0.2	0.8±0.1
Total yield, %	59.3±1.2	58.4±0.8	55.0±0.5	48.5±0.5	41.9±0.5
Kappa Number	39.4±1.9	21.4±1.0	17.6±0.5	14.1±0.5	13.0±0.5
Black liquor,pH (±0.2)	9.5	10.7	12.4	12.8	12.9
Residual Alkali, NaOH, gpl (±0.2)	3.9	7.4	11.0	12.9	17.3
Intrinsic viscosity,g/cm3 (±10)	650	610	570	470	410

Table 3.4B: Effect of AQ doses (0.05 to 0.2 %) at different active alkali charge (12 to 20 %, as Na_2O)and sulphidity(15% to 20% during Kraft delignification of poplar deltoides, using following to conditions, Maximum Temperature: 165°C; Time at Max. Temp : 90 minutes. ;

Active alkali,% (Na_2O)	Sulphidity ,%	AQ doses, %	Screened pulp yield, % (±0.8)	Screening rejects, %	Total pulp yield %	Kappa number	Black liquor,pH (±0.1)	RA , NaOH, (±0.2)
12	15	0.0	43.1	12.5±1.2	55.6±1.6	40.6±2.2	9.5	3.6
		0.05	44.2	12.0±1.2	56.2±1.6	38.2±2.2	9.5	3.7
		0.1	45.7	11.7±1.2	57.4±1.6	37.1±2.2	9.5	3.7
		0.2	54.9	11.7±1.2	57.7±1.6	36.8±2.2	9.5	3.8
		0.0	44.0	15.3±1.0	59.3±1.6	39.4±2.2	9.5	3.9
12	20	0.05	45.3	13.8±1.0	59.4±1.6	38.0±2.2	9.5	3.9
		0.1	46.8	11.7±1.0	58.6±1.6	37.1±2.2	9.5	3.8
		0.2	47.3	10.6±1.0	58.1±1.6	36.6±2.2	9.5	3.7
		0.0	56.7	2.3±0.3	59.0±1.6	27.4±1.6	10.5	6.8
	15	0.05	57.4	2.2±0.3	59.6±1.6	26.8±1.6	10.5	6.8
14		0.1	58.8	2.2±0.3	61.0±1.6	26.0±1.6	10.6	6.7
		0.2	59.0	2.1±0.3	61.1±1.6	25.2±1.6	10.6	6.6
		0.0	55.8	2.6±0.3	58.4±1.4	21.4±1.0	10.7	7.4
14	20	0.05	56.3	2.5±0.2	58.8±1.4	21.0±1.0	10.8	7.6
		0.1	56.7	1.5±0.2	58.3±1.4	20.1±1.0	10.8	7.6
		0.2	57.7	1.3±0.2	58.0±1.4	19.4±1.0	10.8	7.7
16		0.0	54.3	1.6±0.2	55.9±1.2	19.2±1.0	11.9	12.6
	15	0.05	55.6	1.6±0.2	57.2±1.2	18.8±0.8	11.9	12.7
		0.1	56.2	1.5±0.2	57.7±1.2	18.1±0.8	11.9	12.7
		0.2	56.4	1.5±0.2	57.9±1.2	17.9±0.8	11.9	12.7
16		0.0	53.4	1.6±0.2	55.0±1.2	17.6±0.8	12.4	13.0
	20	0.05	54.0	1.4±0.2	55.4±1.2	17.2±0.8	12.4	13.0
		0.1	54.7	1.3±0.2	56.0±1.2	16.7±0.8	12.4	13.1
		0.2	54.9	1.2±0.2	56.2±1.2	16.5±0.8	12.4	13.2
18		0.0	50.1	1.0±0.2	51.1±1.2	15.1±0.5	12.6	14.0
	15	0.05	51.3	1.0±0.2	52.3±1.2	14.8±0.5	12.6	14.0
		0.1	51.5	0.9±0.2	52.4±1.2	14.2±0.5	12.6	14.2
		0.2	51.7	0.8±0.2	52.7±1.2	14.2±0.5	12.6	14.3
		0.0	47.2	1.3±0.2	48.5±0.8	14.1±0.5	12.8	14.4
	20	0.05	47.3	1.2±0.2	48.5±0.8	14.1±0.5	12.8	14.3
18		0.1	47.5	1.2±0.2	48.7±0.8	14.0±0.5	12.9	14.3
		0.2	45.5	1.2±0.2	48.8±0.8	14.0±0.5	12.9	14.3
20		0.0	45.3	0.8±0.1	46.2±0.8	13.6±0.5	12.9	16.2
	15	0.05	46.0	0.8±0.1	46.9±0.8	13.4±0.5	12.9	16.8
		0.1	46.4	0.7±0.1	47.3±0.8	13.3±0.5	12.9	16.6
		0.2	46.6	0.7±0.1	47.4±0.8	13.3±0.5	12.9	16.7
20	20	0.0	41.1	0.8±0.1	41.9±0.8	13.0±0.5	13.0	18.3
		0.05	41.3	0.7±0.1	42.2±0.8	12.8±0.5	13.0	18.2
		0.1	41.4	0.7±0.1	42.3±0.8	12.7±0.5	13.0	18.4
		0.2	41.4	0.7±0.1	42.3±0.8	12.7±0.5	13.0	18.4

**The experimental results for all the response parameters are based on four sets of experiments of pulping at the same conditions and reported as average mean.They normally found not to be equidistant from the mean values but found in this range. The variation in the responding variables were found to be well within the experimental error.*

Table 3.5B: Effect of Sulphidity (0to 25%)and time (30 to 150 min) at 16%Active alkali (as Na_2O) at 165^0C during Kraft delignification of Poplar deltiodes.

Sulphidity, %	Time at Temp. (min.)	Screened pulp yield ,% (±0.8)	Screening rejects,%	Total pulp yield, %	Kappa Number	Lignin ,% (±0.1)
0	30	-	-	-	-	-
	60	50.3	12.7±2.2	63.2±2.5	39.0±2.0	5.9
	90	57.9	4.8±0.5	62.7±2.2	31.6±2.0	4.8
	120	55.0	2.2±0.3	57.2±1.5	25.1±1.4	3.8
	150	54.6	1.7±0.2	56.3±1.2	23.8±1.0	3.6
	180	51.4	1.1±0.1	52.5±0.8	22.5±1.0	3.4
10	30	49.5	14.0±1.7	63.5±2.0	46.5±2.0	7.0
	60	57.8	4.2±0.8	62.0±2.0	35.9±2.0	5.2
	90	55.8	2.1±0.5	57.9±1.5	25.6±1.4	3.8
	120	54.2	1.4±0.3	55.6±1.3	23.2±1.0	3.4
	150	52.1	0.9±0.1	53.0±1.2	22.0±1.0	3.2
15	30	52.2	9.1±1.5	61.3±2.0	38.3±2.0	5.8
	60	57.4	3.8±0.5	61.2±1.5	31.6±1.8	4.7
	90	55.2	2.0±0.2	57.2±1.0	24.2±1.4	3.6
	120	53.8	1.3±0.1	55.1±1.0	21.1±1.0	3.1
	150	52.4	0.9±0.1	52.3±1.0	20.8±1.0	3.1
20	30	53.7	7.6±1.2	60.3±2.0	31.2±1.5	4.6
	60	56.7	3.4±0.8	60.1±1.5	26.3±1.4	3.9
	90	53.4	1.6±0.2	55.0±1.0	17.6±0.5	2.6
	120	51.4	1.1±0.2	52.5±1.0	15.8±0.5	2.4
	150	48.9	0.9±0.1	49.8±0.8	15.2±0.5	2.3
25	30	54.3	6.4±1.1	60.7±2.0	30.3±1.5	4.5
	60	55.2	3.0±0.5	58.2±1.5	24.6±1.2	3.7
	90	52.0	1.2±0.2	53.2±1.0	17.0±0.5	2.5
	120	49.3	0.6±0.1	49.9±0.8	15.1±0.5	2.3
	150	47.7	0.6±0.1	48.3±0.8	14.8±0.7	2.2

Table 3.6B: Characteristics of kraft and kraft-AQ spent liquor of poplar deltiodes at optimum conditions .

Particulars	Kraft	Kraft-AQ
Black liquor pH (±0.1)	12.4	10.8
Residual alkali, gpl (±0.2)	11.0	7.6
Organics,% (±0.5)	71.9	72.1
Inorganic ,% (±0.5)	29.1	27.9
Calorific value,cal/gm (±10)	3760	3990

Table 3.7B: Pulp evaluation data of unbleached kraft pulp of Poplar deltoides at different alkali doses (14 to 20%) using following conditions.
Max. Temp. 165°C, Time at Max Temp. 90 min., Wood to liquor ratio 1:3

Active alkali,% (as Na_2O)	PFI Rev.	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.02)	Tensile Index (N.m/g) (±1.0)	Tear Index ($mN.m^2/g$) (±0.2)	Burst Index ($kPa.m^2/g$) (±0.2)
14	0	700	4.3	0.60	17.0	2.0	0.7
	1000	610	4.8	0.62	32.1	3.3	2.0
	2000	550	5.2	0.66	44.3	4.0	3.0
	3000	460	5.8	0.70	61.2	5.1	4.7
	4000	320	7.4	0.77	68.8	6.9	4.9
	6000	190	15.6	0.79	71.3	5.0	5.1
16	0	690	4.3	0.60	17.4	2.5	0.8
	1000	590	4.8	0.64	33.2	3.5	2.3
	2000	530	5.3	0.68	45.7	4.1	3.2
	3000	450	6.0	0.72	63.2	5.4	4.8
	4000	310	7.8	0.79	70.3	7.2	5.0
	6000	180	15.8	0.81	71.0	5.3	5.2
18	0	680	4.3	0.60	18.2	2.3	0.8
	1000	580	4.9	0.65	34.3	3.3	2.4
	2000	520	5.5	0.70	44.4	3.9	3.3
	3000	440	6.2	0.75	60.1	5.2	4.9
	4000	310	8.1	0.80	65.2	6.5	5.2
	6000	180	16.0	0.83	66.4	4.9	5.0

Table 3.8B: Strength properties of unbleached Kraft-AQ pulp, at 14% active alkali, 20% sulphidity, temperature 165^{0}C,time at temp. 90 min., 0.1% AQ.

PFI Revolutions	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.02)	Tensile Index (N.m/g) (±1.0)	Tear Index (mN.m^2/g) (±0.2)	Burst Index (kPa.m^2/g) (±0.2)
0	680	4.3	0.60	17.2	2.0	0.8
1000	570	5.0	0.65	32.8	3.4	2.3
2000	510	5.6	0.69	44.6	4.3	3.1
3000	410	6.3	0.72	62.6	5.4	4.6
4000	300	8.0	0.76	69.8	7.6	5.0
5000	240	12.4	0.78	71.2	6.7	5.1
6000	180	14.8	0.80	70.3	4.9	4.7

Table 3.9B: Results of Kraft pulping of poplar deltiodes and eucalyptus at a different active alkali (12% to 20% , as Na_2O) , using following conditions .
Maximum Temperature: 165^{0}C
Time at Maximum Temperature : 90 minutes. Wood to liquor ratio : 1:3

Particulars	Poplar deltiodes			Eucalyptus		
Active alkali ,% (as Na_2O)	14	16	18	16	18	20
Sulphidity ,%	20	20	20	20	20	20
Screen yield ,% (±0.8)	55.8	53.6	47.2	45.2	47.8	45.2
Rejects ,% (±0.2)	1.6	1.4	1.3	4.9	2.1	1.8
Total yield ,% (±1.0)	57.4	55.0	48.5	50.1	49.9	47.0
Kappa Number (±0.5)	21.8	15.6	14.1	24.0	21.2	19.1
Black liquor ,pH (±0.1)	10.7	12.4	12.8	9.5	10.0	10.3
Residual Alkali, NaOH, gpl (±0.2)	7.4	11.0	13.0	6.5	9.5	11.3

Table 3.10B: Strength properties of Poplar and Eucalyptus pulps

Particulars	16% Kraft pulp of Poplar deltoides	18% Kraft pulp of Eucalyptus
;ness,CSF (ml) (±10)	320	320
sile Index, (N.m/g) (±1.0)	70.2	71.0
st Index, ($kPa.m^2/g$) (±0.02)	5.0	5.7
r Index, ($mN.m^2/g$) (±0.3)	7.2	6.2

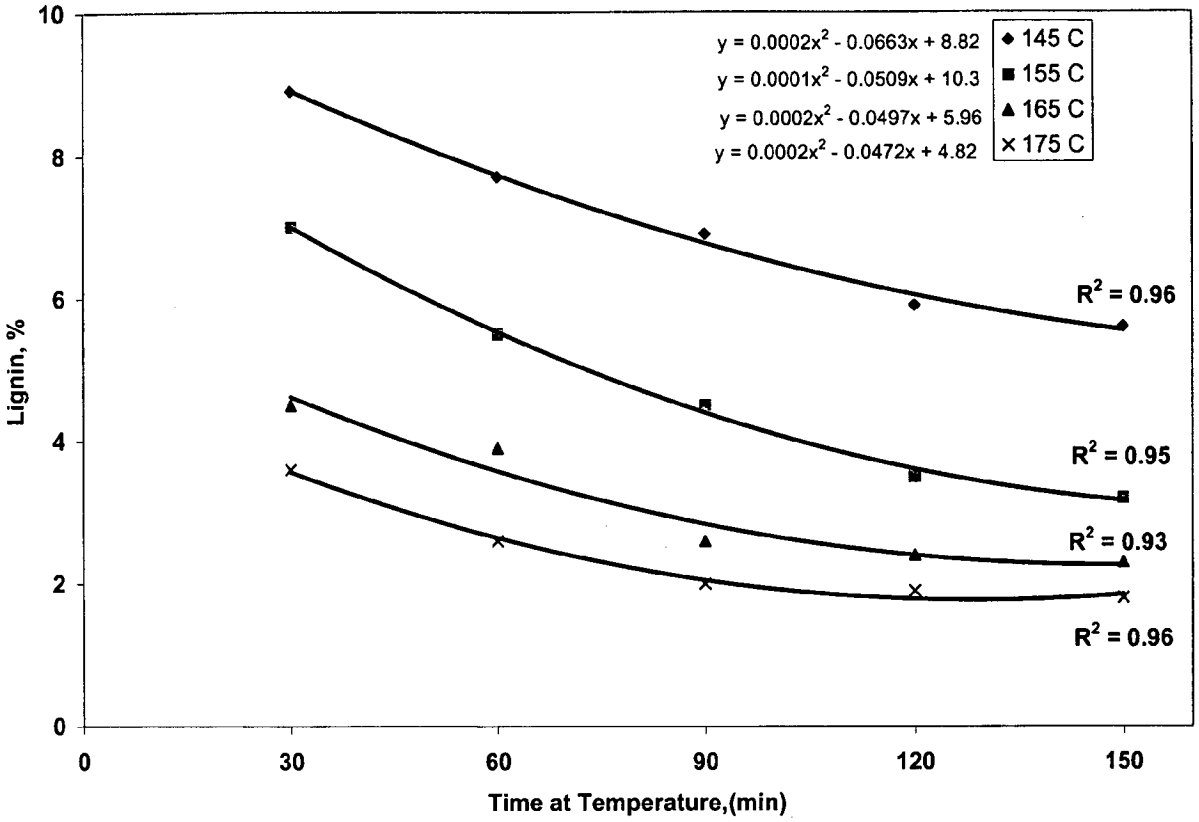


Fig 3.1B: Plots of lignin vs time at different temperatures at 16% AA,20% sulphidity during kraft pulping of Poplar deltoides.

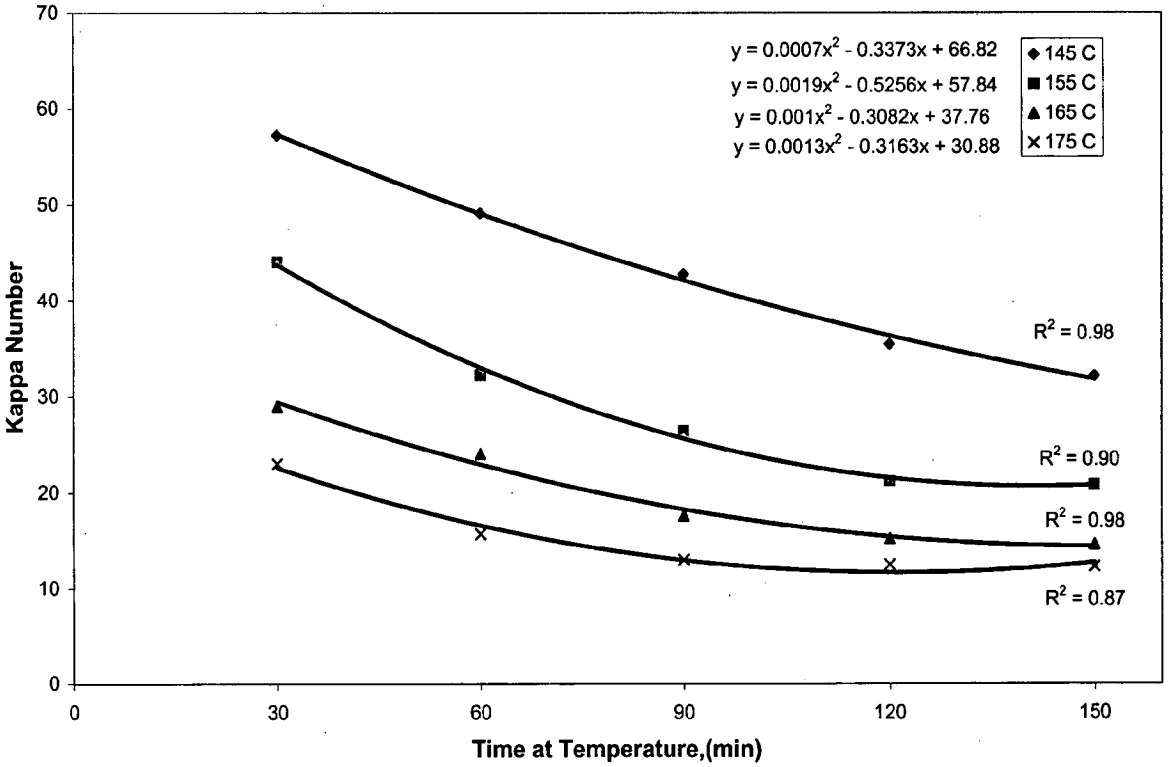


Fig 3.2B: Plots of time vs kappa number at 16% AA asNa O) and 20% sulphidity during kraft pulping of Poplar deltoides.

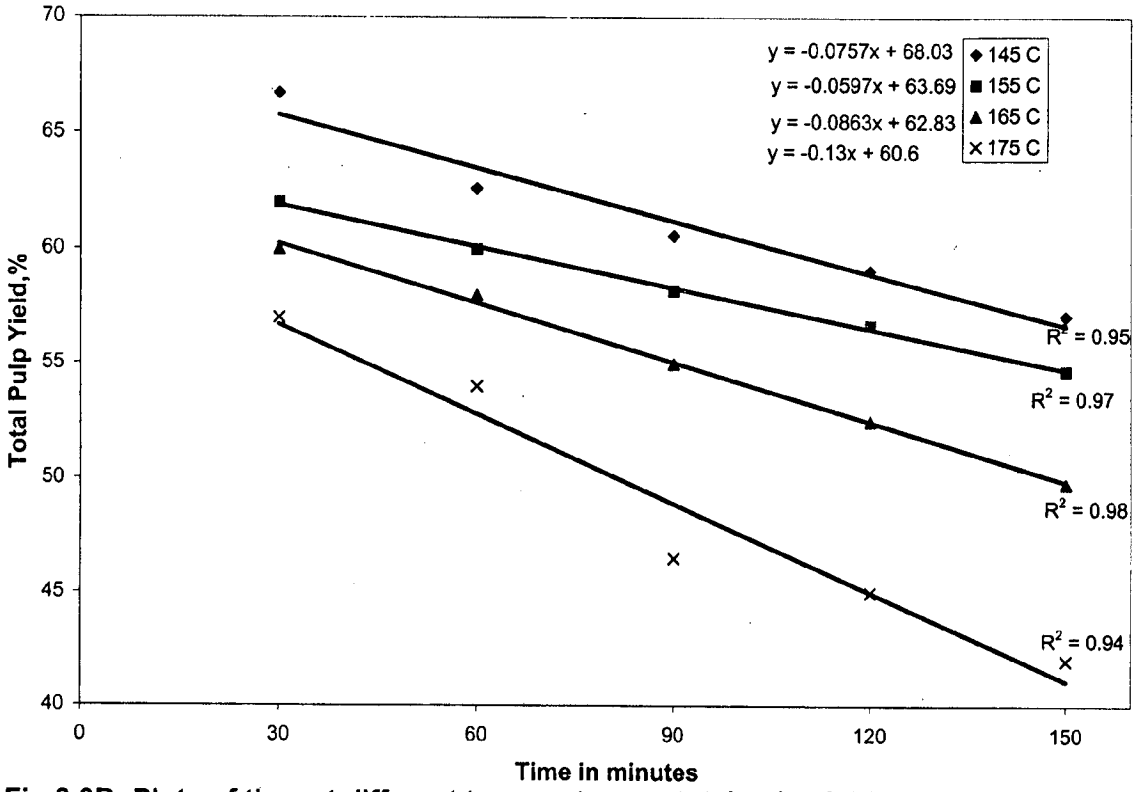


Fig 3.3B: Plots of time at different temperature vs total pulp yield at 16% AA and 20% sulphidity during kraft pulping

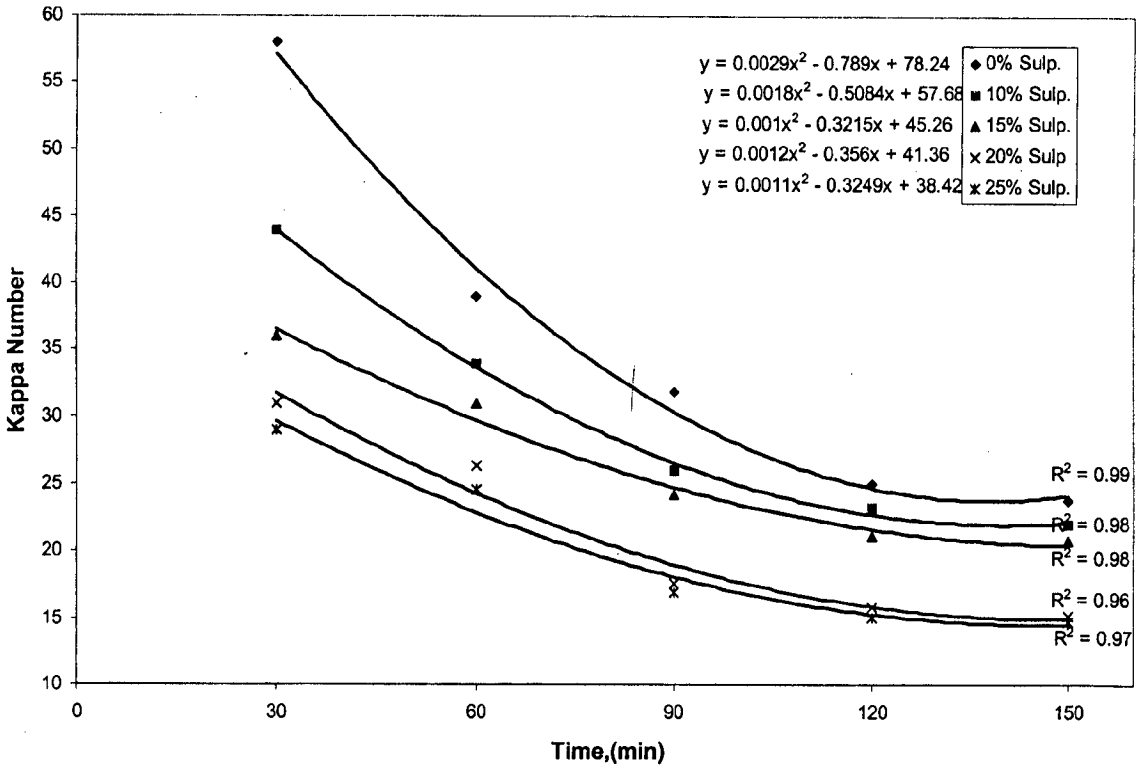


Fig. 3.4B: Plots of kappa number vs time (at temperature) at different sulphidity during kraft pulping using 16% AA at 165 C

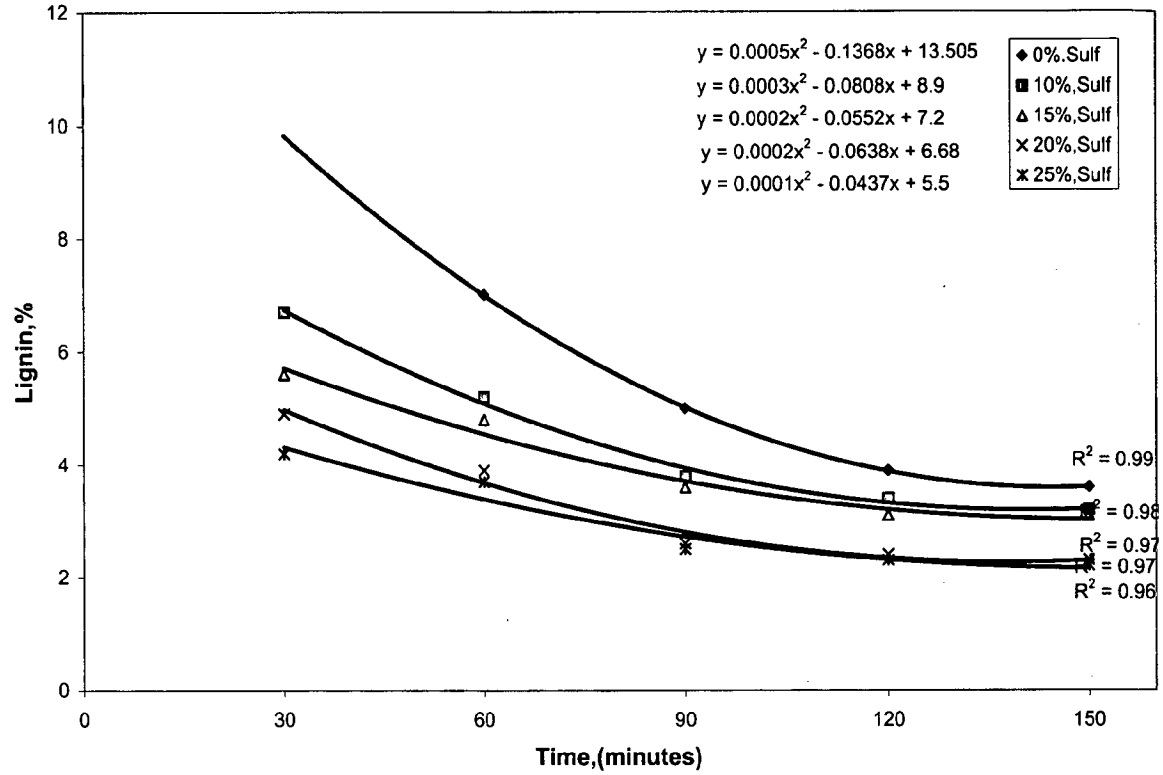


Fig.3.5B: Plots of time vs. lignin content at different sulphidity during kraft pulping at 16% active alkali.

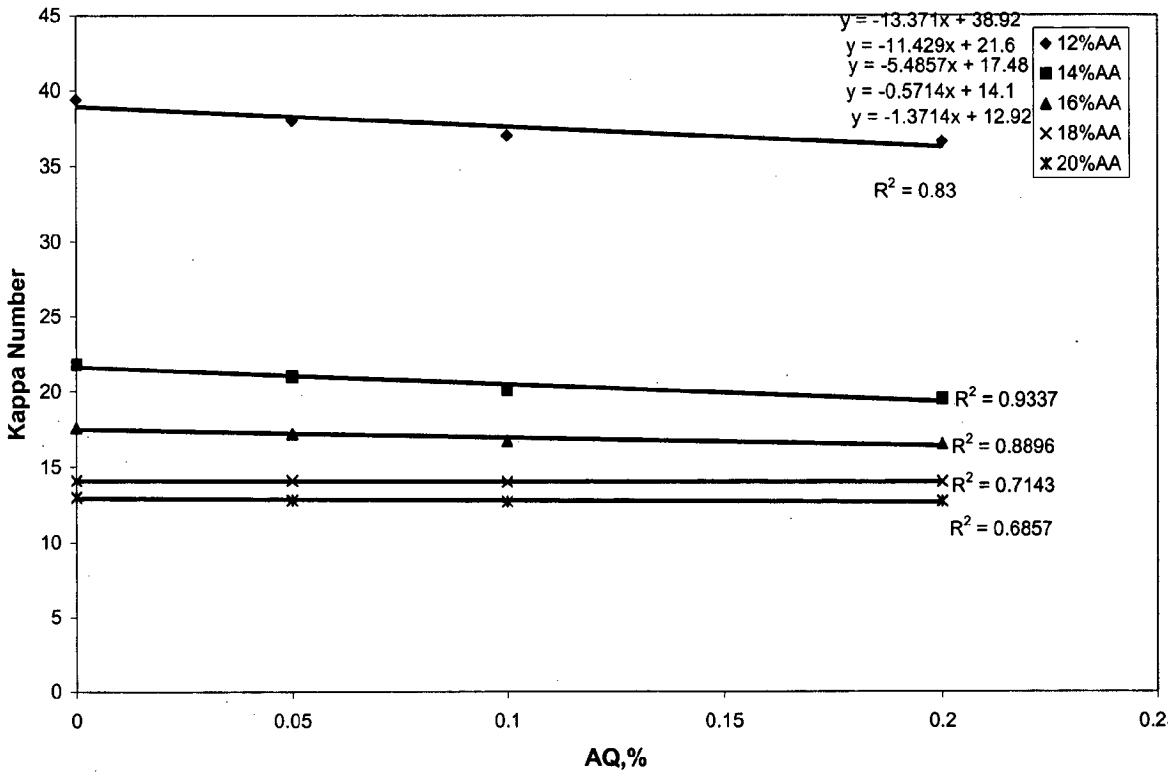


Table 3.6B Effect of AQ on kappa number at different active alkali during kraft-AQ pulping.

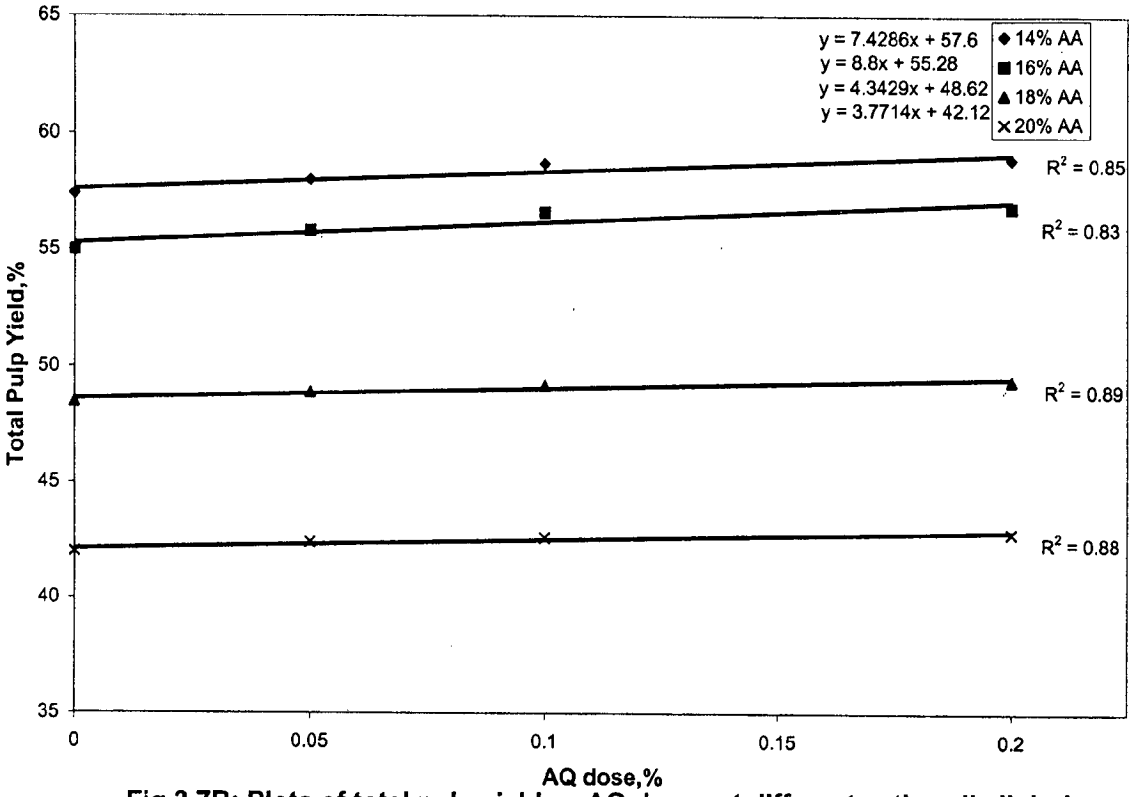


Fig 3.7B: Plots of total pulp yield vs AQ doses at different active alkali during kraft pulping at 165 C for 90 minutes

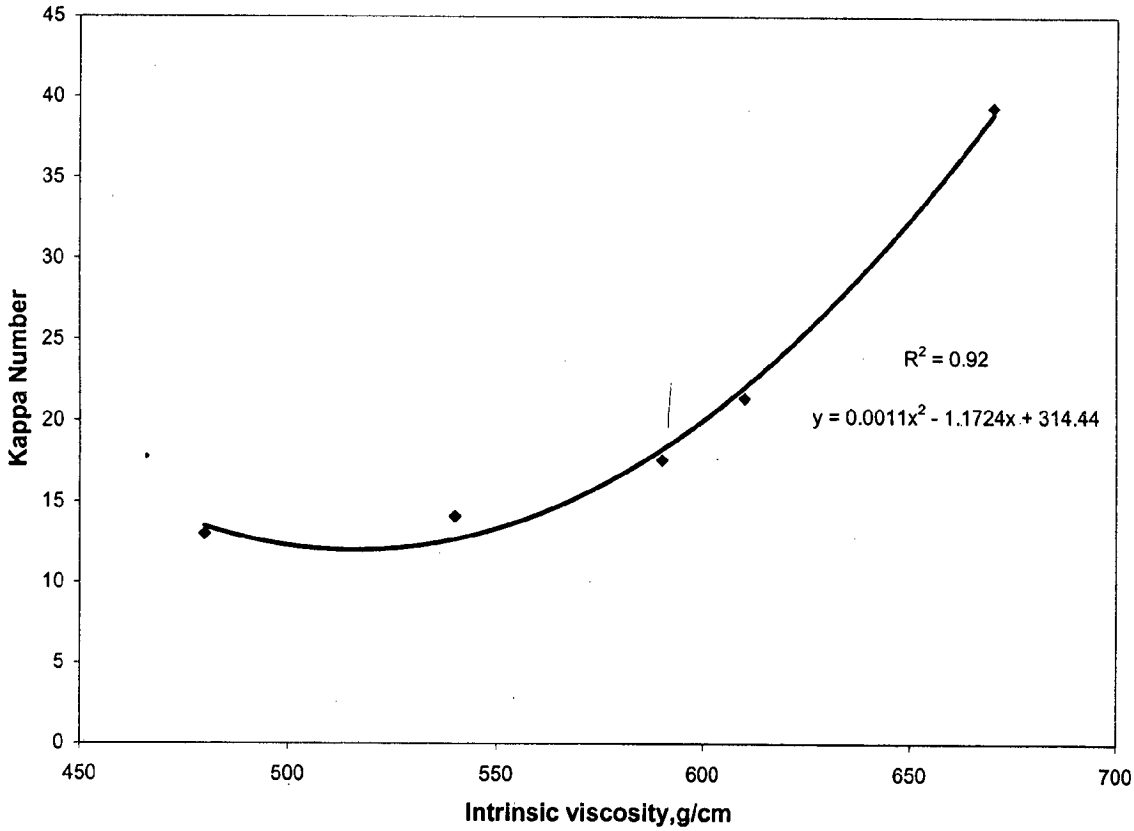


Fig 3.8B: Plots of viscosity vs kappa number of poplar pulps

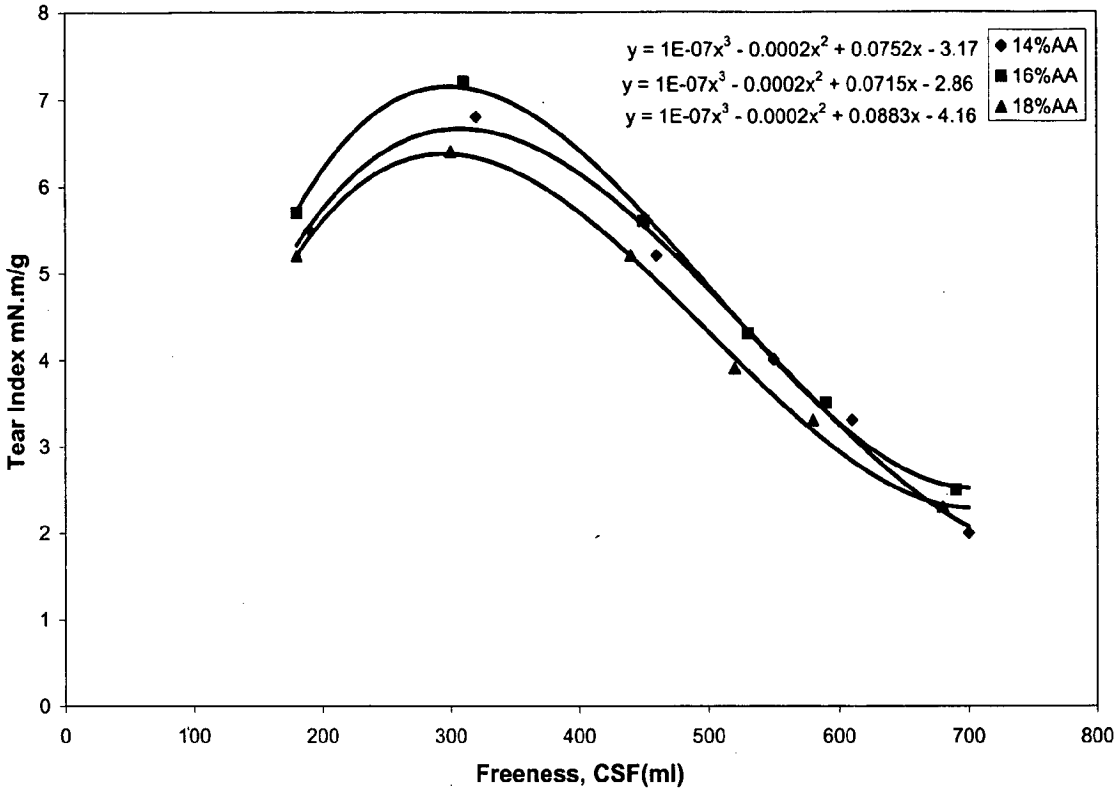


Table 3.9B: Plots of freeness vs tear index at different active alkali during kraft pulping of poplar

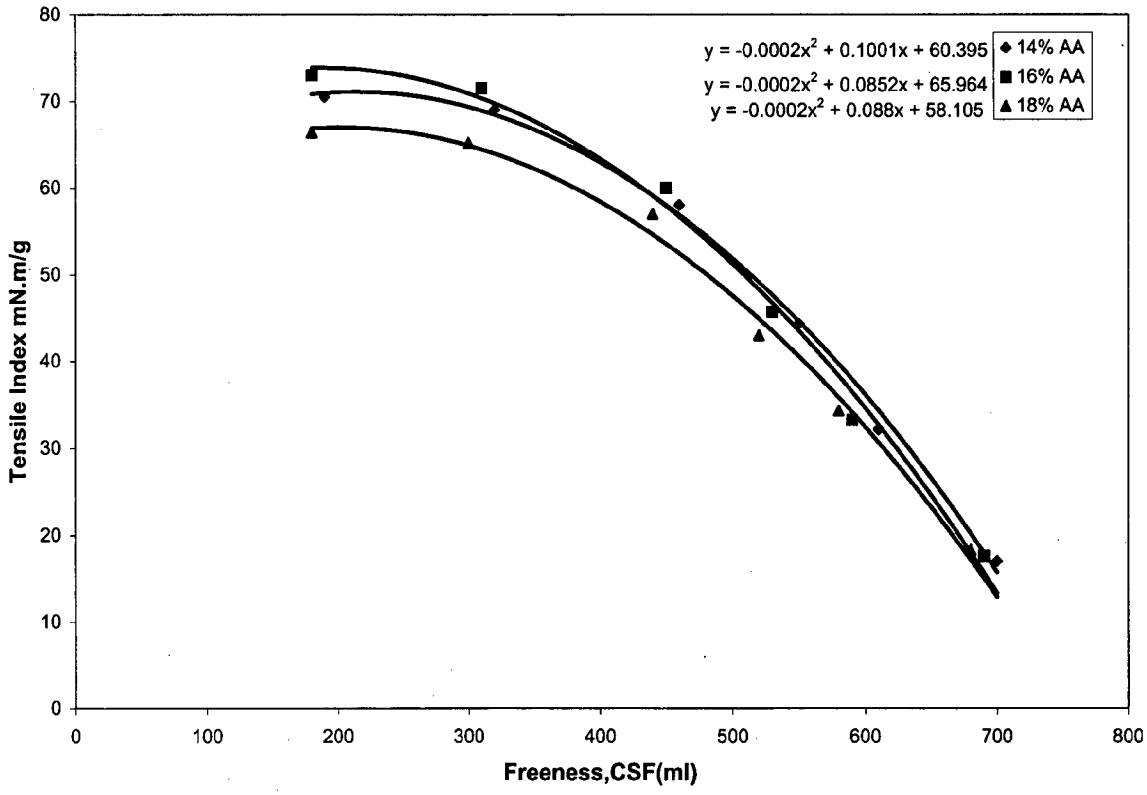


Fig 3.10B Plots of freeness vs tensile index during kraft pulping at different active alkali

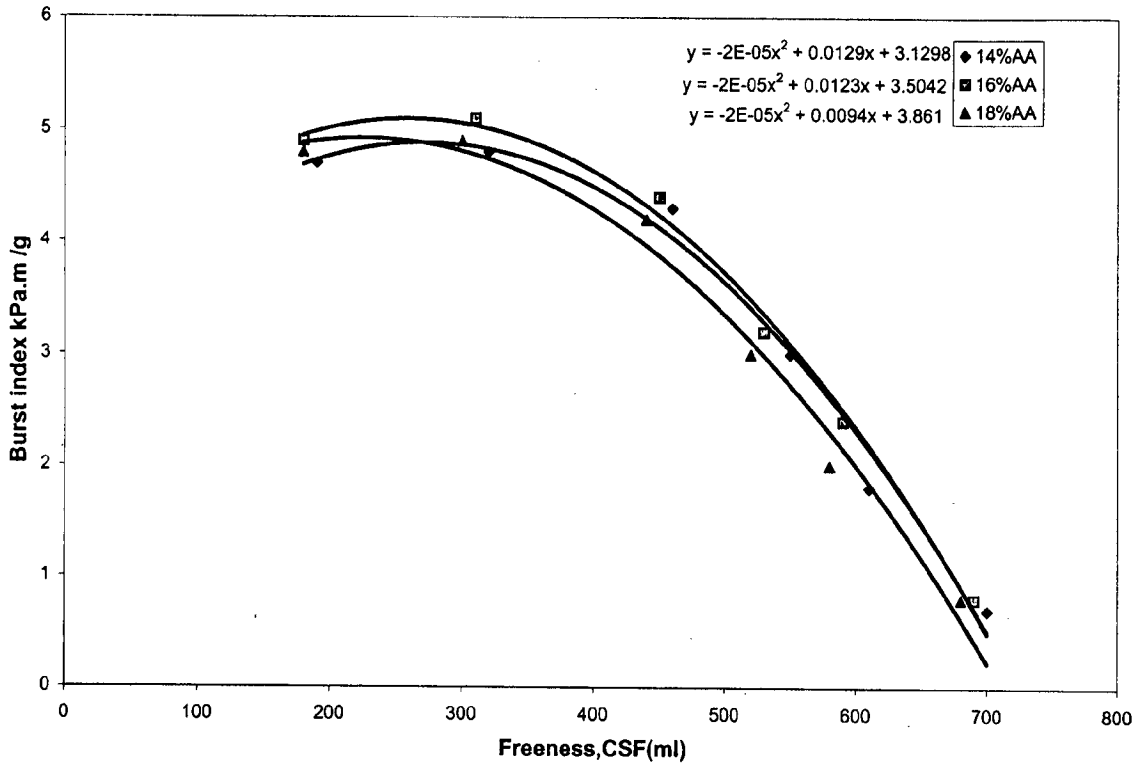


Fig 3.11B: Plots of freeness vs burst index at different AA during kraft pulping of poplar.

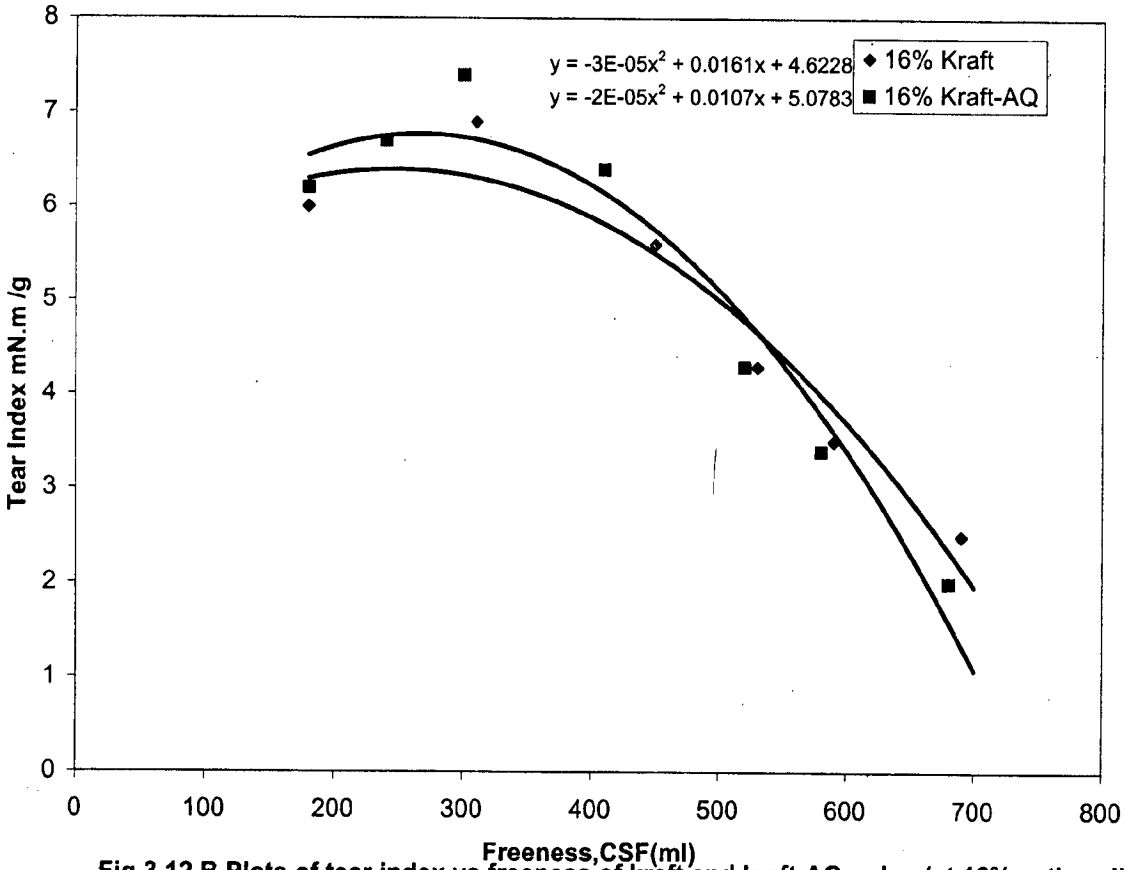


Fig 3.12 B Plots of tear index vs freeness of kraft and kraft-AQ pulps (at 16% active alkali) of poplar.

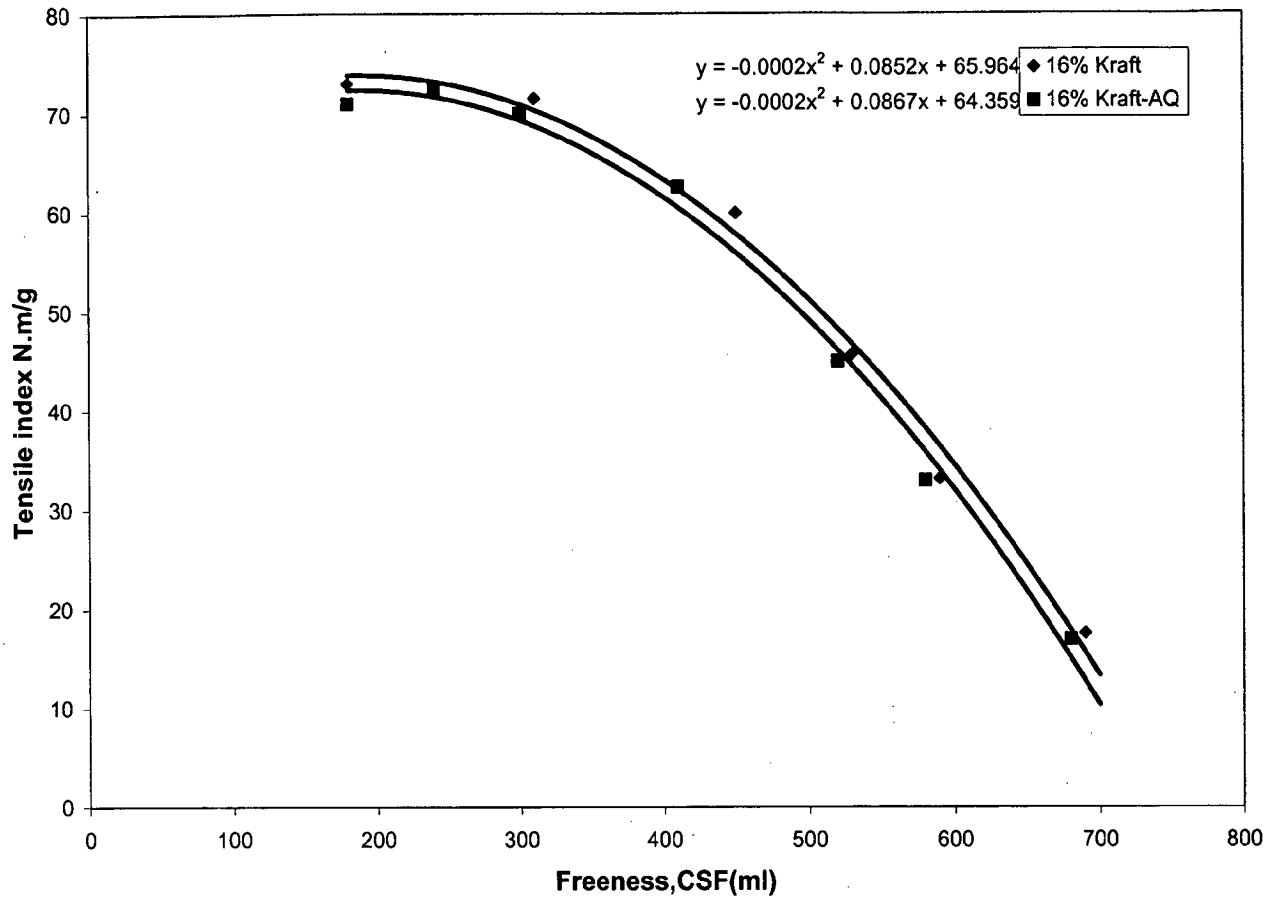


Fig 3.13 B Plots of tensile vs freeness of kraft and kraft-AQ pulps (at 16% active alkali) of poplar.

CHAPTER 3C

POLYSULPHIDE AND POLYSULPHIDE-AQ PULPING

3.1C: Introduction:

Over the past few decades several chemicals were identified by the researchers, which can improve pulp yield, when used as pulp additives (6,73,195,207). Most of these chemicals are capable of inhibiting the 'peeling' reactions during kraft pulping, by converting the carbohydrate aldehyde end groups to alkali-stable alcohols or carboxylic acids. The carbohydrate end groups can be reduced to alcohols with sodium boro-hydrides (6) and to thiols with hydrogen sulfide (207). This can also be oxidized to carboxylic acids with polysulfide or anthraquinone (AQ) (195,73). Among these four additives only polysulfide and anthraquinone have been applied commercially due to their relative cost and easy handling.

The first report of a kraft pulp yield increases in presence of polysulfide, made by dissolving elemental sulfur in kraft cooking liquor, was given by Hagglund in 1946 (70). Subsequently, several kraft mills applied Hagglund's technique to generate polysulfide in their white liquor, was confirmed in their mills (67,95).

However Polysulfide (PS) pulping was introduced in late 1970 as a means of increasing the pulp yields alongwith decreasing the wood and energy costs of kraft pulping (53,85,86). Due to the increasing cost of wood, the efforts have been made to increase the pulp yield. The pulp yield can be increased by increasing the carbohydrate retention during the course of pulping operation. The use of polysulfide or anthraquinone (AQ) or in combination, proved beneficial in improving the pulp yield at the same kappa no. without sacrificing the strength properties (10,163,218). The use of 1-2% polysulfide helps in increasing the pulp yield to the tune of 1.5-2.5% (218).

Environmental concerns about the discharge of chlorinated organic compounds (AOX) from the bleach plant have led to a decrease in the use of chlorine during bleaching. The amount of chlorinated organic compounds depends on the amount of chlorine used during bleaching (10,9,126). The chlorine consumption in bleaching is the function of the kappa no. of the pulp. Hence low kappa no. pulp requires less chlorine and reduces the discharge of chlorinated organic compounds. Pulping towards low kappa no. results in the drop in pulp yield and strength. The use of polysulfide and AQ or PS,AQ both in the kraft pulping reduces the lignin content of the pulp (kappa no.) with almost no effect on pulp yield and strength properties or used to improve the pulp yield at the same kappa no. of conventional kraft pulp.

Polysulfide does not affect the delignification rate significantly but polyslfide (PS) is an effective pulping additive for increasing kraft pulp yield. PS oxidises the reducing end group in polysaccharides to carboxylic groups rendering the polysaccharide in particular glucomannans, stable against the alkali assisted end wise degradation, resulting in an increase in pulp yield (6,10,73,85,86,94,207). In the early stages of the polysulfide pulping, most of the polysulfide is consumed by reacting with the carbohydrates (8,70).

$$R\text{-}CHO + Na_2S_2 + 3\,NaOH \longrightarrow RCOONa + 2Na_2S + 2H_2O$$

This equation depicts the oxidation of the carbohydrate reducing carbonyl end group to carboxylic group thus preventing the extent of peeling reaction and stabilizing the carbohydrates against alkaline degradation. The stabilization of carbohydrates is one of the reason to increase the pulp yield in PS pulping over kraft pulping (4). In the above reaction it has been seen that the reaction of polysulfide and carbonyl end group generates sodium sulfide. The polysulfide at 140^0C generates sodium sulfide also.

$$4Na_2S_2 + 6NaOH \longrightarrow 6\,Na_2S + Na_2S_2O_3 + 3H_2O$$

3.2C: Experimental Methodology :

Polysulfide liquor was prepared in laboratory by reacting sulfur powder with high sulfidity white liquor in the presence of oxygen at about 70-80 ^{0}C for three hours under N_2 atmosphere. The active alkali and polysulfide sulfur contents of the liquor were determined by Tappi method 694 om-90. The polysulfide percent applied on wood is not independent variable and determined by the polyslfide concentration in the liquor. The polysulfide concentration depends upon the sulfidity of the white liquor, higher the sulphidity the more will be the amount of polysulphide formed. During the course of polysulphide pulping, the sulfidity of the polysulphide liquor continuously decreases and attain a low value even than of white liquor. To keep the kappa no. of polysulphide pulp comparable to conventional kraft pulp, the active alkali charge for the polysulphide cooking is kept slightly higher than the conventional kraft pulping.

The chips of poplar deltoides were screened in order to separate the over size chips and undersize chips from the chips of acceptable quality. The chips of poplar deltoides retained on 32 mm screen, were utilized for pulping studies. All the cooks were done in CCL digester using a charge of 300 g o.d. chips at wood to liquor ratio 1:3, maintaining the following cooking conditions:

Time from room temperature to 105 ^{0}C	=	45 minutes
Time from 105 ^{0}C to maximum temperature 165 ^{0}C	=	45 minutes
Time at maximum temperature.	=	120 minutes

3.3C: Optimum Pulping Conditions:

The pulping studies were made using different concenteration of polysulphide to study the optimum ratio of these chemicals for the purpose of delignification. The cooking were also carried out for different time at a temperature of 165 ^{0}C to study the effect of cooking time during the course of delignification reaction. At the end of the cook, the pulp was defibrated

washed and screened with a plate clearance of 0.15 mm. These pulps were evaluated for the screened pulp yield, kappa number and rejects.

3.4C Results and Discussion:

The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions of temperature, pressure, time at temperature with constant active alkali charge. As the pulping experiments are extremum type, no two sets can be identical therefore average of the four / five set of data are shown only. The maximum and minimum deviation of statistically mean value is not shown or the all four sets of data are not shown, merely to reduce the large volume of data.

In the present investigation, data found from the laboratory experiments for a specific set of input parameters such as time, temperature, different alkali with different polisulphide etc. all the data are not reproduce the brevity of rather average data of the set is depicted in tables. However it is observed that there is marginal difference in the set of data which is permitted in this type of experiments. The variation in the responding variables were found to be well within the experimental error.

For the statistic modelling the responding parameters during pulping namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content of the pulp at different alkali with different polisulphide were regressed with the time at temperature as independent variables. The responding variables of pulp evaluation such as tear index, tensile index and burst index were regressed with different freeness as independent variable. In most of the cases the quadratic model ($y = ax^2 + bx + c$, where a, b and c are parameters to be estimated) were obtained. Where y is the responding variable and x is the time at temperature, which is

found to fit well to the data. The quadratic model reflects the behavoir of various pulping conditions and pulp evalution.

3.4.1C Effect of Polysulfide concentration on pulp yield:

The results of the different doses of polysulfide pulping have been reported in table 3.1C. Addition of polysulfide increases the pulp yield. From the results of polyslfide pulping of poplar it has been observed that with the addition of 1% polysulfide, there is an increase of 1.5% in pulp yield in the kappa range of 16-18. Similarly on addition of the polysulfide dose of 2 and 3%, the increase in yield was found to be 2.4% and 2.8% respectively. The results of the effect of PS concentration at 16% and 17% active alkali on pulp yield and kappa number are plotted in figure 3.1C to 3.4C The data fitted statistically smooth curves having concavity upwards with R square values ranging from 0.91-0.99. The R square values indicate the closeness of the fit of the data. From the results of table 3.1Cand 3.2C it has been observed that the increase in pulp yield with polysulfide is more for higher kappa pulps. Use of PS and AQ are less effective for yield improvement in the low kappa range. These results indicate that the yield improvement by PS addition decreases in low kappa number range may be due to in stability of hemicellulose at higher degree of delignification. The increase in pulp yield by the addition of polysulfide or other additives is due to the higher retention of carbohydrate materials in the pulp. The hemicelluloses are less stable than cellulose at higher cooking temperature; longer time and higher active alkali charge degrades the carbohydrate materials and decreases the retention of hemicelluloses. When polysulfide is used alone, it has been observed from the experimental results that the improvement in pulp yield is less effective. On using PS alongwith AQ, the improvement in pulp yield was found to be more pronounced (Table 3.2C). The screened yield obtained with 16% kraft, 16% kraft + 0.1% AQ, Polysulphide 1-3% with 0.1% AQ (at 16% active alkali for 2 hours at temperature) was found to be 53.6, 54.7, 56.8, 57.2 and 57.5 percent respectively. One of the

possible reason to increase in pulp yield during higher polysulfide dose may be due to the low degradation of total carbohydrate material along with higher retention of hemicellulose content. Moreover AQ also helps in preserving carbohydrate material during polysulphide pulping (86,94,109,110).

The yield gain and alkali requirement have a significant impact on both the over all daily liquor requirement and on the load of black liquor solids delivered to liquor recovery operations. The change in black liquor solids can be estimated using data of Green and Grace (8). With AQ/polysulfide, pulp production increases, while the production of black liquor solids decreases by about 5% compared to conventional kraft pulping at a same kappa number. The additional yield gain obtained with AQ actually reduces black liquor solids, even with the small increase in alkali requirement. AQ is required for the full benefits of polysulfide pulping.

From the results it can be concluded that a 2% dose of polysulphide may be considered as optimum dose in order to get better pulp yield without affecting the physical strength properties.

3.4.2C: Effect of Alkali Charge and Sulphidity:

Polysulfide liquor is generated from the oxidation of sodium sulfide in kraft white liquor. Since the generation of PS consumes sodium sulfide, the nominal sulfidity of the PS liquor produced is decreased to about half to that of the original white liquor. When the PS liquor is heated during pulping, a portion of polysulphide in the liquor is converted back to sodium sulfide. Despite of this reversion, the sulphidity of PS cook remains lower than that of conventional kraft cooks. The lower sulfidity of PS liquor needs to increase the active alkali in PS cook for obtaining pulp with same kappa no. as in conventional 16% kraft cook. Therefore in PS pulping, a little higher active alkali charge (17%) was used in order to obtain the pulp with same kappa no. The results of the kraft pulping, polysulphide pulping alongwith AQ have been reported in tables 3.3C and 3.4C. It has been observed that the kappa no. of conventional kraft

pulp is comparable to that of polysulphide pulping with 17% active alkali along with 2% PS concentration. The effect of polysulphide pulping at 16% and 17% active alkali charge alongwith 1-3% polysulphide concentration on pulp yield and kappa no. are plotted in figure 3.1C to 3.4C. The R square values ranges from 0.91-1, which indicate the closeness of the fit of the data.. These results indicates that for obtaining lower kappa number pulp, a little higher active alkali is required during polysulphide as compared to kraft pulping.

3.4.4C: Effect of AQ (Alongwith PS):

The effect of AQ on polysulphide pulping was studied using 0.1% AQ, at 16% and 17% active alkali with 1-3% PS and the results have been reported in table 3.2C and 3.4C. On using 1%, 2%, 3% PS with 16% active alkali along with 0.1% AQ, increase the screened pulp yield to the tune of 2.1, 2.5% and 2.8% respectively, as compared to kraft-AQ (16% active alkali + 0.1% AQ) process, while a net increase in pulp yield to the tune of 3.1, 3.6 and 3.9% respectively was observed in comparison to kraft process (16% active alkali). The results reported in table 3.1C and 3.2C clearly indicate that the magnitude of increase in pulp yield decline on increasing the time of cooking or it can be said that the magnitude of increase in pulp yield also showed a declining trend with respect to decrease in kappa number. On using PS (1%, 2%, 3%) at 16% active alkali alone increases the pulp yield to the tune of 1.4%, 2.0% and 2.2% respectively, as compared to 16% kraft process. The effect of time on kappa no. and pulp yield during PS-AQ pulping at 16% and 17% active alkali are plotted in figure 3.5C to 3.8C. The R square values ranges from 0.68-0.99, which indicate the closeness of the fit of the data. The regression co-efficient between total pulp yield, kappa number, screened yield at different active alkali at same time and temperature indicates strong dependence of these parameters of pulping conditions. These data clearly indicate that the PS and AQ have a combined effect on increasing pulp yield. The similar type of findings have also been reported in literature (23,86,94). One possible

mechanism may be that PS participates in AHQ-lignin and AQ-carbohydrate redox system; where partial regeneration or stabilization of PS takes place. The combined effect of PS-AQ is likely to be more pronounced in the early stages of the cooking, since at a temperature above 140^0C, the PS readily undergoes thermal decomposition (38). The AQ also oxidize the C-2 and C-3 hydroxyl groups in sugar units to form carbonyl group. Thus the combined use of PS and AQ has the optimum effect in order to get the maximum benefit for carbohydrate stabilization.

The pulping studies also showed that by using AQ at the same conditions of polysulphide pulping decreases kappa no. by 10 to 15%. The kappa number obtained by polysulfide cooking is higher than the conventional kraft pulp at the same active alkali level. The effect of time on kappa number during the pulping at 16% and 17% active alkali are plotted in figure 3.7C and 3.8C. The use of polysulphide and AQ decreases the kappa number and the kappa number so obtained is quite comparable to conventional kraft at the same active alkali level. The kappa number of conventional kraft, 1% PS-AQ, 2% PS-AQ, 3% PS-AQ (all at 16% active alkali) are 15.2, 17.6, 16.8 and 16.0 respectively.

3.5C: Pulp Evaluation:

These pulps were evaluated for screened pulp yield, rejects, and kappa number (table 3.1C and 3.3C). The beating of the PS and PS-AQ pulps to different freeness levels was carried out in PFI mill according to Tappi method 248cm-85 and hand sheets of 60 gsm were prepared according to Tappi method T-205. The hand sheets were evaluated for strength characteristics according to Tappi 220 on-88 method after condioning at 27± 1°C and relative humidity 65±2%. The results of the pulp evaluation are reported in table 3.5C and 3.6C.

The pulp evaluation data of the polysulfide and polysulfide-AQ pulps are reported in table-3.5C and 3.6C. The results of the tear strength shows that PS, PS-AQ pulps have slightly lower tear than the conventional kraft pulp. The tear index of kraft, 2% PS, 2% PS-AQ pulp at the

freeness of around 310 (ml) CSF are 7.2, 6.8, 7.1 respectively. The tear index of PS-AQ pulp has been found to be comparable to the conventional kraft pulp. The tensile index of polysulfide pulp has been found to be slightly lower than that of kraft pulp, at equal freeness level. The tensile index values at around 310 ml CSF of 16% kraft, 2% PS, 2% PS + 0.1% AQ pulps at 16% active alkali are 71.0, 65.3 and 67.7 respectively. The PS and PS-AQ pulps have slightly lower burst values than the conventional kraft pulp. The plots of pulp freeness versus tear, tensile and burst index at different PS pulping of poplar deltoides are shown in fig.3.9C, 3.10C and 3.11C. The regression co-efficient between tear, tensile and burst index at different freeness 0.81 -0.95 (not reported in figures), which indicates strong dependence of these parameters.

Fig.3.13C shows the tear tensile relationship for the handsheets of kraft, PS, PS-AQ pulps at different freeness levels. The PS and PS-AQ pulps shows slight decrease in tear strength when refined to lower CSF, while on the other hand, the tensile index values shows a slight improvement at the same freeness level. These results indicate that pulping to higher kappa number produces the pulp with higher tear while the low kappa pulping has lower tear due to higher carbohydrate degradation. The burst index values of PS and PS-AQ pulps have been found to be slightly lower than that of kraft pulp.

The effect of freeness on the tear, tensile and burst for kraft, PS and PS-AQ pulps have been plotted in figures 3.9C, 3.10C and 3.12C. These figures clearly indicated that the burst and tensile values improves upto 300ml CSF while the tear declines. The tensile and burst index depends on the extent of pulping and refining conditions. The more delignified pulp shows poor tensile and burst index due to higher carbohydrate degradation. Although the difference in burst strength of kraft, PS and PS-AQ pulps have been found to be small. The freeness value data indicate that the PS-AQ pulp can be refined with lesser energy than the conventional kraft pulps, due to comparatively higher retention of hemicellulose contents.

3.6C Conclusions:

The use of PS and PS-AQ shows a significant increase in the pulp yield. When PS is used alone, the increase in pulp yield was found to be around 2.6%, on using 2% PS at 16% active alkali. In the combination of PS-AQ, the pulp yield increases significantly (around 3.1%). PS and PS-AQ processes can be used to decrease the kappa number at the same yield or increase the yield at the same kappa number. However, in polysulfide pulping, slightly higher active alkali is used then kraft pulp because the sulfidity of the polysulfide liquor falls during PS formation.
AQ can be used to decrease the additional alkali burden imposed while using PS. To provide the effectiveness of AQ in presence of PS, a lower nominal sulfidity of PS liquor is to be used. At an identical PS charge and active alkali, AQ afford greater reduction in kappa number.

The pulping studies shows that when polysulphide is used alone (without AQ), no significant decrease in kappa number was found even on increasing the active alkali by almost 1%. If PS and AQ are used in combination, the decrease in kappa no. was found to be significant with slight increase in active alkali (around 1%).

The PS-AQ pulp was found to be easily beatable than kraft pulps. The tear and burst values of the PS pulps were found to be slightly lower, while the tensile index values were found to be comparable with that of kraft pulp.

Table 3.1C: Effect of time on different polysulphide concentration during polysulphide pulping of Poplar deltiodes at 165 ^{0}C

Pulp	Time at Temperature (min.)	Screened pulp yield , % (±0.8)	Screen rejects, % (±0.2)	Total pulp yield, % (±1.0)	Kappa number	Lignin , % (±0.1)
16 % AA	60	56.2	3.4	60.1	26.3±1.0	4.0
20%,Sulf	90	53.6	1.6	55.2	17.6±0.5	2.4
(Kraft Pulp)	120	51.4	1.1	52.5	15.8±0.5	2.4
	60	60.3	5.7	66.3	35.0±1.5	6.2
16%,AA	90	57.2	3.2	60.4	28.2±1.0	4.6
12%,Sulf.	120	55.1	1.5	56.6	18.5±0.6	2.7
1%,PS	150	53.1	1.3	54.4	16.9±0.5	2.6
	60	63.2	5.0	68.2	34.3±1.5	5.5
16%,AA	90	59.0	2.8	61.8	28.3±1.0	4.3
12%,Sulf.	120	55.6	1.8	57.6	17.9±0.5	2.7
2%,PS	150	54.7	1.3	56.0	16.6±0.5	2.5
	60	64.8	4.2	69.0	33.0±1.5	5.5
16%,AA	90	60.1	2.6	62.7	27.0±1.0	4.3
12%,Sulf.	120	55.8	1.4	57.8	17.2±0.5	2.6
3%,PS	150	55.5	1.1	56.6	15.8±0.5	2.45
	60	58.2	4.2	62.4	35.0±1.5	5.9
17%,AA	90	56.0	3.0	59.0	27.6±1.0	4.4
12%,Sulf.	120	54.3	1.4	56.6	16.4±0.5	2.5
1%,PS	150	51.7	1.2	52.9	15.4±0.5	2.4
	60	60.1	3.9	64.0	32.6±1.5	5.5
17%,AA	90	58.2	2.7	60.2	26.1±1.0	4.0
12%,Sulf.	120	55.2	1.4	56.6	17.2±0.5	2.3
2%,PS	150	53.2	1.0	54.2	14.3±0.5	2.2
	60	60.6	4.0	64.6	31.2±1.5	5.2
17%,AA	90	58.6	2.8	61.4	24.5±1.0	3.8
12%,Sulf.	120	55.2	1.3	56.5	14.9±0.5	2.3
3%,PS	150	54.0	1.0	55.0	14.3±0.5	2.2

Table 3.2C: Effect of time on different polysulphide concentration during polysulphide –AQ (0.1%) pulping of Poplar deltiodes at 165 ^{0}C

Pulp	Time at temperature (min.)	Screened pulp yield , % (±0.8)	Screen rejects, % (±0.2)	Total pulp yield, % (±1.0)	Kappa number	Lignin , % (±0.1)
16 % AA	60	57.5	3.2	60.7	24.0±1.0	3.6
20%,Sulf	90	54.7	1.3	56.0	17.8±0.5	2.7
(Kraft Pulp)	120	52.0	0.9	52.9	15.2±0.5	2.2
16%,AA	60	60.9	5.1	66.0	38.0±1.5	5.9
12%,Sulf.	90	59.2	3.0	62.2	29.1±1.2	4.4
1%,PS	120	56.8	1.4	58.2	17.6±0.5	2.4
	150	54.0	1.0	55.0	17.0±0.5	2.3
16%,AA	60	62.2	4.5	66.7	35.6±1.5	5.2
12%,Sulf.	90	60.1	2.6	62.7	26.3±1.0	3.8
2%,PS	120	57.2	1.5	58.7	16.8±0.5	2.3
	150	55.9	1.1	57.0	16.5±0.5	2.2
16%,AA	60	63.4	4.3	67.7	34.1±1.5	5.2
12%,Sulf.	90	61.3	2.4	63.7	25.6±1.0	3.8
3%,PS	120	57.5	1.3	58.8	16.0±0.5	2.2
	150	56.2	1.1	57.3	15.8±0.5	2.2
17%,AA	60	61.0	4.7	65.7	36.6±1.5	5.5
12%,Sulf.	90	58.1	2.6	60.7	26.2±1.0	3.9
1%,PS	120	55.7	1.2	56.9	15.7±0.5	2.2
	150	53.5	1.0	54.5	15.2±0.5	2.2
17%,AA	60	63.2	4.4	67.6	35.4±1.5	5.5
12%,Sulf.	90	60.3	2.5	62.8	26.0±1.0	3.9
2%,PS	120	57.0	1.2	58.1	14.7±0.5	2.2
	150	55.3	0.9	56.2	14.0±0.5	2.2
17%,AA	60	63.6	4.4	68.0	32.6±1.5	5.3
12%,Sulf.	90	60.6	2.4	63.0	24.1±1.0	3.7
3%,PS	120	57.2	1.1	58.3	13.9±0.5	2.1
	150	55.7	0.9	56.6	13.7±0.5	2.1

Table 3.3C: Effect of active alkali, sulphidity and polysulphide concentration on pulp and black liquor properties, at following conditions

Max. Temperature : 165^0C
Time at Temperature : 120 Minutes
Bath Ratio : 1:3

Active alkali , % as Na_2O	14	14	14	16	16	16	16	17	17	17
lphidity, %	20	13	13	20	12	12	12	12	12	12
lysulphide, %	-	1	2	-	1	2	3	1	2	3
reened Pulp Yield,% (±0.8)	55.8	57.2	57.9	53.6	55.0	56.2	56.5	54.3	55.1	55.2
reen Rejects, % (±0.2)	1.6	1.7	1.8	1.4	1.5	1.4	1.3	1.4	1.4	1.3
tal Pulp Yield, % (±1.0)	57.4	58.9	59.7	55.0	56.5	57.6	57.8	55.7	56.5	56.5
ıppa number(±1.0)	21.8	23.1	24.0	15.6	17.6	16.9	16.2	16.4	15.2	14.9
ack liquor properties										
I (±0.1)	10.7	10.6	10.6	12.3	12.2	12.2	12.2	12.4	12.4	12.4
sidual Alkali, gpl (±0.2)	7.4	6.9	7.0	11.8	11.1	11.3	11.7	12.8	13.0	13.0
L Solids(±0.3)	16.2	16.0	16.1	17.0	17.2	17.4	17.3	17.2	17.2	17.0

Table 3.4C: Effect of active alkali, sulphidity and polysulphide,AQ concentration on pulp and black liquor properties, at following conditions

Max. Temperature : 165^0C
Time at Temperature : 120 Minutes
Bath Ratio : 1:3

Active alkali , % as Na_2O	14	14	14	16	16	16	16	17	17	
Sulphidity, %	20	13	13	20	12	12	12	12	12	
Polysulphide, %	-	1	2	-	1	2	3	1	2	
AQ ,%	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	(
Screened Pulp Yield,% (±0.8)	56.7	58.9	59.3	52.0	56.8	57.2	57.4	56.7	57.0	5
Screen Rejects, % (±0.2)	1.6	1.7	1.7	0.9	1.4	1.3	1.3	1.2	1.1	1
Total Pulp Yield, % (±1.0)	58.3	60.6	61.0	52.9	58.2	58.7	58.8	57.9	58.1	5
Kappa number(±1.0)	20.1	23.3	23.7	15.2	17.6	16.8	16.0	14.8	14.2	1
Black liquor properties										
pH (±0.1)	10.8	10.7	10.7	12.4	12.4	12.4	12.4	12.5	12.5	1
Residual Alkali, gpl(±0.2)	7.6	7.1	7.1	12.2	12.5	13.2	12.6	13.2	13.2	1
B/L Solids (±0.3)	16.0	16.1	16.2	16.6	16.3	16.4	16.5	16.7	16.7	1

Table 3.5 C: Strength properties of PS pulps at various freeness levels

Pulp	PFI Rev.	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.0.2)	Tensile Index (N.m/g) (±1.0)	Burst Index ($kPa.m^2/g$) (±0.2)	Tear Index ($mN.m^2/g$) (±0.3)
16%,AA	0	690	4.3	0.60	17.4	0.8	2.5
20%,Sulph	2000	540	5.4	0.69	45.7	3.2	4.1
(kraft pulp)	4000	320	7.6	0.76	71.0	5.0	7.2
	6000	180	15.6	0.79	72.6	4.4	5.3
16%,Kraft	0	700	4.3	0.61	16.1	0.7	2.2
12%,Sulph	2000	540	5.4	0.70	43.2	2.8	3.8
1%,PS	4000	310	7.8	0.76	67.0	4.4	6.6
	6000	180	15.8	0.79	68.3	4.2	4.9
16%,Kraft	0	690	4.3	0.62	16.0	0.7	2.3
12%,Sulph	2000	530	5.6	0.72	42.1	2.6	4.0
2%,PS	4000	310	8.0	0.78	65.3	4.1	6.8
	6000	180	16.2	0.79	66.7	3.9	5.1
16%,Kraft	0	690	4.3	0.62	16.0	0.7	2.3
12%,Sulph	2000	520	5.7	0.73	42.4	2.5	4.1
3%,PS	4000	300	8.1	0.76	64.8	3.9	6.9
	6000	170	16.6	0.79	65.9	3.8	5.1
17%,Kraft	0	680	4.5	0.64	16.8	0.7	2.3
12%,Sulph	2000	510	6.0	0.72	44.8	2.9	3.9
1%,PS	4000	300	8.3	0.76	68.4	4.6	6.7
	6000	180	16.4	0.79	69.7	4.3	4.9
17%,Kraft	0	680	4.5	0.65	16.6	0.7	2.4
12%,Sulph	2000	500	6.2	0.75	44.3	2.8	4.1
2%,PS	4000	290	8.4	0.79	67.3	4.4	6.9
	6000	170	16.8	0.80	68.2	4.1	5.0
17%,Kraft	0	680	4.5	0.66	16.5	0.7	2.5
12%,Sulph	2000	500	6.4	0.74	44.0	2.7	4.1
3%,PS	4000	290	8.5	0.79	66.4	4.4	7.0
	6000	170	17.2	0.81	67.0	4.2	5.1

Table 3.6C: Strength properties of PS-AQ pulps at various freeness levels

Pulp	PFI Rev.	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.02)	Tensile Index (N.m/g) (±1.0)	Burst Index ($kPa.m^2/g$) (±0.2)	Tear Index ($mN.m^2/g$) (±0.3)
16%,AA	0	680	4.3	0.62	17.8	0.8	2.7
20%,Sulph	2000	520	5.7	0.68	46.2	3.4	4.4
(kraft pulp)	4000	320	7.6	0.76	71.0	5.2	7.5
0.1%AQ	6000	180	16.0	0.78	72.3	4.8	5.4
16%,Kraft	0	680	4.4	0.62	16.5	0.8	2.4
12%,Sulph	2000	520	5.8	0.69	44.8	3.0	3.9
1%,PS	4000	310	7.9	0.76	68.3	4.7	6.9
0.1%AQ	6000	170	16.8	0.78	69.2	4.3	5.2
16%,Kraft	0	670	4.4	0.60	16.5	0.7	2.5
12%,Sulph	2000	510	6.2	0.72	44.6	2.9	4.1
2%,PS	4000	300	8.0	0.76	67.7	4.3	7.1
0.1%AQ	6000	170	17.1	0.78	68.9	4.0	5.2
16%,Kraft	0	670	4.4	0.61	16.6	0.7	2.6
12%,Sulph	2000	500	6.3	0.72	55.0	2.7	4.1
3%,PS	4000	290	8.3	0.76	67.1	4.0	7.2
0.1%AQ	6000	170	17.0	0.79	68.0	3.8	5.2
17%,Kraft	0	670	4.4	0.63	17.5	0.7	2.5
12%,Sulph	2000	490	6.5	0.73	45.0	3.2	4.0
1%,PS	4000	290	8.4	0.77	69.3	4.9	6.8
0.1%AQ	6000	180	16.9	0.79	70.1	4.5	5.1
17%,Kraft	0	670	4.4	0.62	17.3	0.7	2.5
12%,Sulph	2000	490	6.5	0.71	44.1	3.0	4.2
2%,PS	4000	290	8.6	0.76	68.0	4.6	7.1
0.1%AQ	6000	170	17.4	0.79	69.2	4.2	5.0
17%,Kraft	0	660	4.4	0.63	16.9	0.7	2.6
12%,Sulph	2000	470	6.7	0.72	43.6	2.8	4.2
3%,PS	4000	280	8.8	0.77	67.1	4.5	7.3
0.1%AQ	6000	170	17.8	0.79	68.0	4.2	5.3

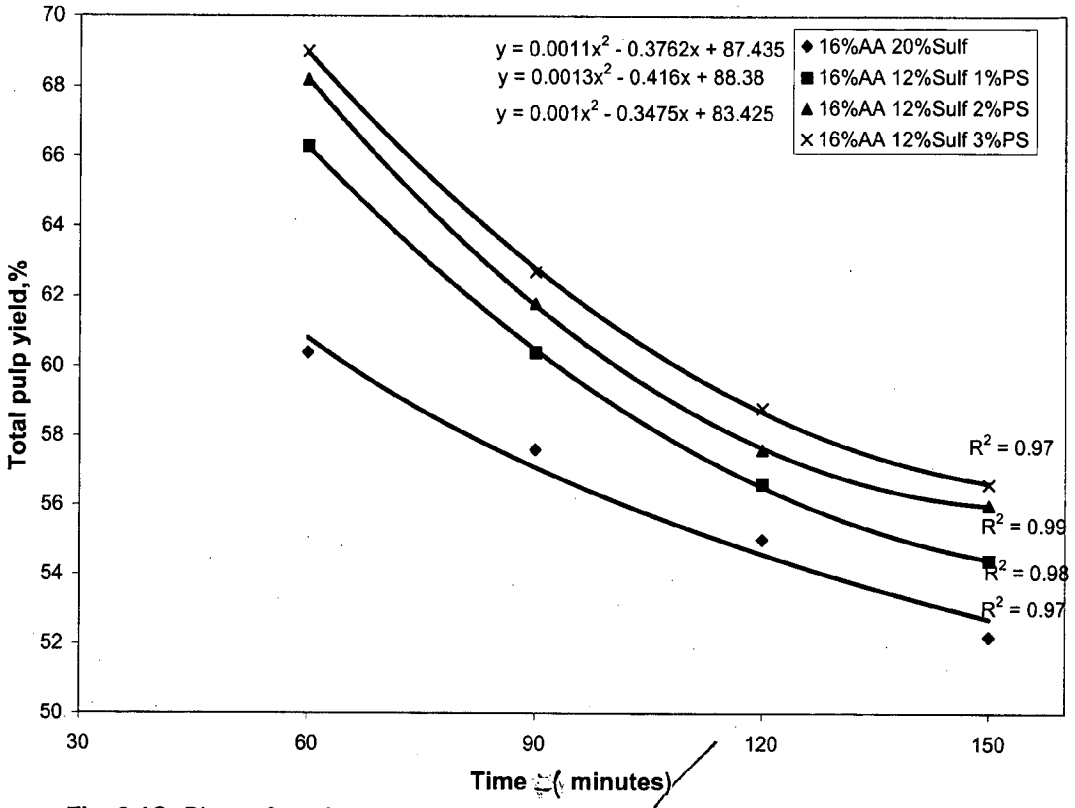


Fig. 3.1C: Plots of total pulp yield vs time at temperature (165 C) during polysulphide pulping at 16% active alkali of Poplar

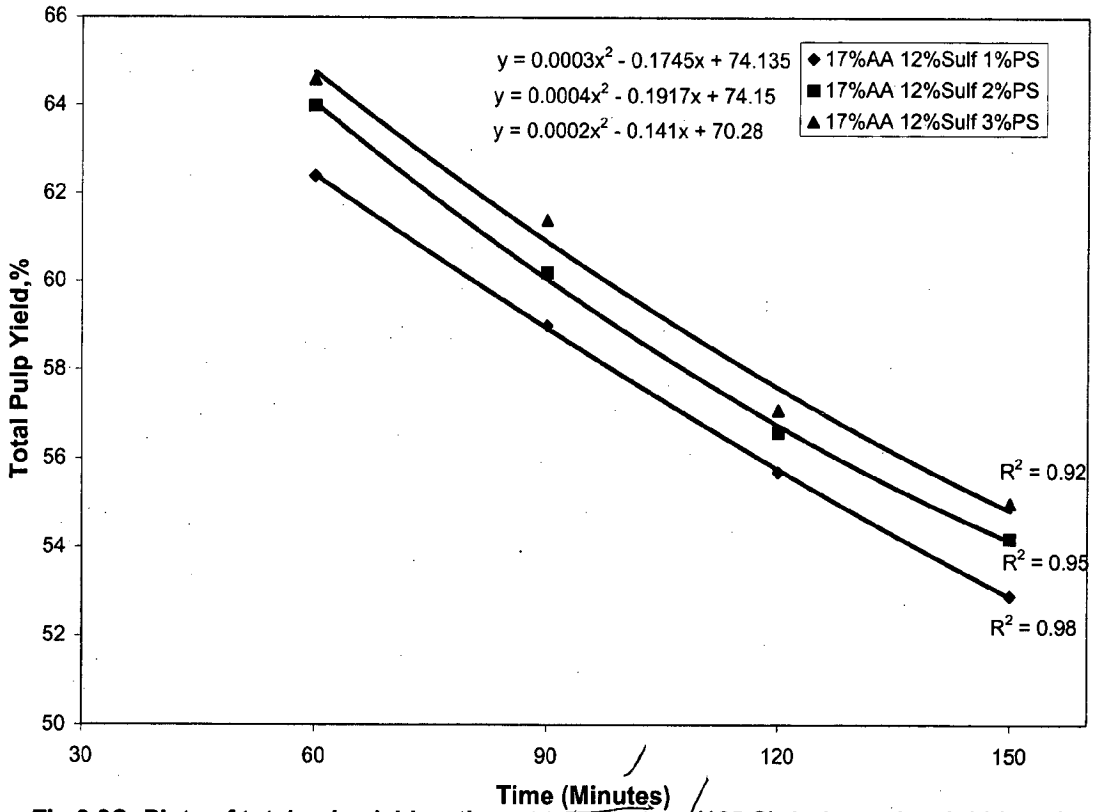


Fig 3.2C: Plots of total pulp yield vs time at temperature (165 C) during polysulphide pulping of Poplar deltoides

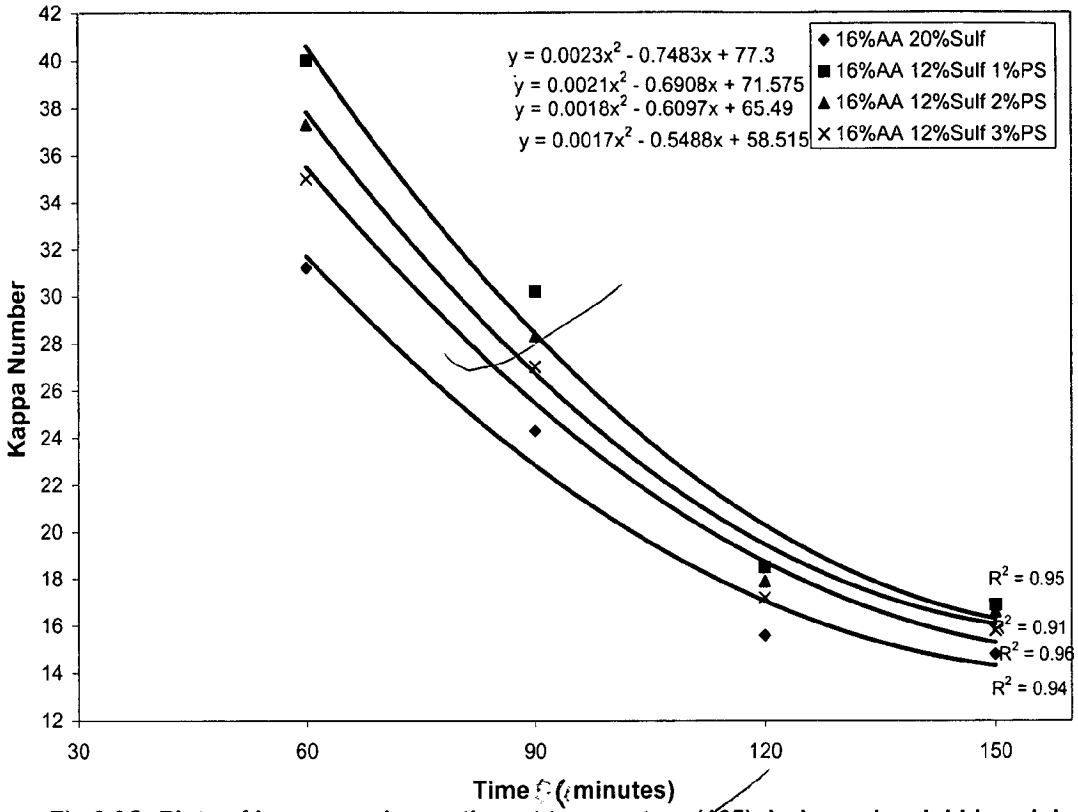


Fig 3.3C: Plots of kappa number vs time at temperature (165) during polysulphide pulping of Poplar deltoides.

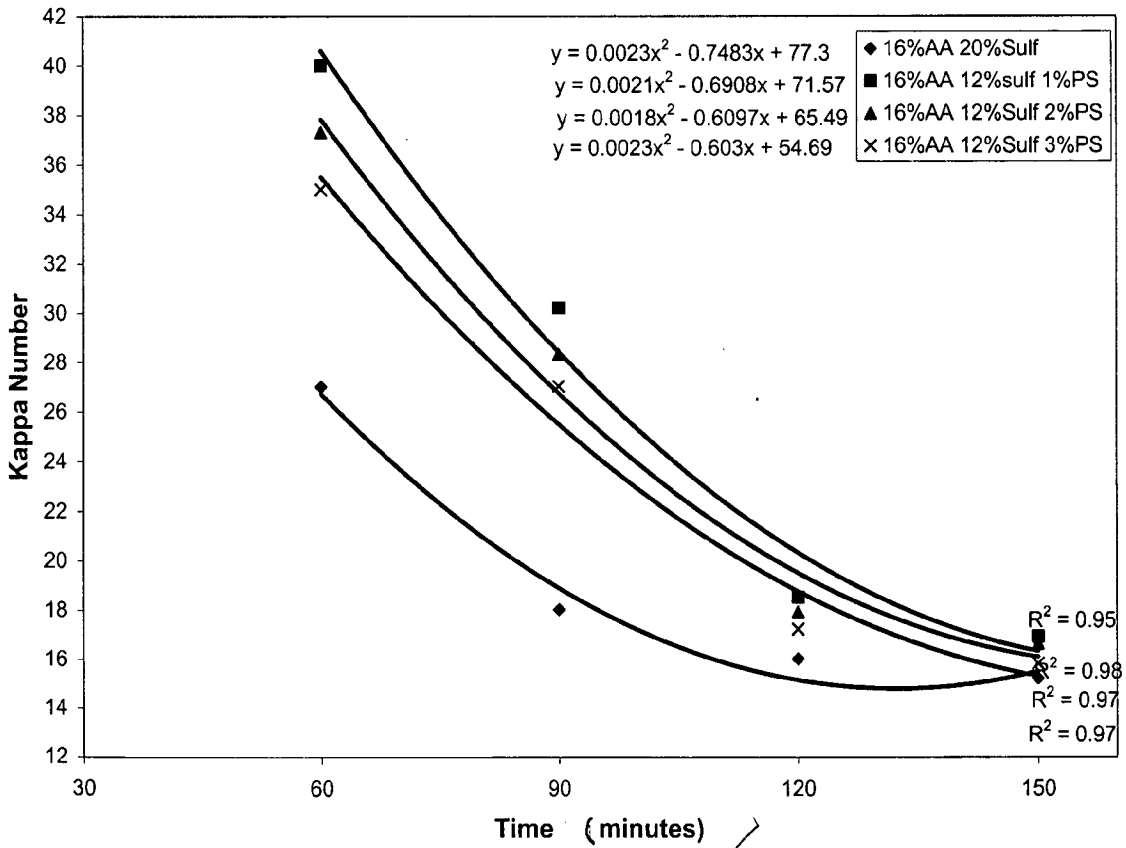


Fig. 3.4C: Plots of kappa number vs time (at temperature) at different polysulphide doses (16% active alkali) during polysulphide pulping.

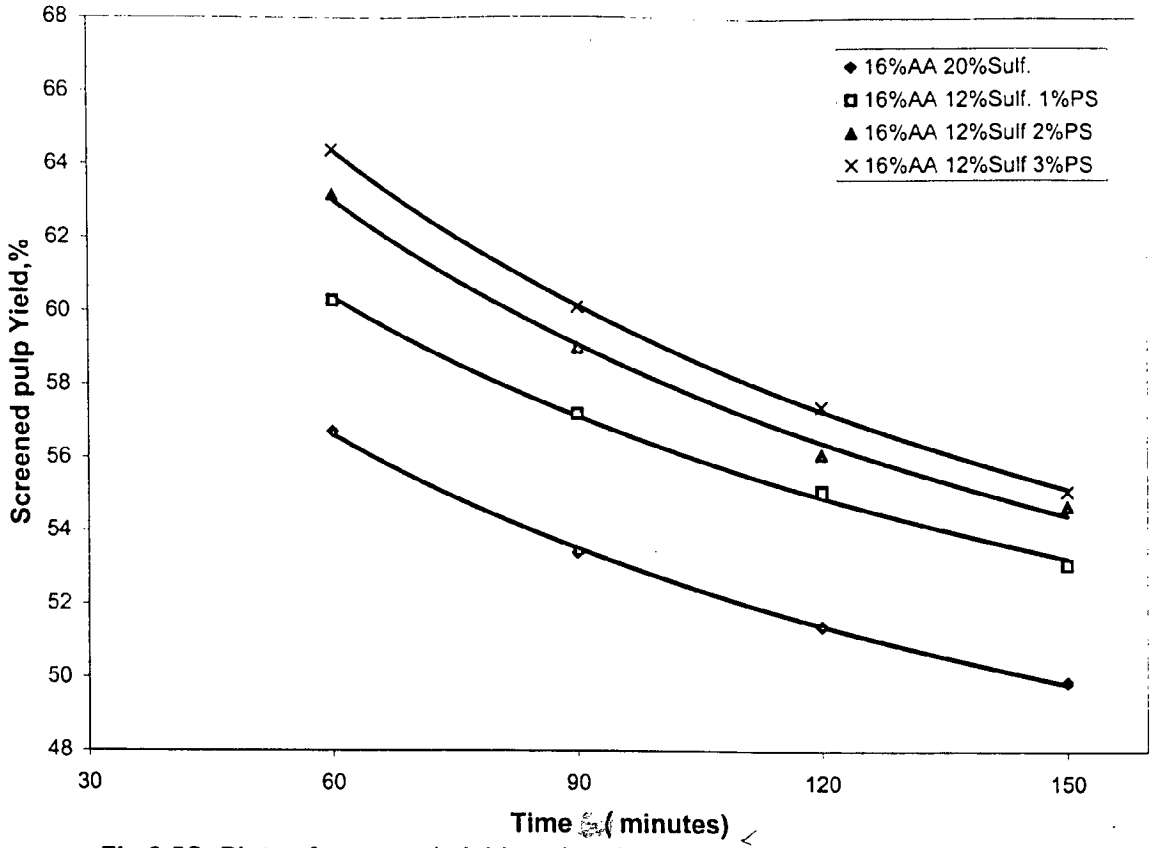


Fig 3.5C: Plots of screened yield vs time (at temp.) at different polysulphide doses at16% active alkali during polysulphide pulping.

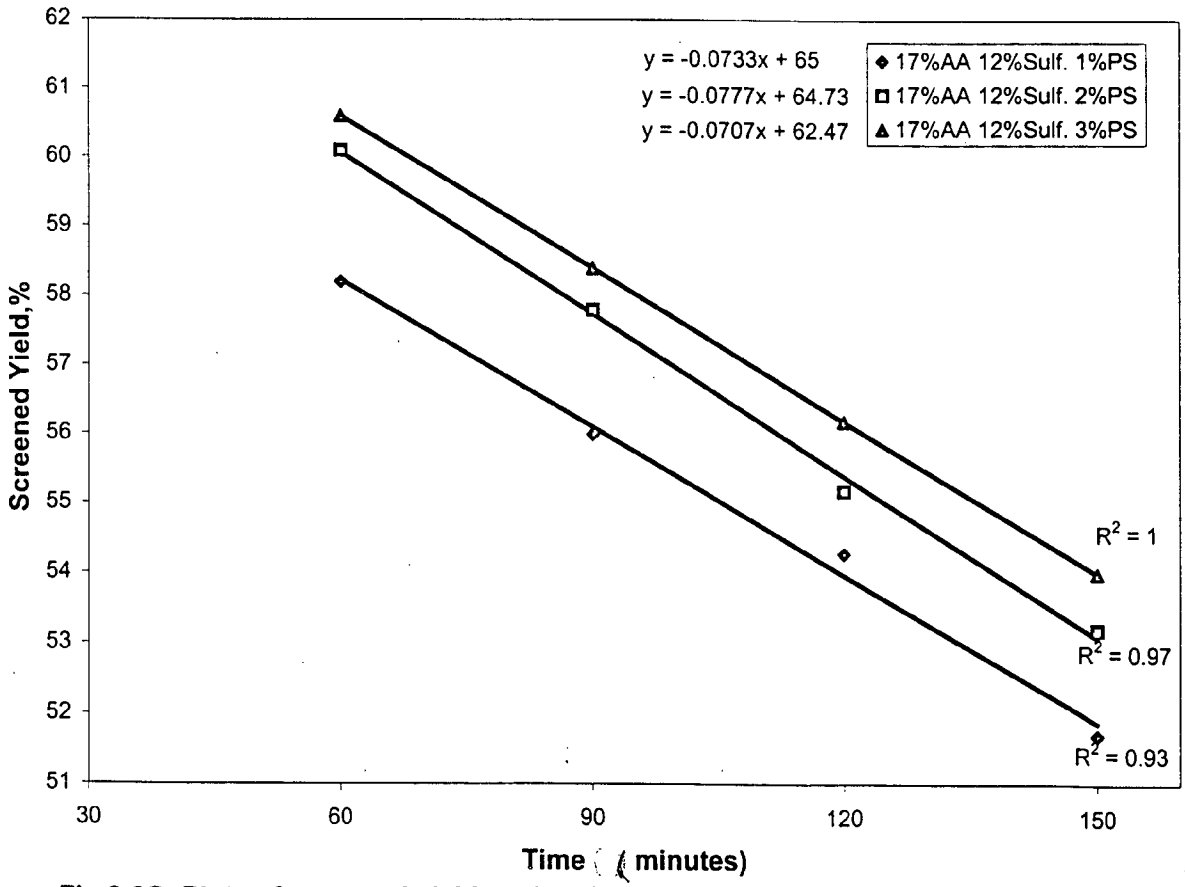


Fig 3.6C: Plots of screened yield vs time (at temp) at different polysulphide doses at 17% active alkali during polysulphide pulping.

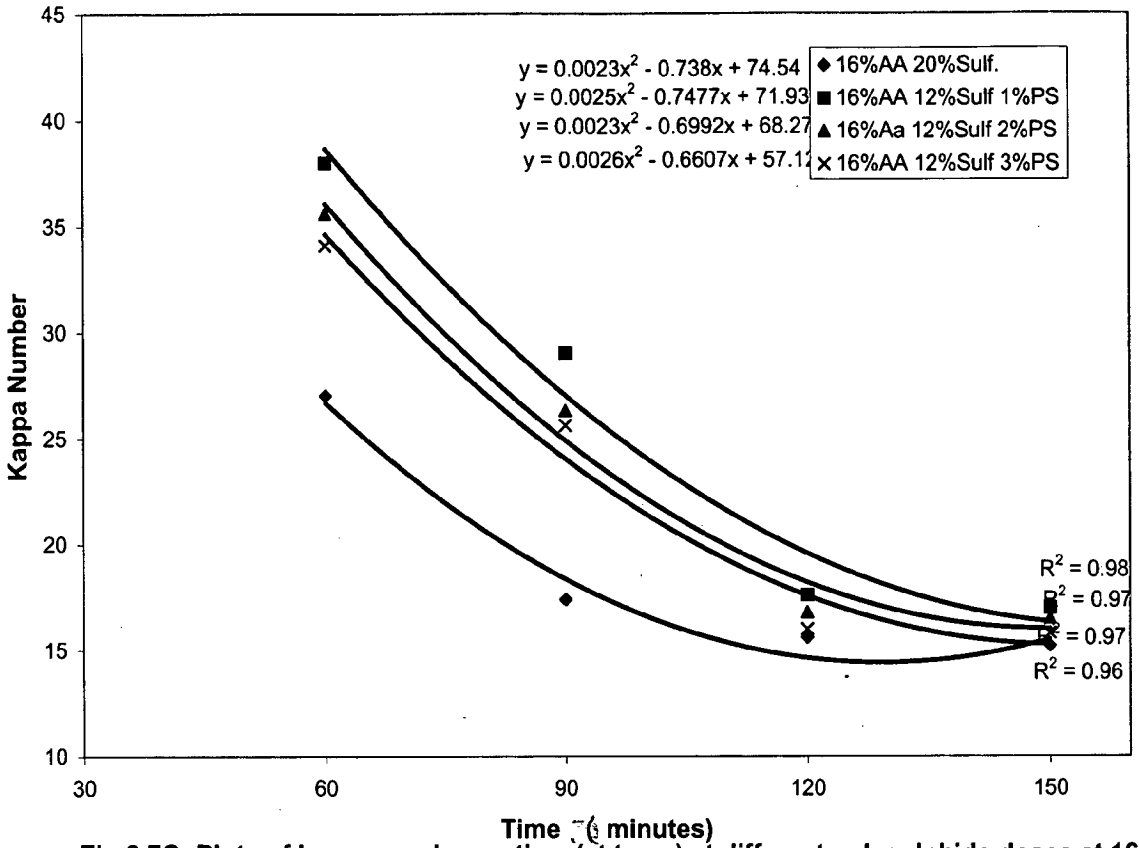


Fig 3.7C: Plots of kappa number vs time (at temp) at different polysulphide doses at 16% active alkali during polysulphide AQ pulping of Poplar.

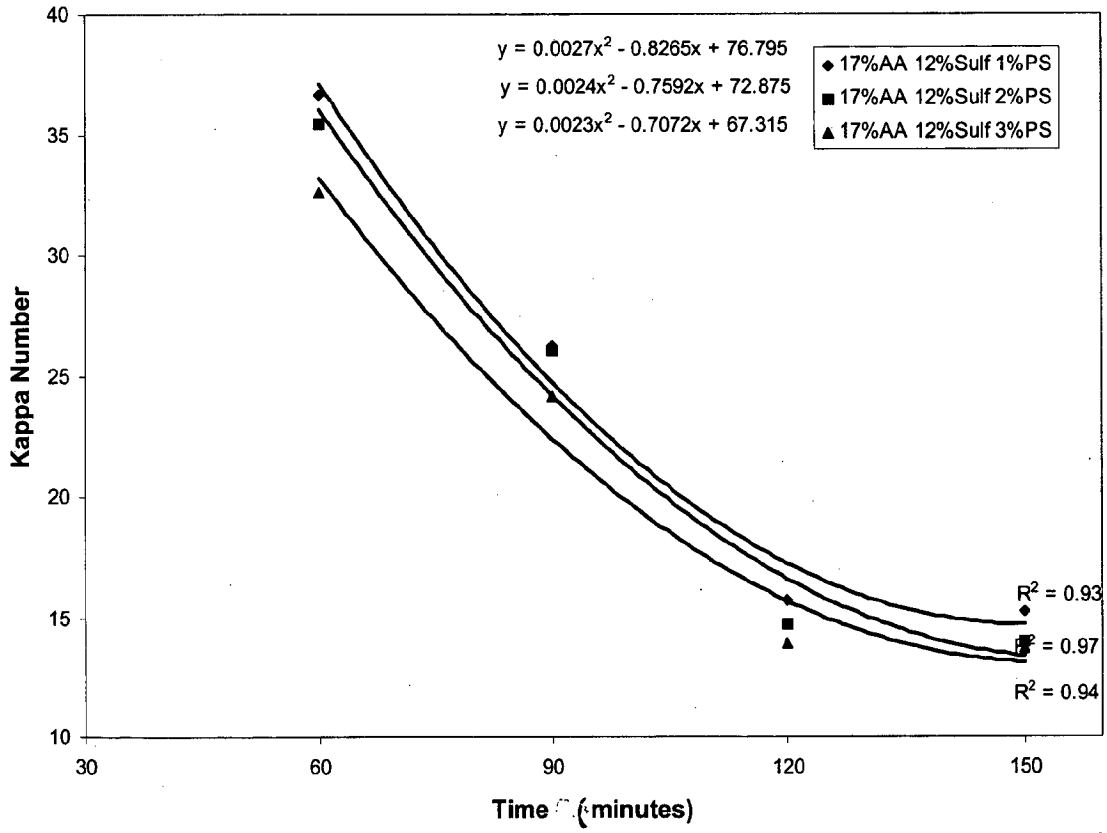


Fig 3.8C: Plots of kappa number vs time (at temp) at different polysulphide doses at 17% active alkali during polysulphide AQ pulping of Poplar.

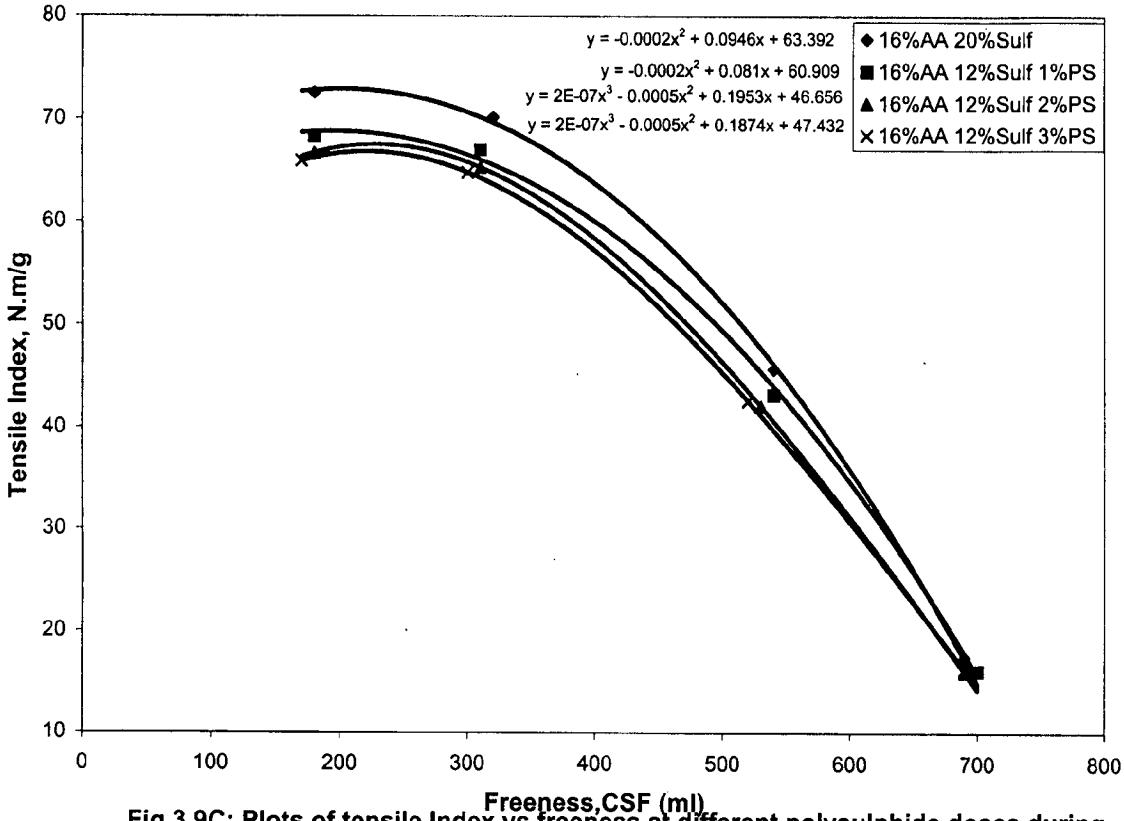


Fig 3.9C: Plots of tensile Index vs freeness at different polysulphide doses during polysulphide pulping at16% active alkali.

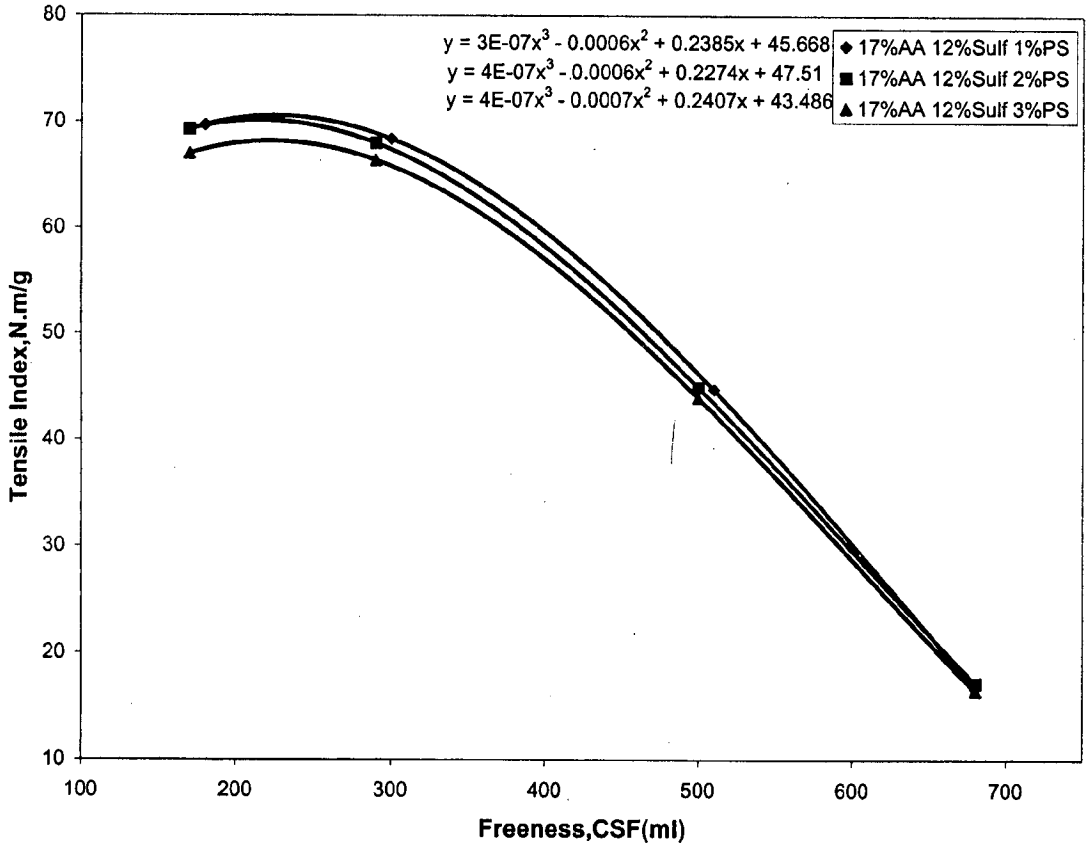


Fig 3.10C: Plots of tensile Index vs freeness at different polysulphide doses during polysulphide pulping at 17% active alkali

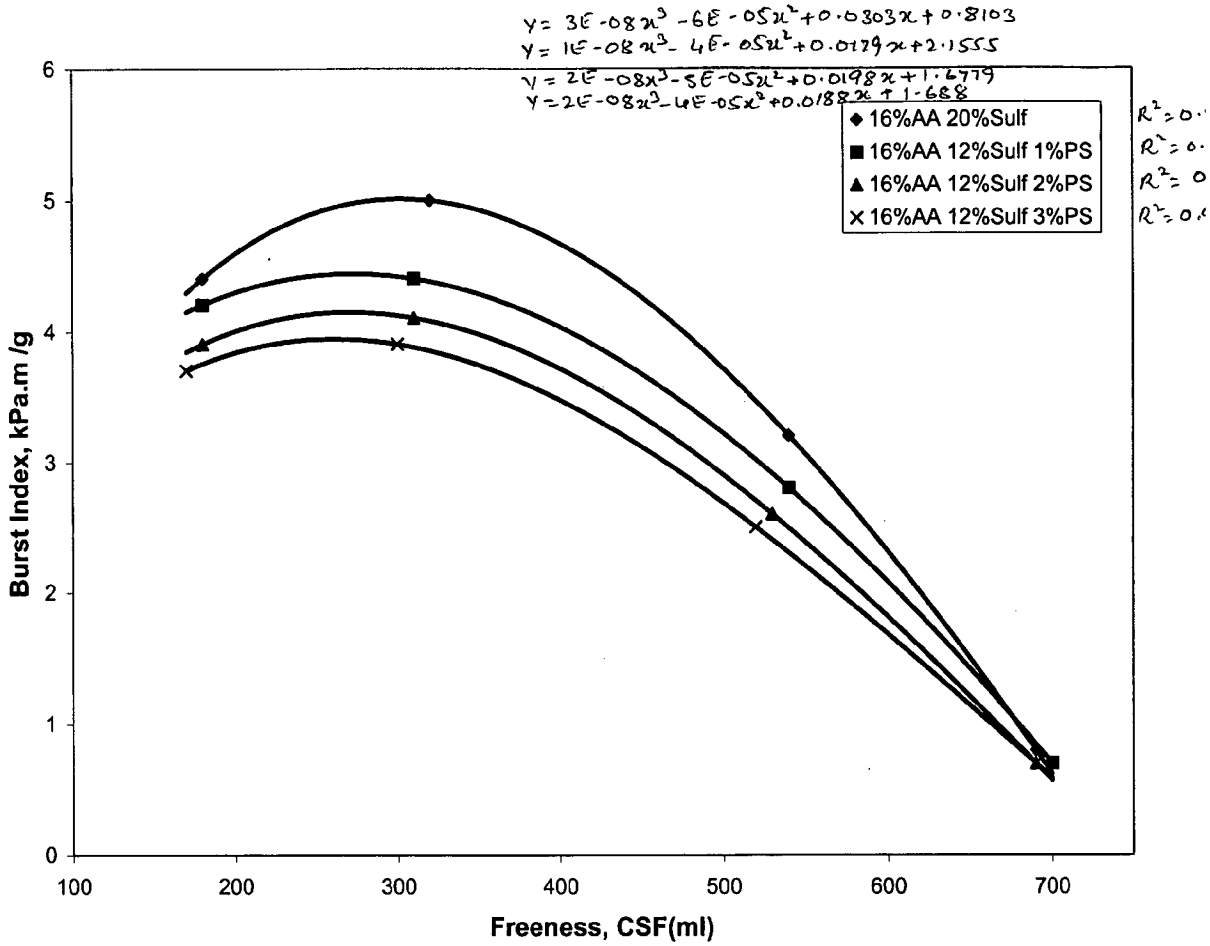


Fig 3.11C: Plots of burst Index vs freeness at different polysulphide doses during polysulphide pulping at 16% active alkali.

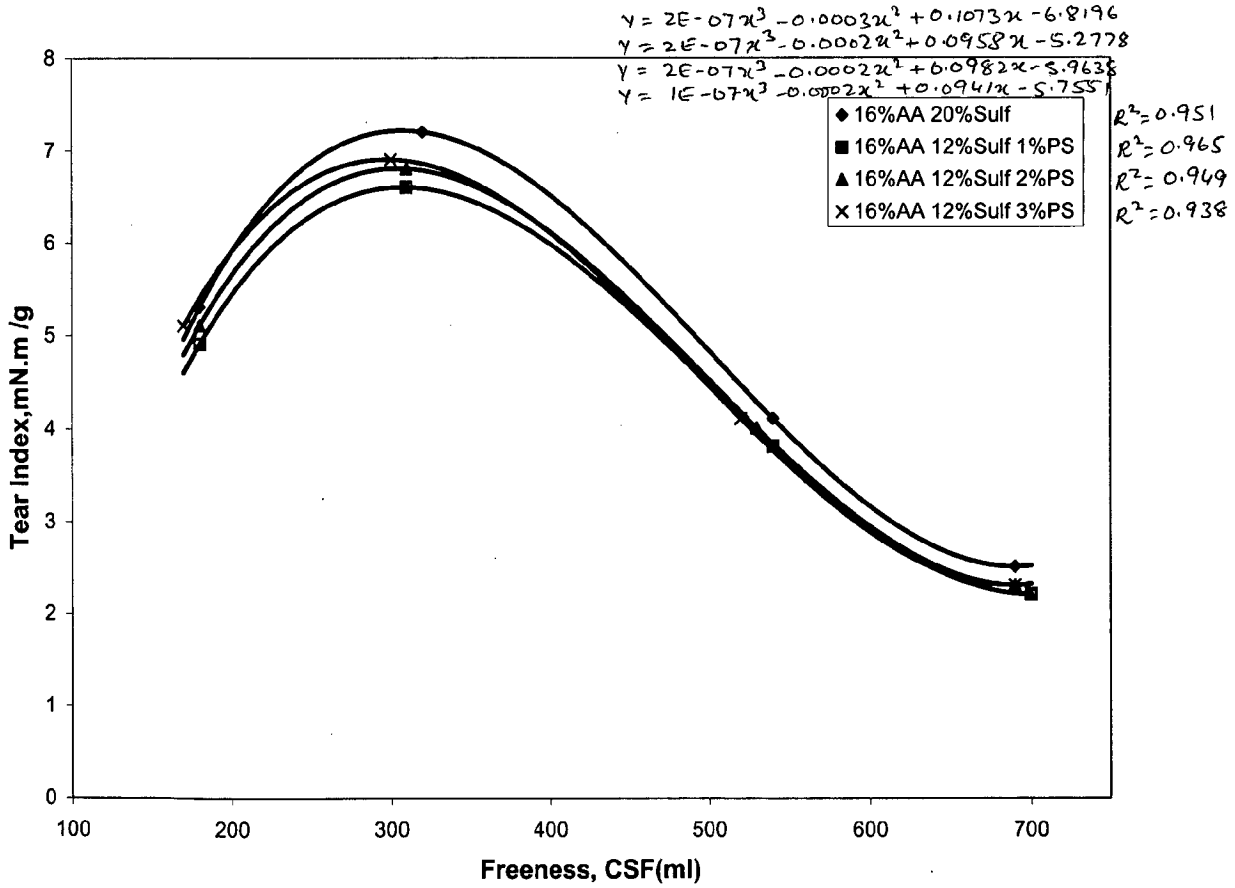


Fig 3.12C: Plots of tear Index vs freeness at different polysulphide doses during polysulphide pulping at 16% active alkali.

CHAPTER 3D

ALKALINE SULPHITE AND ALKALINE SULPHITE-AQ PULPING

3.1D Introduction:

High yield sulphite pulping of hardwoods has been investigated for making a low cost pulp for the production of newsprint, printing papers and tissue papers. Sulphite pulping under strong alkaline conditions using sodium sulphite (Na_2SO_3) and sodium hydroxide, to produces a pulp having strength properties comparable to kraft pulp (74,75,179). The alkaline sulphite approach does not produce odoriferous sulphides. Ingruber, made extensive studies in the field of alkaline sulphite pulping (74,75,76).

One of the attractive features of the AS-AQ process is its comparable characteristics with the conventional kraft process (75). Its inherent advantage to produce stronger pulps as kraft without kraft odor with low requirement of caustic soda. It necessitates the operation and maintenance of large units for the recausticisation of the spent pulping liquor at considerable expense and energy consumption. With the moderately alkaline process, the necessary alkalinity can be provided by soda ash, which is available directly from the recovery process. Therefore, the recausticization unit can be completely eliminated. The AS-AQ process is advantageous over the common kraft process, in terms of economy, product flexibility and elimination of kraft odor (74,180). The most promising initial application of the process is in the production of liner board and packaging grades of paper. Although alkaline sulphite processes have not achieved much industrial success in the pulping. The use of AS-AQ process are now being used commercially for making linerboard, corrugating medium and newsprint (76,163).

In the sulphite cook, a sulphonation reaction makes lignin hydrophillic, part of the lignin is broken down to the extent that it is dissolved, parts of the lignin is less hydrolysed and is still in the fiber contributing to the hydrophilicity of the pulp and improving its bonding ability.

The anthraquinone (AQ), has been found to be most effective pulping additive, accelerating delignification and protects carbohydrate degradation in alkaline environment (76). With the addition of AQ, both the cooking kinetics as well as the composition and the properties of the resulting pulp are profoundly altered (74). This process was not commercialized because of its slower delignification rate in comparison to kraft process. The use of AQ was found to be very effective in accelerating the sulphite delignification rate (75). It has been observed that the AQ addition has been generally much more effecting the alkaline sulphite process than the kraft process (179,212).

3.2:D Experimental Methodology:

The methods of raw material preparation have been discussed on page 39. For the optimum pulping conditions, the chips of Poplar deltoides were cooked in CCL digester, having 6 bombs of 2.5-litre capacity each, using a wood charge of about 300 gm o.d. chips, at a wood to liquor ratio of 1:3. Following time schedule for heating the digester was adopted.

Time from room temperature to 105 ^{0}C. = 45 minutes

Time from 105 ^{0}C to maximum temperature = 45 minutes

of cooking (180 ^{0}C)

3.3:D Optimum Conditions For Pulping:

The pulping studies were made using different ratios of sodium sulphite to sodium hydroxide in order to study the optimum ratio of these chemicals for the purpose of delignification. The cooking were also carried out for different time and temperature, to study the effect of cooking time and temperature during the course of delignification reaction. At the end

of the cook, the pulp was defibrated, washed and screened with a plate clearance of 0.15 mm. These pulps were evaluated for the screened pulp yield, kappa number and rejects. The spent liquors were analysed for pH and residual chemicals.

3.4: D Results and Discussion:

The experimental results for all the response parameters namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content are based on four sets of experiments of pulping at the same conditions of temperature, pressure, time at temperature with constant active alkali charge.

In the present investigation, data found from the laboratory experiments for a specific set of input parameters such as time, temperature, different alkali with different polisulphide etc. all the data are not reproduce the brevity of rather average data of the set is depicted in tables. However it is observed that there is marginal difference in the set of data which is permitted in this type of experiments. The variation in the responding variables were found to be well within the experimental error.

The statistic modelling the responding parameters during pulping namely total pulp yield screened pulp yield, screening rejects, kappa number and lignin content of the pulp were regressed with the time at temperature as independent variables. The responding variables of pulp evaluation such as tear index, tensile index and burst index were regressed with different freeness as independent variable. In most of the cases the quadratic model ($y = ax^2 + bx + c$, where a, b and c are parameters to be estimated) were obtained. Where y is the responding variable and x is the time at temperature, which is found to fit well to the data. The quadratic model reflects the behavoir of various pulping conditions and pulp evalution.

3.4.1:D Effect of Sodium Sulphite:

The results of pulping experiments of poplar deltoides at constant temperature and time with varying doses of sodium sulphite (6% to 12%, as Na_2O) (keeping the sodium hydroxide dose constant), are reported in table 3.1D. These results indicate that the amount of sodium sulphite charge has a considerable influence on the rate of delignification reaction. The pH of spent liquors were found to be less than 10. The data of table 3.1D have been plotted in figure 3.1D and 3.2D. The R square indicate the closeness of the fit of the data which indicates strong dependence of these parameters of pulping conditions. Which indicates that total pulp yield and kappa number showed a continuously decreasing trend with an increase in sodium sulphite doses (6-12%), which is responsible for enhance delignification. However, the screened pulp yield increases from 47.3% (at 6% Na_2SO_3) to 56.7% (at 9% Na_2SO_3); further addition of the sodium sulphite shows a decrease in screened pulp yield. Thus from the data of table 3.4.1D, a 10% Na_2SO_3 dose with 10% NaOH may be considered as the optimum dose for the alkaline sulphite delignification of Poplar deltoides.

3.4.2:D Effect of Time and Temperature:

The effect of time was studied in the series of experiment at constant doses of Na_2SO_3 and NaOH; and temperature, with varying time (60 to 210 minutes). The results of these experiments are reported in table 3.2D. These results (table 3.2D) and the plots of kappa no. vs sodium sulphite dose (fig.3.3D) and plots of total pulp yield vs time (fig.3.4D) indicates that the rate of delignification was found to be comparatively low in early stages of cooking, as already reported in literature (74,75,76,179), as lot of alkali is being consumed for neutralizing the extraneous component rather than delignification. Therefore, due to slower rate of delignification more time (at temperature) is required to achieve the desired degree of delignification. The

figures 3.4D also indicate a sharp drop in pulp yield beyond a time of 150 minutes due to degradation of carbohydrate materials corresponding to residual phase of delignification. The R square values indicate the closeness of the fit of the data which indicates strong dependence of these parameters of pulping conditions. Thus a time at temperature for 150 minutes may be taken as optimum time for AS pulping.

The studies on effect of temperature were conducted at optimum level of parameters except temperature, which was varied from 150 ^{0}C to 190 ^{0}C. These experiments were conducted at different temperature (varying from 150 to180 ^{0}C) keeping all other cooking parameters constant (time at maximum temperature 180 minutes, and wood to liquor ratio of 1:3). The results of these experiments are reported in table 3.3D, table 3.4D and figure 3.5D and 3.6D (R square values 0.96, 0.94 respectively indicating the closeness of the fit of the data). These data clearly indicate that both the pulp yield and kappa number decreased with increase in time and temperature. It has also been observed that beyond a temperature of 180 °C, the kappa number remained almost practically constant while a significant drop in yield has been observed and this may be due to the depolymerisation of carbohydrates contents. Therefore, a temperature of 180 °C may be considered as an optimum temperature for AS pulping of poplar deltoides.

3.4.2:D Effect of Alkali Concentration:

The effect of alkali concentration was studied in a series of experiment conducted at constant temperature of 180 °C, time 2.5 hours with varying alkali dose of NaOH (6 to 10%; as Na_2O). The results of these experiments are reported in table 3.4D. Table 3.4D and figures 3.7D and 3.8D indicate that the rate of delignification showed an indirect proportional relationship with both pulp yield and kappa number. On increasing the NaOH charge from 6% to 14% (as Na_2O), the kappa number decreased from 59.3 to 16.2 and the total pulp yield decreased from 72.4% to 50.1% respectively. Figure 3.7D and 3.8D shows that there is a continuous decrease in

both the pulp yield and kappa number during the entire course of delignification. The sharp decrease in pulp yield and kappa number or high rate of delignification is undoubtedly due to the high alkali concentration in the cooking liquors.

3.4.4D: Effect of AQ:

As discussed earlier, AQ has an advantageous effect in increasing the pulp yield as well as to enhance delignification. The effect of AQ during AS pulping was studied using different doses of AQ i.e. (0.05, 0.1, 0.2%) with10% Na_2SO_3 and 10% NaOH. The results of these experiments are reported in table 3.5D. The addition of small amount of AQ (0.1%) during alkaline sulphite pulping showed a significant influence on both pulping characteristics and strength properties. The AQ assist in accelerating the rate of delignification during AS-AQ pulping, comparable to kraft alongwith a gain in pulp yield with initial higher brightness values (76,180).

3.5D: Pulp Evaluation:

The beating of the AS and AS-AQ pulps to different freeness levels was carried out in PFI mill according to Tappi method 248cm-85 and hand sheets of 60 gsm were prepared according to Tappi method T-205. The hand sheets were evaluated for strength characteristics according to Tappi 220 on-88 method after condioning at 27± 1°C and relative humidity 65±2%. The results of the pulp evaluation are reported in table 3.5C and 3.6C. were beaten in PFI mill at 2000, 4000, 6000 revolutions, to obtain different freeness levels. The handsheets were made as per TAPPI standard method. The results of evaluation of the physical strength properties of unbleached AS and AS-AQ pulps of poplar deltoides are reported in table 3.6D and 3.7D respectively. The initial freeness of both the pulps were found to be higher. The freeness of unbeaten AS and AS-AQ pulp were found to be 700 CSF. The burst index and tear index increases upto a freeness level of around 300 CSF and beyond that the burst index and tear index

both showed a decline trend as shown in figure 3.11D and 3.12D respectively, while the tensile shows a slight increase as shown in fig 3.10D. The regression co-efficient between tear, tensile and burst index at different freeness 0.80 -0.94 (not reported in figures), which indicates strong dependence of these parameters.

The strength properties showed a declining trend as a result of over beating beyond a optimum level, whereas tear index first showed a little enhancement and then a continuous sharp decline. The drop in tear index at high level of tensile strength is not caused by an increase in the ratio of fiber fracture to pull out. It is the result of fiber damage brought about by tearing. It also appears that these fibers are more susceptible to weakening by prolong beating. Therefore, these pulps should not be beaten beyond their optimum freeness level of about 300 ml. CSF.

3.6D: Conclusions:

By using the AS-AQ pulping process, one can get most of the advantages of the kraft pulping process alongwith a substantial gain in the initial brightness of AS pulp. The same rate of delignification can be obtained with strongly alkaline sulphite cooking using 0.1% AQ at a 10 °C higher temperature. Paper making properties are exceptionally good despite of higher yield. The pulp yield of AS-AQ pulping is around 5% higher than the kraft process at a kappa number 24. At lower kappa pulping the increase in pulp yield is around 2%. Although the chemical charge in AS-AQ pulping is considerably higher and the cooking time is also more but the overall quality of the AS-AQ pulp is quite comparable with that of kraft process with initial higher brightness values. The AS and AS-AQ pulping requires mechanical action to fiberize the stock before screening. The lower kappa number AS-AQ pulps have comparable strength properties with that of kraft process.

Table 3.1D: Effect of Sodium Sulphite during AS pulping of Poplar deltoides at 180°C,for 150 minutes.

Chemical Charge, % on o.d Wood (as Na_2O) Na_2SO_3	NaOH	Screened pulp yield, % (±0.8)	Screen rejects, %	Total pulp yield, % (±1.2)	Kappa number	pH (±0.1)
6.0	10	47.3	18.1±1.5	65.4	55.0±2.0	8.8
7.0	10	51.8	11.2±1.2	63.0	48.3±1.8	9.2
8.0	10	53.9	7.3±1.0	61.2	39.2±1.5	9.4
9.0	10	56.7	3.9±0.5	60.6	33.2±1.2	9.6
10.0	10	56.4	2.3±0.2	58.7	25.1±1.0	9.7
11.0	10	55.0	1.9±0.2	56.9	23.4±1.0	9.8
12.0	10	54.3	1.8±0.2	56.1	22.1±1.0	9.8

Table 3.2D: Effect of time at constant chemical charge during AS pulping of Poplar deltoides at 180°C.

Chemical Charge, % on o.d Wood (as Na_2O) Na_2SO_3	NaOH	Time at Temp, (min)	Screened pulp yield, % (±0.8)	Screen rejects, %	Total pulp yield, % (±1.2)	Kappa number	pH (±0.1)
10	10	60	44.4	27.2±2.0	71.6	74.6±3.0	11.2
10	10	90	54.1	14.2±1.5	68.3	58.2±2.0	11.1
10	10	120	57.3	7.4±1.0	64.7	39.3±1.5	11.0
10	10	150	56.4	2.3±0.2	58.7	25.1±1.0	10.8
10	10	180	55.1	2.1±0.2	57.2	23.7±1.0	10.7
10	10	210	51.2	1.3±0.2	52.5	18.4±0.8	10.7

Table 3.3D: Effect of Temperature (150 to 190°C) during AS pulping of Poplar deltoides using 10% Na_2SO_3 and 10%NaOH.

Chemical Charge, % on o.d Wood (as Na_2O)		Temp, (°C)	Screened pulp yield , % (±0.8)	Screen rejects, %	Total pulp yield, % (±1.2)	Kappa number	pH (±0.1)
Na_2SO_3	NaOH						
10	10	150	54.8	14.2±1.3	69.0	60.2±2.0	11.0
10	10	160	60.6	5.9±0.5	66.5	47.2±1.5	10.9
10	10	170	59.8	3.4±0.2	63.2	38.1±1.2	10.8
10	10	180	56.4	2.3±0.2	58.7	25.1±1.0	10.7
10	10	190	53.2	1.1±0.1	54.3	19.8±1.0	10.7

Table 3.4D: Effect of Sodium hydroxide (at constant dose of sodium sulphite) during AS pulping of Poplar deltoides at 180°C,for 150 minutes.

Chemical Charge, % on o.d Wood (as Na_2O)		Screened pulp yield , % (±0.8)	Screen rejects, %	Total pulp yield, % (±1.0)	Kappa number (±1.0)	pH (±0.1)
Na_2SO_3	NaOH					
10	6	43.7	28.7±2.0	72.4	59.3	9.9
10	8	48.2	17.8±1.3	65.0	42.9	10.3
10	10	56.4	2.3±0.2	58.7	25.1	10.7
10	12	52.6	1.3±0.1	53.9	19.9	11.2
10	14	51.1	1.0±0.1	50.1	16.2	11.4

Table 3.5D: Effect of AQ at constant chemical charge during AS pulping of Poplar deltoides at 180°C,for 150 minutes.

Chemical Charge, % on o.d Wood (as Na_2O)		AQ, (%)	Screened pulp yield , % (±0.8)	Screen rejects, % (±0.2)	Total pulp yield, % (±1.0)	Kappa number (±1.0)	pH (±0.1)
Na_2SO_3	NaOH						
10	10	0.05	57.1	1.9	59.0	23.2	10.7
10	10	0.10	58.2	1.7	59.9	22.8	10.7
10	10	0.20	58.4	1.7	60.1	22.5	10.7

Table 3.6D: Strength properties of unbleached AS pulp of Poplar deltoides at optimum condition as mentioned below.
Maximum temperature: 180°C
Time at temperature: 150 min
NaOH ; 10%, Na_2SO_3 :10%
Wood to liquor ratio : 1:3

PFI Revolutions	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.0.2)	Tensile Index (N.m/g) (±1.2)	Tear Index ($mN.m^2/g$) (±0.2)	Burst Index ($kPa.m^2/g$) (±0.2)
0	700	4.2	0.60	16.1	1.7	0.6
2000	530	5.3	0.69	38.1	3.6	2.2
4000	330	7.7	0.76	59.4	5.8	3.9
6000	190	17.0	0.80	61.2	5.2	3.6

Table 3.7D: Strength properties of unbleached AS-AQ pulp of poplar deltoides at optimum condition as mentioned below.
Maximum temperature: 180°C
Time at temperature: 150 min
NaOH ; 10%,Na_2SO_3 :10% ,AQ 0.1%
Wood to liquor ratio : 1:3

PFI Revolutions	Freeness CSF (ml) (±10)	Drainage time (sec.) (±0.1)	Apparent Density (gm/cm^3) (±0.0.2)	Tensile Index (N.m/g) (±1.2)	Tear Index ($mN.m^2/g$) (±0.2)	Burst Index ($kPa.m^2/g$) (±0.2)
0	690	4.2	0.60	16.3	1.8	0.6
2000	510	5.3	0.69	40.9	3.8	2.3
4000	290	7.9	0.76	59.7	5.9	4.1
6000	180	17.8	0.80	60.8	5.4	3.9

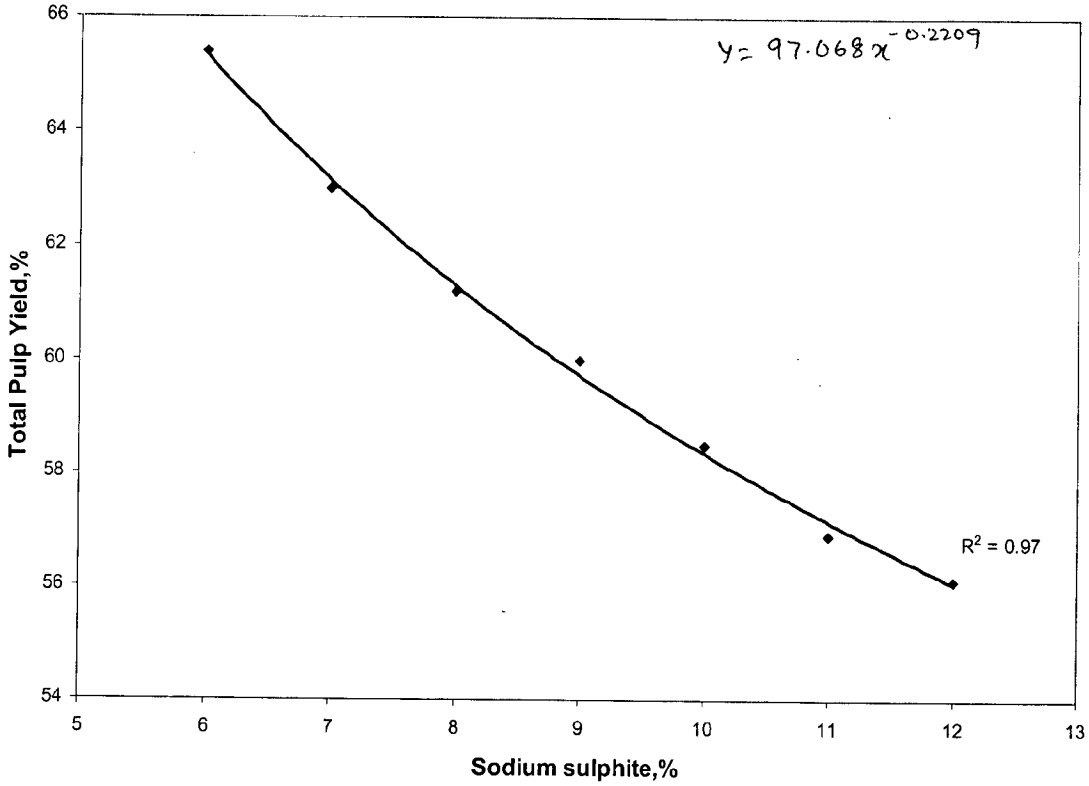


Fig 3.1D: Plots of effect of sodium sulphite doses vs total pulp yield during alkaline sulphite pulping using 10% NaOH.

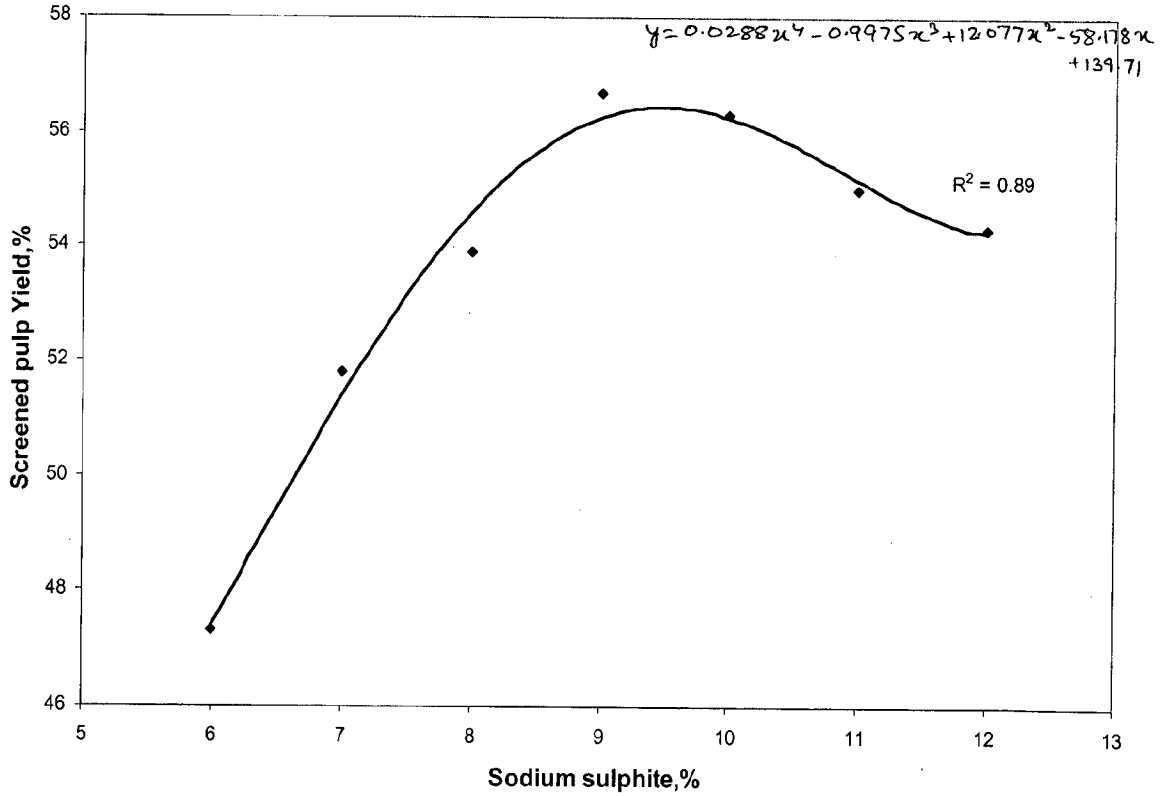


Fig 3.2D: Plots of effect of sodium sulphite doses vs screened pulp yield during alkaline sulphite pulping using 10% NaOH.

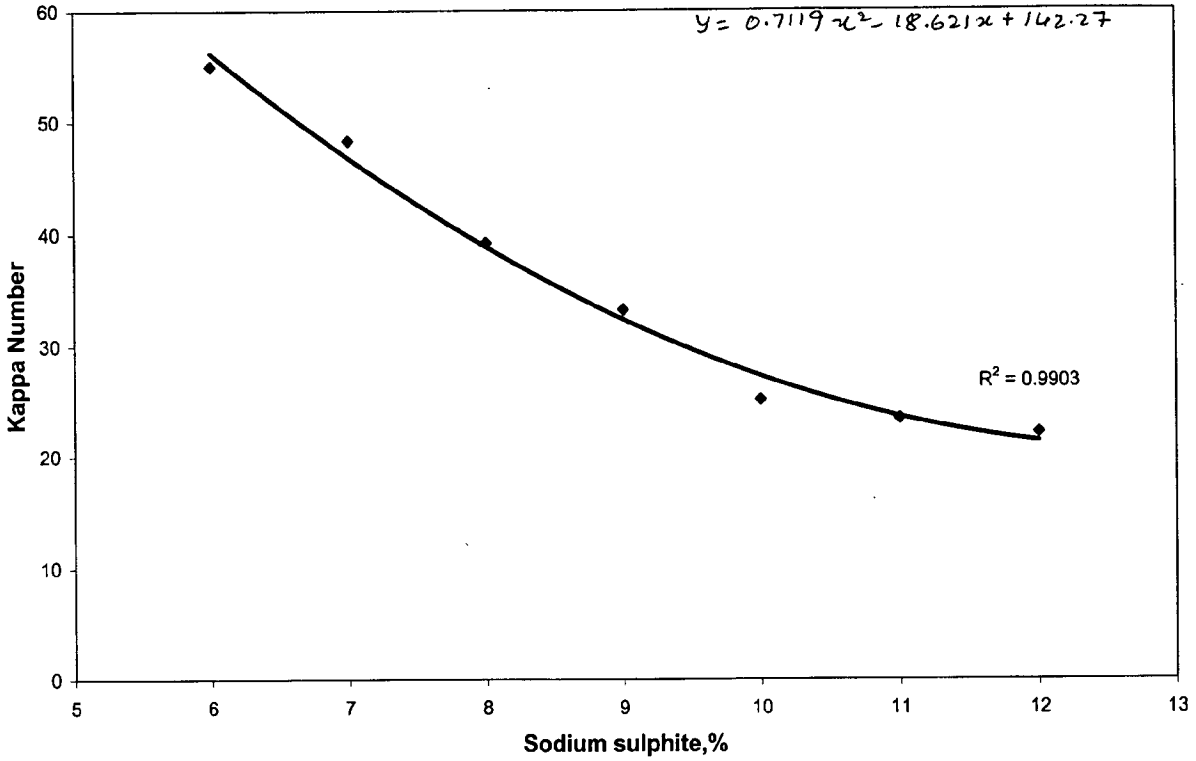


Fig 3.3D: Plots of effect of sodium sulphite doses vs kappa number during alkaline sulphite pulping using 10% NaOH.

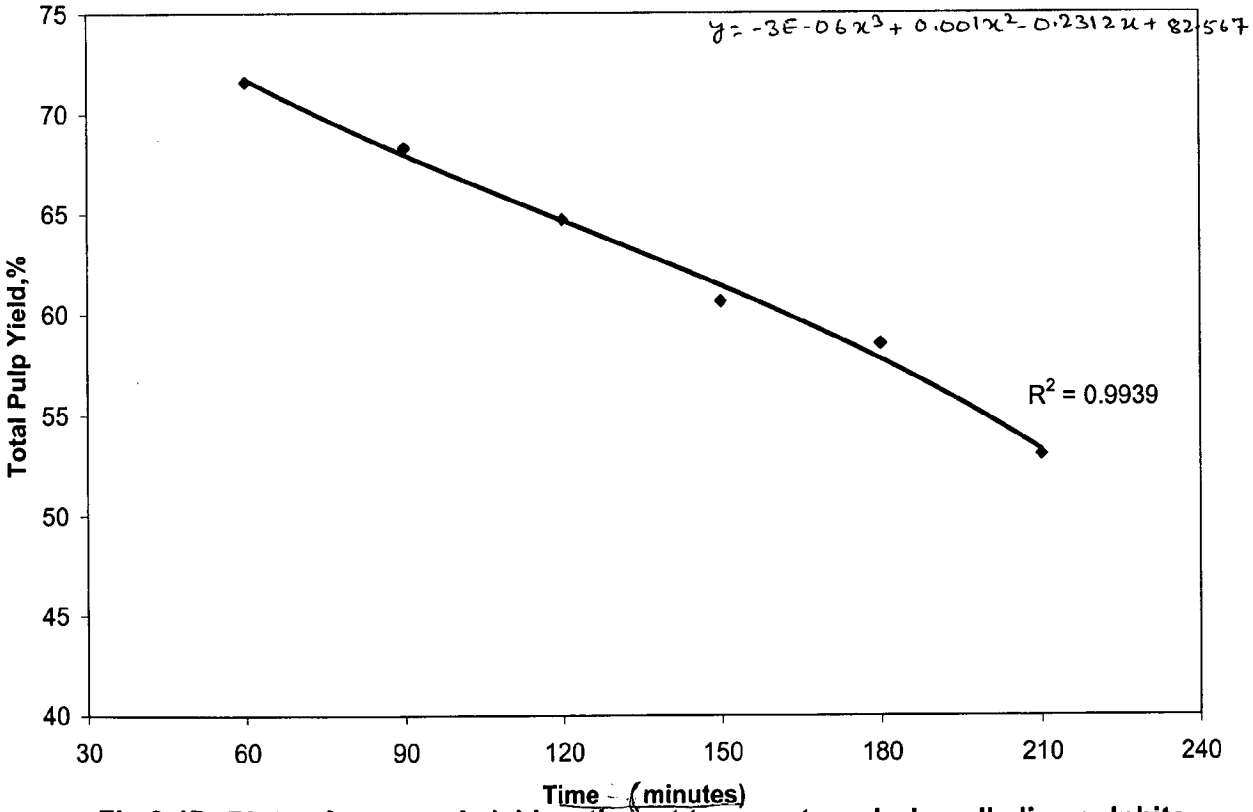


Fig 3.4D: Plots of screened yield vs time at temperature during alkaline sulphite pulping using 10% NaOH and 10% Na2SO3.

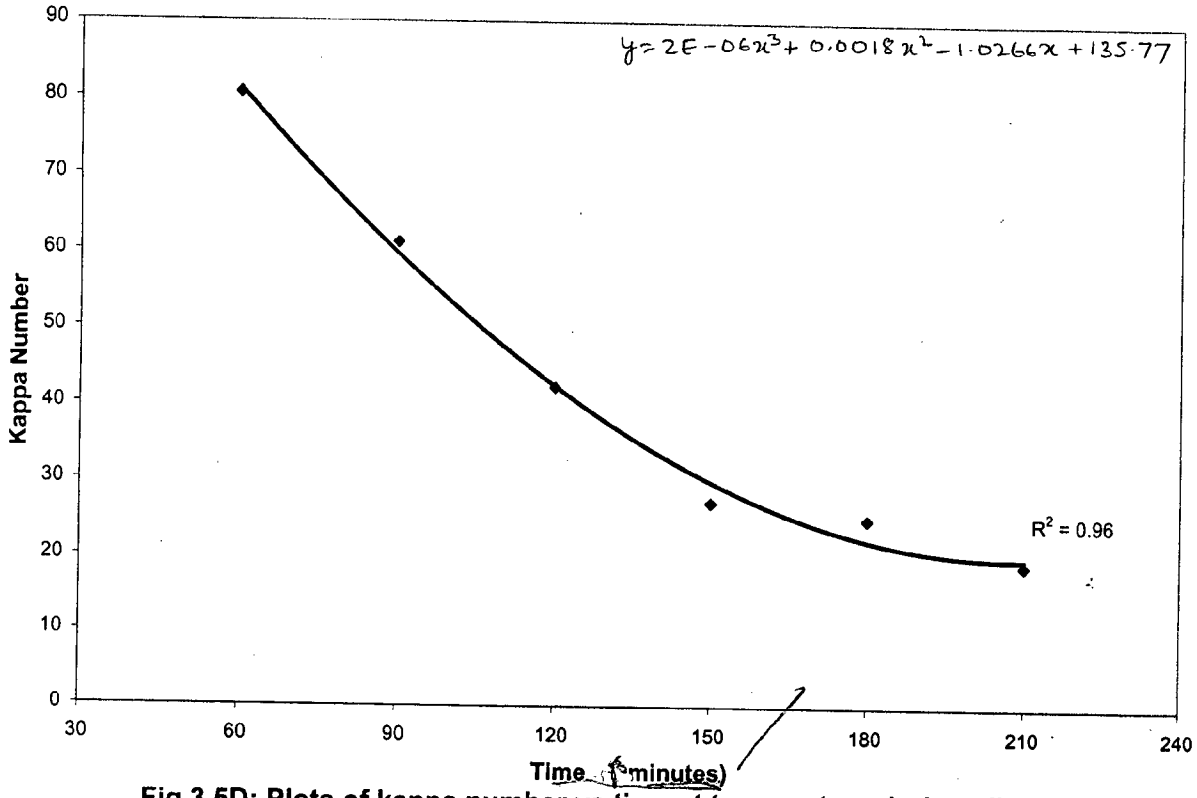


Fig 3.5D: Plots of kappa number vs time at temperature during alkaline sulphite pulping using 10% NaOH and 10% Na2SO3.

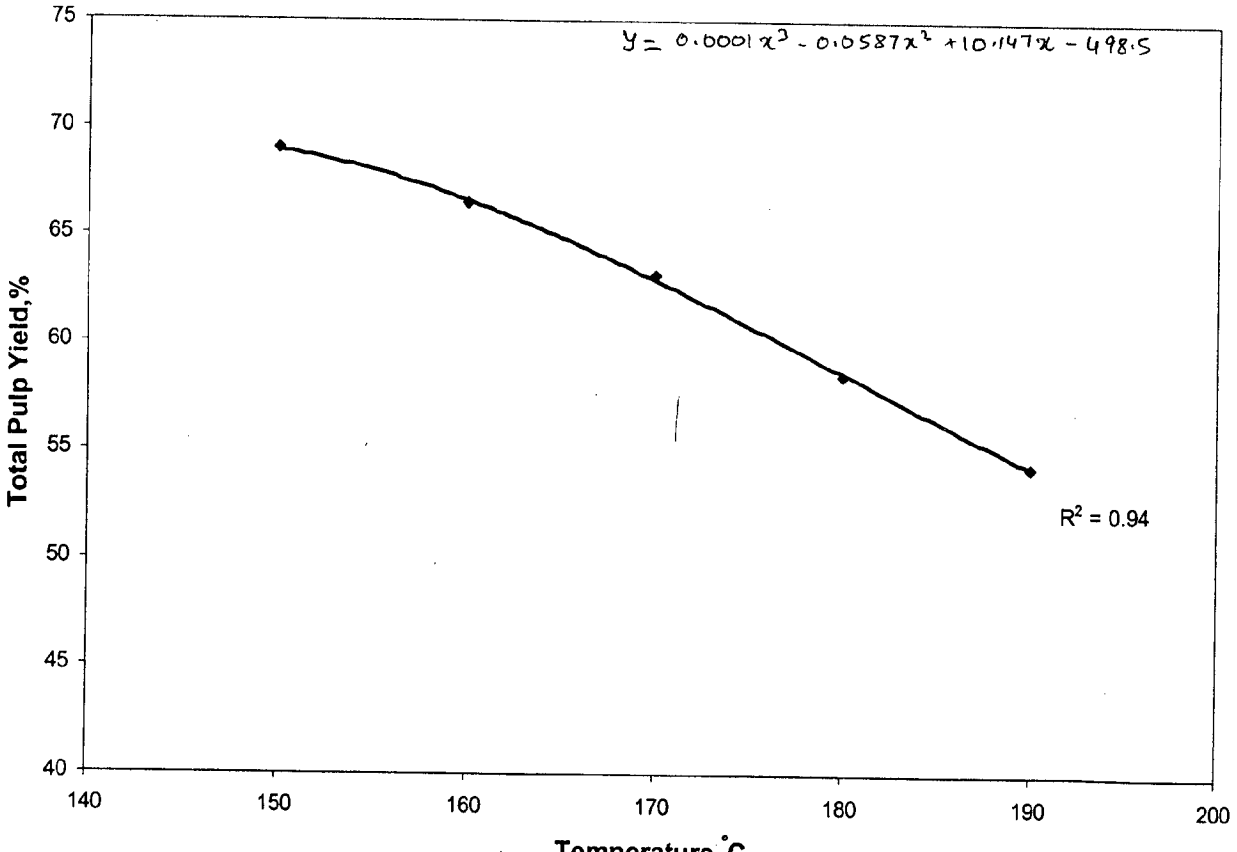


Fig 3.6D: Plots of total pulp yield vs temperature during alkaline sulphite pulping using 10% NaOH and 10% Na2SO3 for 180 minutes.

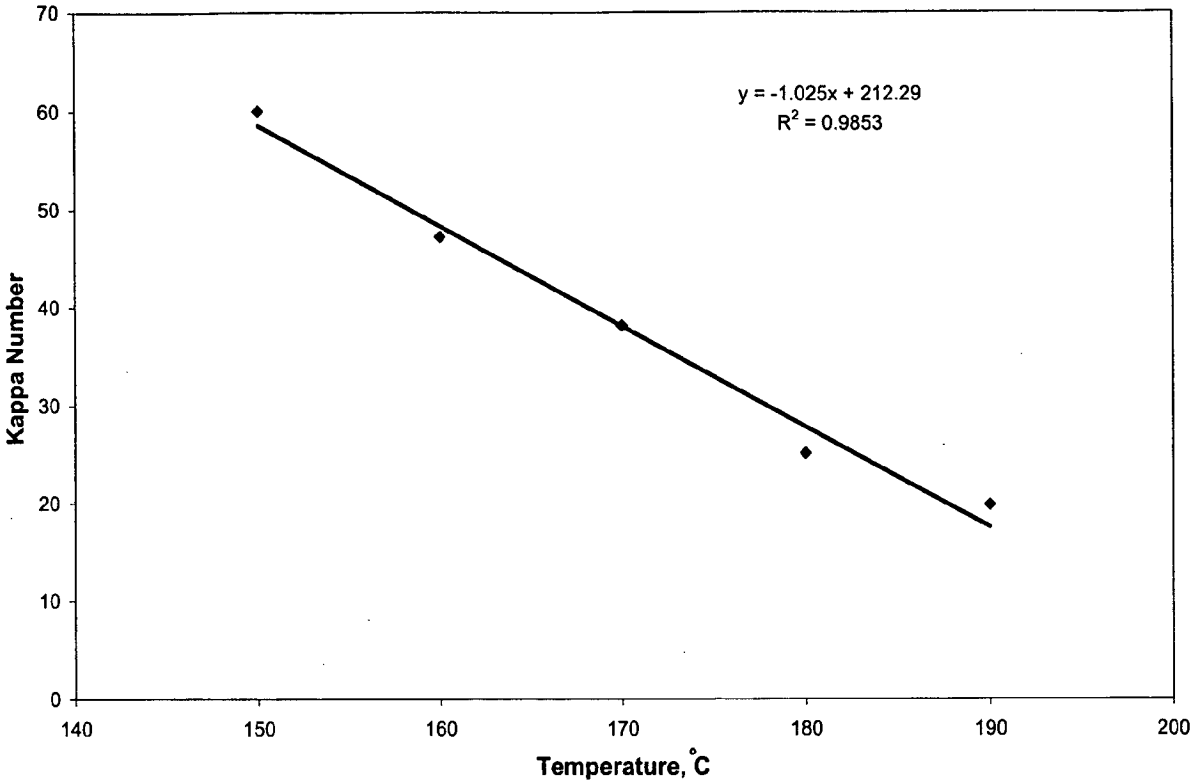


Fig 3.7D: Plots of kappa number vs temperature during alkaline sulphite pulping using 10% NaOH and 10% Na2SO3 for 180 minutes.

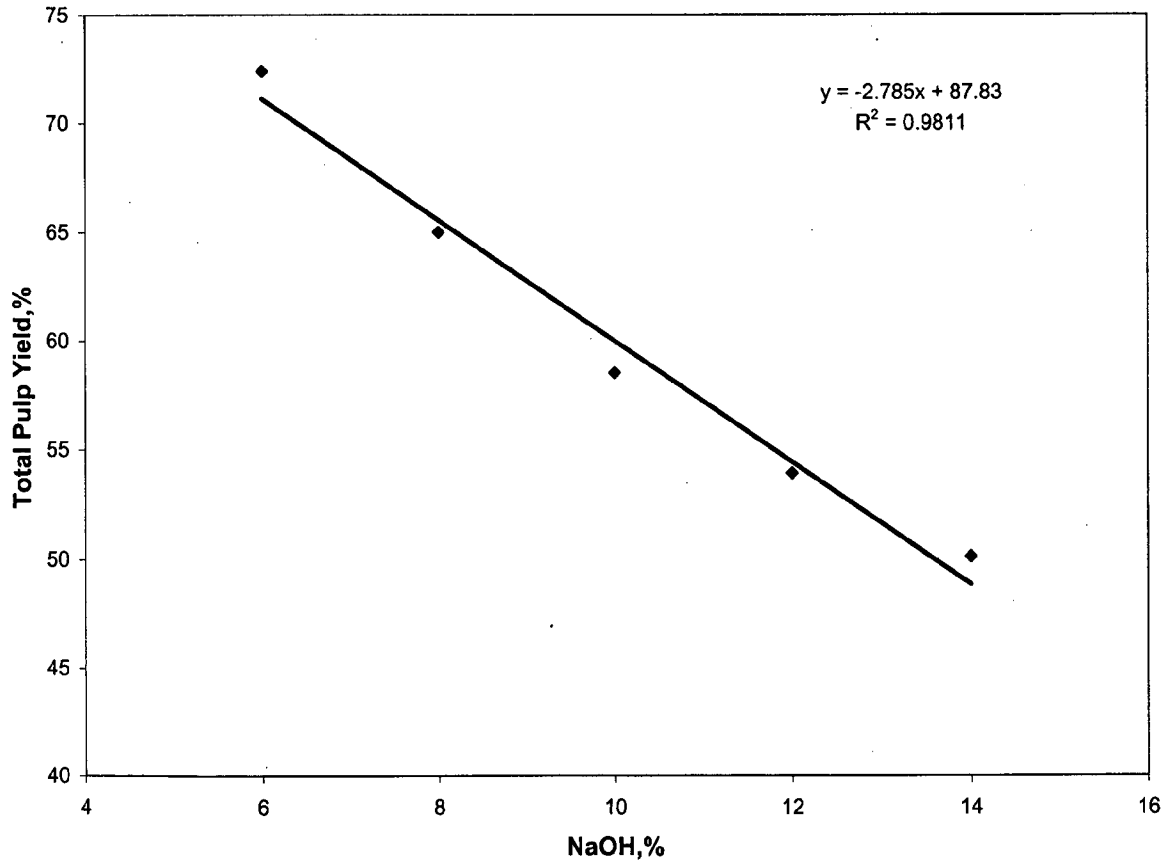


Fig 3.8D: Plots of alkali dose vs total pulp yield using 10% Na 2SO3 during alkaline sulphite pulping of Poplar

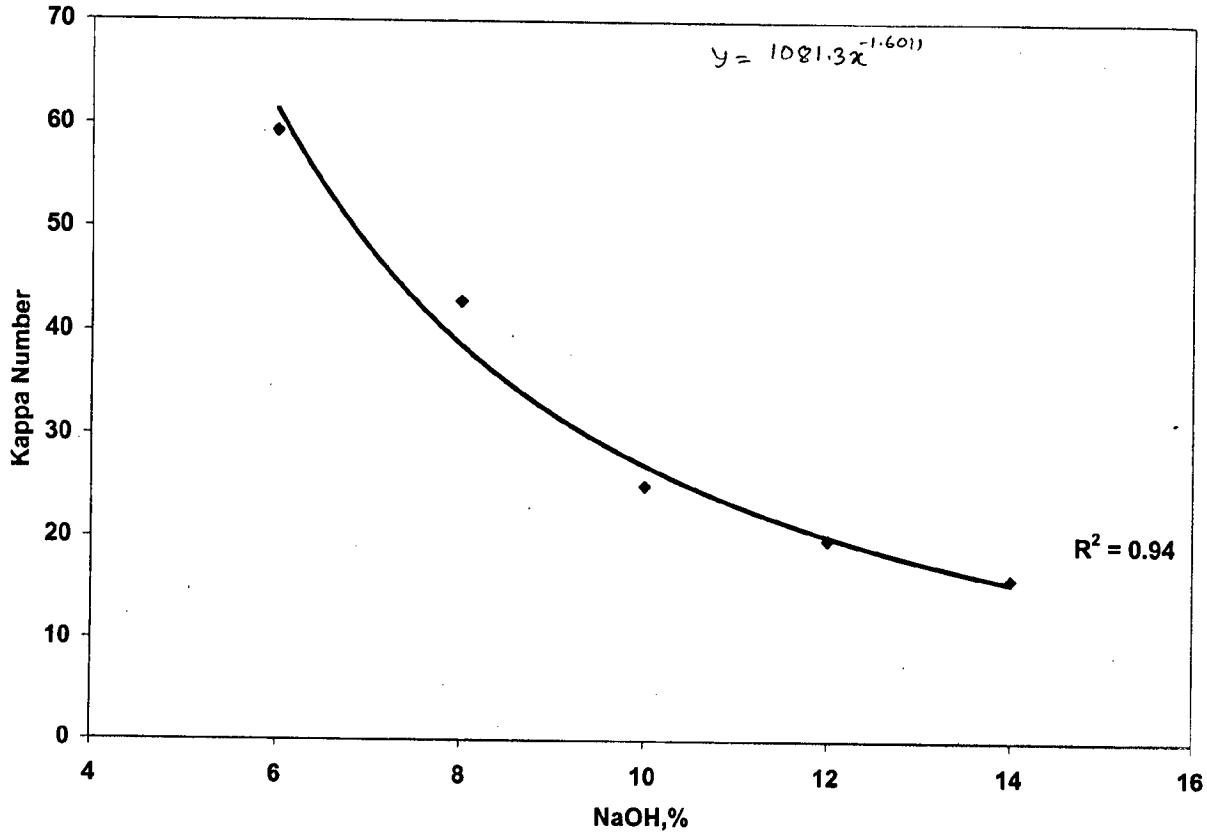


Fig 3.9D: Plots of alkali dose vs kappa number using 10% Na2 SO3 during alkaline sulphite pulping of Poplar

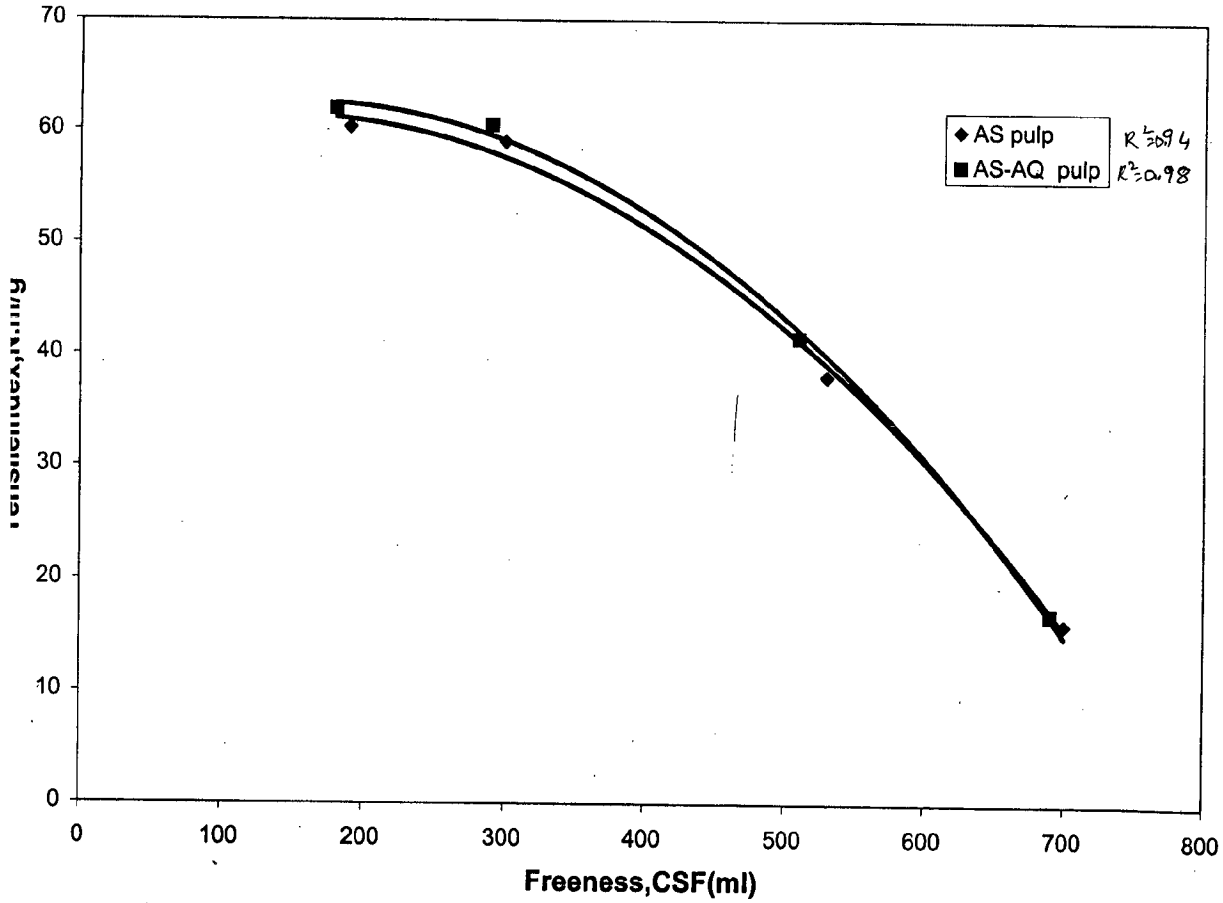


Fig 3.10D: Plots of tensile vs freeness of alkaline sulphite and alkaline sulphite-AQ pulps

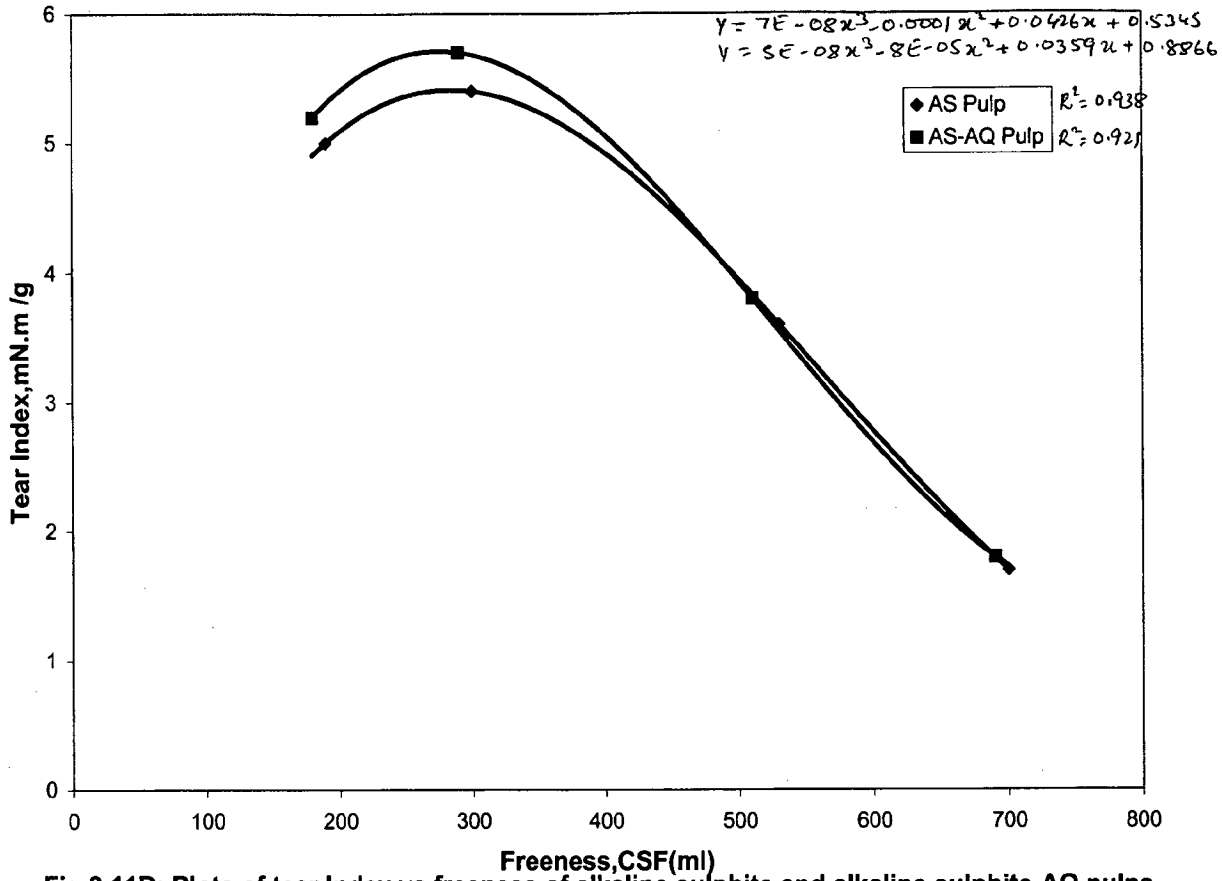


Fig 3.11D: Plots of tear Index vs freeness of alkaline sulphite and alkaline sulphite-AQ pulps

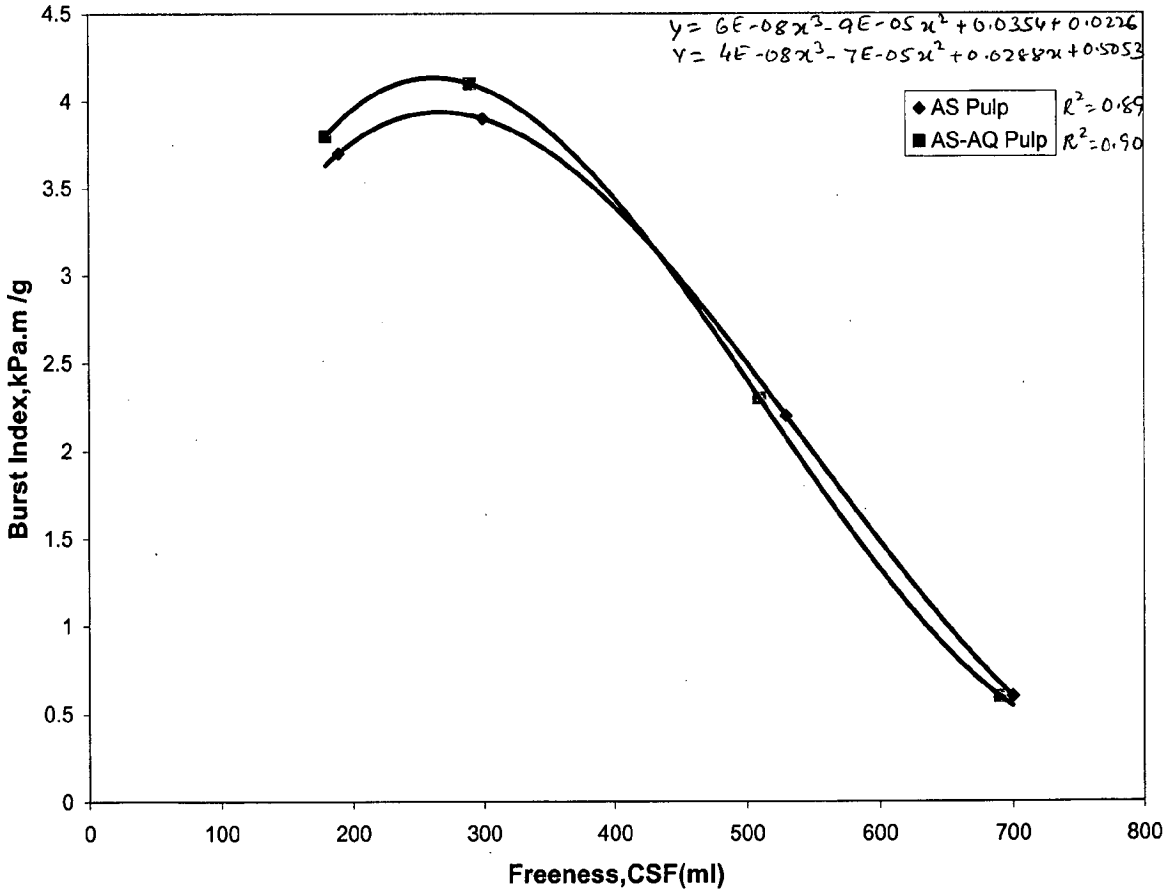


Fig 3.12D Plots of burst Index vs freeness during alkaline sulphite and alkaline sulphite-AQ pulps

CHAPTER 4

STUDIES ON THE PULP BLEACHING

Pulp bleaching is the chemical treatment of cellulosic fibre to increase the brightness either by lignin removal or by lignin decolouring, lignin is coloured and one of the principle constituents of wood. If it is present in the pulp, it darkens with age and cause deterioration of the strength properties of paper. Bleaching of the pulp by lignin removal not only leads to higher brightness but also increases the brightness stability of the final product. Bleaching chemicals cleans the pulp by bleaching shives and dirt particles.

The chemicals commonly used for pulp bleaching includes oxidants, alkali for the chemical pulps and for mechanical pulps reducing agents such as sodium hydrosulfite (sodium thionite) is used these chemicals are mixed with pulp suspention and the mixture is retained at prescribed pH, temperature and consistency for specific period.

The bleaching reactions that occur are highly complex due to the complexity of lignin and wide variety of reactive bleaching species present. The progress of bleaching reaction is monitered by measuring pulp lignin content, pulp brightness and residual chemicals. Bleaching chemicals are frequently applied sequentially with intermediate washing between treatment stages

Different bleaching chemicals are described in Table-1. The main oxidants are chlorine, chlorine dioxide, hypochlorite, oxygen and hydrogen peroxide. With the discovery of ways to use chlorine gas for the bleaching of pulps in 1930, chlorine has become the predominant chemical for delignification of pulp which is less expensive. Chlorine dioxide has the particular advantage of being able to brighten pulp without causing severe damages to the cellulose. Oxygen is extremely expensive and can be used for delignification of pulp. Oxygen

delignification removes almost half of the lignin present in the pulp without causing severe damages to the cellulosic fiber. Oxygen delignification reduces almost half of the bleaching chemicals.

One of the most important aspects of chemical pulp bleaching is the selectivity of the bleaching chemicals. Selectivity is the relative reaction of the chemical with lignin compared to cellulose. Unbleached pulp has a high lignin content and so less selective chemicals like oxygen and chlorine may be used. However, with further delignification resulting in a low lignin concentration in pulp, more reaction with carbohydrates takes place and pulp strength suffers Chlorine dioxide and hydrogen peroxide are highly selective, reacting rapidly with lignin but very little with cellulose. The highly selective chemicals are used in the latter stages of bleaching where the lignin content is low and the cellulose is susceptible to degradation. Also chlorine dioxide and hydrogen peroxide is more expensive that than chlorine and oxygen. Oxidizing agents accepts electrons and are thereby reduced. The substances they react with give up electrons and are thereby oxidized. The oxidation-reduction reactions commonly used in bleaching and the number of electrons transferred per molecule is shown in Table-2. In comparing bleaching chemicals, the efficiency with the oxidant degrades lignin is considered Oxygen requires three to four times as many oxidizing equivalents to achieve the same degree of delignification as chlorine. When chlorine dioxide is used as a substitute for 50% of the chlorine in a chlorination stage the same degree of delignification can be achieved with fewer oxidizing equivalents. The oxidizing chemicals must often be supplemented with alkali for instance. NaOH or oxidized white liquor must be used in oxygen stage and NaOH must be used in the extraction stage. The role of extraction stage is to remove the lignin made potentially soluble by the previous acidic oxidizing stage during bleaching stage (oxidizing stage) and to reactivate the

pulp for further oxidation. The changes in bleaching chemical usage may also require capital outlay.

Process conditions are very important in determining the efficiency of bleaching reactions and also strongly influence selectivity and, in some cases, particle elimination. Chemical consumption during a bleaching stage is the single most important parameter. Chemical application is set by proportioning chemical to pulp with adjustments made based on information about brightness target levels or delignification achieved. The pH has an important role on most bleaching reactions and may be controlled by addition of alkali or acid before or with the bleaching chemical.

The extent to which the applied chemicals are consumed depends on the kinetics of the chemical reaction and the reaction time. Time is specified in equipment design but is difficult to adjust because it is linked to equipment size and production rate. Because most bleaching reaction rates, increase with temperature, the reaction rate and therefore the extent of reaction is most commonly controlled by temperature adjustment

Other factors, which must be taken into account in bleaching chemical comparison, are selectivity, particle bleaching, and environmental concerns. As far as selectivity is concerned one should consider the relative rate of reaction of the chemical with lignin as compared to cellulose. In delignification one can rank chemicals as follow: D > C>O> and in brightening D, D>H. Shives removal capacity is another imported factor and can be ranked as follow D>H, C>O, P>Z. Environmental concerns are having a very strong influence on selection of bleaching chemicals. The use of hypochlorite results in production of substantial quantities of chloroform, a well-known carcinogen, therefore in the developed countries, the use of hypochlroite is strongly shifted. Chlorine dioxide is replacing chlorine is first stage. Substitution of chlorine dioxide for chlorine has a profound affect on the formation of chlorinated dioxins, the dioxin

formation being significantly decreased when chlorine use is decreased. Some mills ar concerned about the discharge of chlorinated organic matter in effluent and so non-chlorin bleaching agents, such as oxygen and hydrogen peroxide are increasingly being considered.

Bleaching chemicals are applied in multi-stage sequences where in chemicals are mixe with pulp, a period of retention time is provided and then spent chemicals and dissolve impurities are removed by washing. The bleaching sequence is broken down in two-segmen delignification and brightening stage. In the delignification segment the bulk of the residua lignin associated with the pulp is degraded and solubilized by a single oxidant or th combination of the oxidants such as chlorine, chlorine dioxide, oxygen, ozone etc. Th traditional mode of delignification uses chlorine followed by extraction with sodium hydroxide In India most of the mills uses the traditional mode of delignification. Chlorine dioxide may b added in small amounts to the chlorination stage to preserve pulp strength. Sequentia substitution of chlorine dioxide for chlorine may be practiced for economy or for environmenta reasons.

Oxygen is another effective delignifying agent, which is widely used to enhance th delignification and extraction stage. The main advantages of oxygen bleaching are related to its beneficial effect on the saving of the oxidizing chemicals during bleaching, because oxygen is less expensive. The another advantage of oxygen delignification is the effect on the environmental parameters as it leads to major decrease in biochemical oxygen demand (BOD), chemical oxygen demand (COD) and color. The main disadvantage of its is the high capital costand increased demand on chemical recovery system.

Brightening stage principally involves chlorine dioxide, hypochlorite and hydrogen peroxide with increasing environmental pressure to eliminate organochlorine. Hypochlorite

stages are rapidly eliminating more and more as hydrogen peroxide is being used to supplement brightening capacity.

In multi-stage bleaching, process conditions must be optimized to achieve best results. In each stage it is important to control chemical consumed, temperature, time, residual oxidant and pH.

Table-2 Oxidising Equivalents (145)

Reduction

$Cl_2 + 2e^-$ ---- 2Cl

$ClO_2 + 2H_2O + 5e^-$ --- Cl + 4OH

O2 + 2H2O + 4e---- 4OH-

$NaOCl + H_2O + 4e^-$ --- NaCl + 2OH-

$N_2O_2 + 2H^+ + 2e^-$ --- $2H_2O$

Oxidation

$H_2CO + 2OH^-$ --- $HCOOH + H_2O + 2e^-$

Weight	Formula Transferred	Electrons Weigth*	Equivalent 50 kg chlorine	kg. Equivalent to
Cl2	71	2	35.5	50
ClO2	67.5	5	13.5	19
O2	32	4	8	11
H2O2	34	2	17	24
NaOCl	133**	2	66.5	94

*Formula weight per electron transferred.

**Formula weight includes NaOCl plus NaCl since Cl_2 plus2NaOH is required to make NaOCl and NaCl is co-produced.

Table-2 Chemicals Used in Bleaching (145)

Oxidants	Form	Function	Advantages	Disadvantages
Chlorine	Gas	Oxidize and chlorinate lignin	Effective, economical delignification.Good particle removal.	Organochlorine formati Highly corrosive
Hypochlorite	$Ca(OCl)_2$or NaOCl Solution	Oxidise,brighten and solubilize lignin.	Easy to make and use.	Can cause loss of pulp Strength if used improp Chloroform formation.
Chlorine-Dioxide	-40 gpl as Cl_2 7-10 gpl ClO_2 solution in water	1) Oxidize, Brighten and Solubilize lignin 2) In small amounts with Cl_2 protects against degradation of pulp.	Achieves high brightnes Without pulp degradatio Good particle removal.	Must be made on site. e Some organochlorine formation. Highly corro
Oxygen	Gas used with NaOH solution	Oxidize and Solubilize lignin	Low chemical cost. Provides chloride-free effluent for recovery.	Used in large amounts r expensive equipment. can cause loss of pulp s
Hydrogen Peroxide	2-5% solution Gas in low	Oxidize and brighten Lignin in chemical and high yield pulps.	Easy to use. Low capital cost	Expensive, poor particl bleaching.
Ozone*	Concentration in Oxygen	Oxidize,brighten And solubilize Lignin.	Effective. Provides chloride-free effluent for recovery.	Expensive. Degrades pu Poor particle bleaching
Reductant				
Hydrosulfite (for mechanic pulps only	Solution of $Na_2S_2O_4$ or made On-site from $NaBH_2$ solution Plus SO_2	Reduce and decolourize lignin in high yield pulps	Easy to use. Low capital cost.	Decomposes readily. Limited brightness gain
Alkali Sodium Hydroxide	5-10% NaOH solution	Hydrolyse chlorolignin & solubilize lignin	Effective and economica	Darkens pulp.
Enzymes				
Xylanase	Isolated from Fermented process	Catalyze xylan hydrolysi and aid in lignin removal	Easy to use, low capital cost	Limited effectiveness, c
Chelants				
EDTA or DTPA	Liquid	Removes metal ions	Improves peroxide selectivity and efficienc	Cost

CHAPTER 4 A

OXYGEN DELIGNIFICATION

4.1A Introduction :

India is a developing country with the burgeoning market for paper and its products. Paper industry is highly polluting industry and most polluting part in this industry is the effluent generated in pulp bleaching. So far in India, much attention has not been given on the environmental protection from pulp and paper industry, but the time has come to think it seriously. In developed countries, the mills have already forced to take care of environmental protection and they have taken measures like closed bleach plant system, replacing chlorine and chlorine compounds with other bleaching agents such as oxygen, ClO_2, enzymes, ozone etc. The bleaching response of these chemicals is effective and the effluent generated using these chemicals is very low.

Strict legislation of the state and central pollution control board in our country and increasing cost of energy, chemicals and other utilities, alongwith increasing demand of high brightness paper, have forced to think to do the necessary modification of the present delignification and bleaching practices, in Indian paper industries.

Formation of organochlorine compounds during bleaching of chemical pulp, have attracted attention during recent years. Earlier, measures were taken by the pulp and paper industry to solve the chlorine problem focussed on improving effluent treatment methods. Now-a-days, the emphasis of research in this area has shifted more towards improving the process.

The goal is to increase the efficiency and selectivity of pulping process, reducing the amount of lignin in the pulp for bleaching (41,42,43).

As far as the environmental impact of chlorine is concerned, it is important to restrict the use of chlorine to the minimum extent possible manner in bleaching processes, since the amount of chlorine required is directly related to the kappa number of the pulp to be bleached (17,92). Therefore, the pulp which is to be bleached should have lower kappa number so that the use of oxidizing chemicals is reduced.

Oxygen bleaching consumes less expensive chemicals than non-oxygen sequences (92). The significant fact has been the ability of oxygen stage to contribute towards pollution abatement. Oxygen delignification plays an important role in reducing chemical consumption during bleaching. Oxygen delignification reduces the kappa number of the pulp upto 50%, which in turn decreases, the bleach chemical demand during the bleaching of the pulp. The decrease in the demand of bleaching chemicals such as chlorine and chlorine dioxide which in turn reduces the formation of chlorinated organic by-products in the bleach plant effluent (22). Oxygen is less expensive and decreases the chemical cost during bleaching. During oxygen delignification, the presence of alkali plays an important role in activating the phenolic groups for further oxidation. The use of peroxide also enhances oxygen delignification, although the degradation of carbohydrates is enhanced (199). Oxygen delignification kinetics are complex and vary for different wood species and pulping process. Delignification proceeds fast during the first five to ten minutes of the oxygen stage and then proceeds at a much slower rate for the remaining delignification. lignin content when expressed with a single lignin model. The kinetics are characterised by a high apparent reaction order with respect to the McDonough (1996) reviews oxygen delignification chemistry, which is quiet complicated due to the complexity of the lignin structure, as well as the number of different oxygen species formed during the reaction. The

The mechanism of oxygen bleaching have been studied using model compounds (Gierer and Imsgard, 1977,Gunggren and Johansson1989, 1994) and by examining residual and dissolved lignin moieties (BerryandFleming 1987). The oxygen molecules can be reduced to different species; HO_2 -, H_2O_2, O_2 -, HO_2 and HO. Free phenolic hydroxyl groups are thought to play a major role in O_2 delignification. The phenolic group is ionized under strong alkaline conditions, generating a site with high electron density, which undergoes transfer of a single species. The degradation products are prominently organic acid and carbon dioxide (Miller etal 1995) Johanssan and Gunggran (1994) studied the reactivity of lignin model and found that phenolic structure with a conjugated side chain like stilbene and enol ethers reacts vary rapidly during oxygen bleaching (128,107). Where as structures like propyl guaiaiol and β - aryl ethers are more resistant. Some of the free radicals reaction mechanisms were thought to produce new cross-linked structures that had even lower reactivity. The degradation kinetics for a wide variety of lignin model compounds could be fit to a high degree of confidence to first order kinetic equation (107,121,128)

There are two disadvantages of using oxygen, first is the tendency of oxygen to attack carbohydrate alongwith lignin, and second is the difficulty in getting oxygen to the reaction site within the fiber wall. The most important factor that governs the selectivity during oxygen delignification is the presence of transition metal ions content of the pulp, since these ions catalyze the generation of harmful species. One approach in dealing with the problem is to remove the metals ions by acid washing prior to oxygen delignification, while another is by adding some chelating compounds to the pulp that inhibit carbohydrate degradation. The protectors of greatest commercial importance are the magnesium (II) salts. Which are normally applied at levels as low as 0.05 to 0.1% (as Mg++, on o.d. pulp basis). As discussed earlier, another advantage of oxygen delignification is a substantial reduction in the discharge of

pollutants. Since the dissolved solids are washed from the oxygen delignified pulp and recycled back to the chemical recovery system (17, 38,92,96).

Almost all the lignin in unbleached kraft pulp can be removed with an oxygen stage, this has been shown by Olm and Teder (140). The practical extent of delignification is limited by the degradation of carbohydrates in the pulp. If the oxygen delignification have been allowed to proceed for longer period, the degradation of carbohydrate is increased and the strength properties of the pulp decreases. Therefore this limits the oxygen delignification to 40-50% (122,123.196). Oolf Samuelson showed that the polysulphide pulps have more pronounced oxygen delignification (141).

Oxygen delignification is used almost with all the ECF and TCF bleaching sequences to reduce the kappa number (lignin content) of the pulp which in turn decrease oxidising chemicals (40-43). Therefore, the oxygen delignification process could have a significant impact on the economic feasibility of ECF and TCF bleaching. The prices of oxygen is expected to rise more slowly than that of other bleaching agents, the economy of oxygen should be even better in future (58).

4.2A Experimental Methodology:

The soda, soda-AQ, kraft and kraft-AQ pulps were delignified with oxygen in the electrically heated Weverk rotatory digester of capacity 0.02 m^3 incorporated with the valves for the charge of oxygen. During oxygen delignification, the oxygen was fed into digester at a temperature of 70 ^0C to the oxygen pressure of 5 kg/cm^2 in all sets of experiments. The experiments on oxygen delignification were conducted at different temperature, time (at temperature), alkali charge, keeping the oxygen pressure of 5kg/cm^2 as constant, in all the experiments. After the oxygen delignification, the pulp was washed, and evaluated for pulp

yield, kappa number and the viscosity of the pulps were determined by ther TAPPI standard T-236 & T- 230 test methods (192).

4.3A: Results and Discussions:

4.3.1A: Effect of NaOH Concentration:

Oxygen reacts with lignin in alkaline medium, at elevated temperature and pressure. The advantage of using the NaOH is to activate the phenolic groups of the lignin for oxygen delignification. The effect of alkali on oxygen delignification has been studied on soda pulp at different NaOH concentration of 1%, 1.5%, 2.0%, 2.5% at 105 ^{0}C. The conditions and the results has been reported in table 4.1A. It has been observed that on increasing the alkali dose, the extent of delignification also increases. Higher carbohydrate degradations have also been observed in the higher alkali dose. Thus from the data of these experiments, an alkali dose of 2% NaOH may be considered as an optimum dose for the oxygen delignification, based on reduction in kappa number alongwith loss in pulp yield.

4.3.2A Effect of Time and Temperature:

The effect of temperature during oxygen delignification has been studied on the soda pulp of poplar deltoides with a kappa number 20.1. The effect of temperature have been studied at 95 ^{0}C,105 ^{0}C, 120 ^{0}C using 2% alkali at different time, and at constant oxygen pressure of 5kg /cm^2. The results of these experiments have been reported in table 4.2A. These results indicates that on increasing the temperature, the rate of reaction increases. The delignification reaction during oxygen bleaching is a chemical process. The increase in temperature increases the rate of delignification, but at the higher temperature of 120 ^{0}C, the reaction of molecular oxygen with carbohydrates also increases, thereby increasing the degradation of carbohydrates materials which results in severe pulp yield loss. From these results, it has been observed that the rate of

delignification is comparatively slower at 95 ^{0}C. Keeping in view the full advantages of oxygen delignification, a temperature of 105 ^{0}C may be considered to be optimum.

The results of these experiments also revealed that the kappa number decreases as the reaction time increases. Edward and Evans showed that oxygen delignification reaction has been of first order with respect to the lignin content of the pulp (40,41). Moreover, the kappa number continues to decrease even after very longer reaction time. The study of Edward and Evans showed that a kappa number of 3 could be achieved if the oxygen bleaching is carried out at 130 ^{0}C for 6 hours (40,41). Thus a time of 45 minutes at 105 ^{0}C seems to optimum in order to get the maximum benefits of reduction in kappa number alongwith low degradation of carbohydrate materials during oxygen delignification of poplar pulps.

4.4A: Oxygen Delignification of Soda and Soda-AQ Pulp:

The soda and soda-AQ pulps (prepared at 16% and 18% active alkali) were oxygen delignified at the optimum conditions, viz. 10% consistency, temperature 105 ^{0}C, 2% NaOH (on o.d. pulp basis) and time at temperature 45 minutes. The results of these experiments have been reported in table 4.3A. The initial kappa number of soda and soda-AQ pulps at 16% and 18% active alkali were 24.1, 21.8, 18.2, 17.2 respectively. After oxygen delignification these kappa numbers were reduced to 12.3, 11.2, 9.8, 9.2, thereby indicating that about half of the remaining lignin of the pulp can be removed by oxygen prior to the usual bleaching operation. The viscosity of these unbleached pulps were 530, 550,500, 520 cm^3/g respectively which were reduced to 470, 490, 440 and 450 respectively after oxygen delignification. This little drop in viscosity shows a minor degradation of cellulosic fibre during oxygen delignification. The completely bleached oxygen delignified pulps have slightly lower strength properties as

compared to the pulps bleached by using the same bleaching sequences without oxygen. The details are further discussed in chapter 3B, 3C,3D.

4.5A Oxygen Delignification of Kraft and Kraft-AQ Pulps:

The kraft and kraft-AQ pulps (obtained at 14% and 16% active alkali with 20% sulphidity) were oxygen delignified at the optimum conditions viz. 10% consistency, 2% NaOH charge 0.1% $MgSO_4$ and time at temperature 45 minutes. The results of these experiments have been reported in table 4.4A. The incoming kappa numbers of kraft and kraft AQ pulps obtained at 14% and 16% active alkali were 21.4, 20.1, 17.6, 16.7 respectively. When these pulps were oxygen delignified, the kappa number of out going pulps were 11.3, 10.9, 9.5, 8.6 respectively. These results indicate that more than 45% of the remaining lignin present in the pulp can be removed during oxygen delignification before the start of usual bleaching of the pulp. The original viscosity of these unbleached pulps were 610, 640, 570, 590 cm^3/g respectively which were reduced to 540, 570, 510,530 cm^3/g respectively as a result of oxygen delignification. This little drop in viscosity shows a minor degradation of fiber during oxygen delignification.

4.6A: Conclusion :

Oxygen delignification plays an important role in reducing the kappa number of the pulp. The results of experiments revealed that the oxygen delignification removes about half of the residual lignin of the pulp, thereby decreasing the kappa number upto 50%. The chlorine demand for the bleaching depends on the kappa number of the pulp. Thus the oxygen delignification reduces the amount of the bleach chemicals to the same extent for the bleaching of the pulp. The chlorine used during bleaching of pulp produce chloro organic compounds, which increases the pollution load in the environment, which is of more concern. Since, oxygen delignification reduces the use of oxidizing chemicals, which in turn reduces the environmental pollution load drastically, which is one of the most significant advantages of oxygen delignification. Moreover

oxygen is less expensive apart from the cost of equipments. During oxygen delignification, at optimum conditions there is slight loss in the viscosity of the pulps; this means that there is slight degradation of carbohydrates materials by the oxygen. The oxygen-delignified pulps have slightly lower strength properties. These slight losses in strength properties are insignificant in the light of the advantages of oxygen delignification in terms of getting pulps with ultra brightness with very low environmental pollution load.

Table 4.1A: Effect of Alkali at different time (at temperature) during oxygen delignification of kraft pulp at 105 ^{0}C

Kappa number of pulp = 20.1

Consistency = 10% $MgSO_4$ = 0.1%

NaOH,% (on o.d. pulp)	Time at temperature,(min)	Kappa number (±0.2)	% decrease in kappa number	Loss in pulp yield, % (±0.1)
1.0	15	18.6	06	1.6
	30	16.9	17	2.9
	45	15.4	23	3.2
	60	14.9	26	3.5
1.5	15	17.1	15	1.7
	30	15.2	24	2.9
	45	13.7	34	3.6
	60	12.8	37	4.1
2.0	15	15.1	25.1	1.9
	30	11.3	44.0	3.1
	45	10.9	46.8	3.8
	60	10.3	48.9	4.8
2.5	15	13.3	34.0	3.2
	30	10.5	48.2	4.4
	45	9.8	51.5	5.2
	60	9.3	54.2	6.2

Table 4.2A: Effect of temperature at different time (at temperature) during oxygen delignification of kraft pulp at 105 ^{0}C

Kappa number of pulp = 20 .1 Oxygen pressure charged= 5 kg/cm^2

NaOH = 2% Consistency = 10%

$MgSO_4$ = 0.1%

Temperature, C	Time (min)	Kappa number (±0.2)	% decrease in kappa number	Loss in pulp yield,% (±0.1)
95	15	15.7	22.0	1.7
	30	12.0	40.0	2.9
	45	11.5	44.3	3.6
	60	10.9	46.8	4.1
105	15	15.1	25.1	1.9
	30	11.3	44.0	3.1
	45	10.9	46.8	3.8
	60	10.3	48.9	4.8
120	15	13.9	30.8	2.5
	30	9.7	51.7	3.3
	45	8.8	56.3	4.4
	60	8.4	57.7	5.1

4.3A: Effect of oxygen delignification on soda and Soda-AQ pulps of poplar deltiodes.

Pulp consistency 10% Temperature 105 ^{0}C
Oxygen Pressure 5kg/cm^2 $MgSO_4$ 0.1%

Particulars	16% Soda pulp	16% Soda-AQ pulp	18% Soda pulp	18% Soda AQ pulp
NaOH,%	2.0	2.0	2.0	2.0
Oxygen reaction time (min)	45.0	45.0	45.0	45.0
Kappa no.				
Incoming	24.1	21.8	18.2	17.2
Outgoing	12.3	11.2	9.8	9.2
Decrease,%	49.2	48.0	47.5	47.1
Pulp yield, %	96.2	96.7	97.1	97.8
Pulp viscosity, cm^3/g				
Before O_2 delignification	530	550	500	520
After O_2 delignification	470	490	440	450

4.4A: Effect of oxygen delignification on kraft and kraft-AQ pulps of poplar deltiodes.

Pulp consistency 10%
Temperature 105 C
Oxygen Pressure 5kg/cm^2 $MgSO_4$ 0.1%

Particulars	14% Kraft pulp	14% Kraft –AQ pulp	16% Kraft pulp	16% Kraft –AQ pulp
NaOH,%	2.0	2.0	2.0	2.0
Oxygen reaction time (min)	45.0	45.0	45.0	45.0
Kappa no.				
Incoming	21.4	20.1	17.6	16.7
Outgoing	11.3	10.9	9.5	8.6
Decrease,%	47.3	46.5	45.0	44.2
Pulp yield, %	96.6	97.2	97.1	97.5
Pulp viscosity, cm^3/g				
Before O_2 delignification	610	640	570	590
After O_2 delignification	540	570	510	530

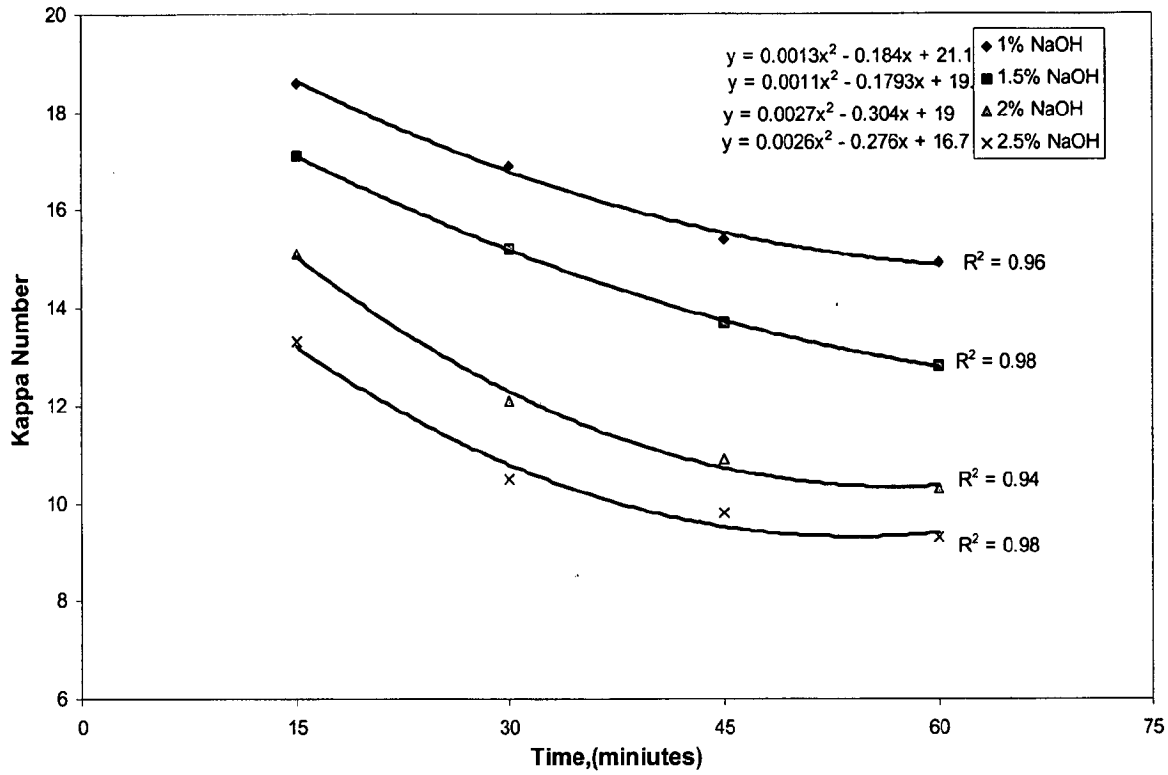


Fig 4.1A Effect of time on kappa no. at different alkali % during oxygen delignification

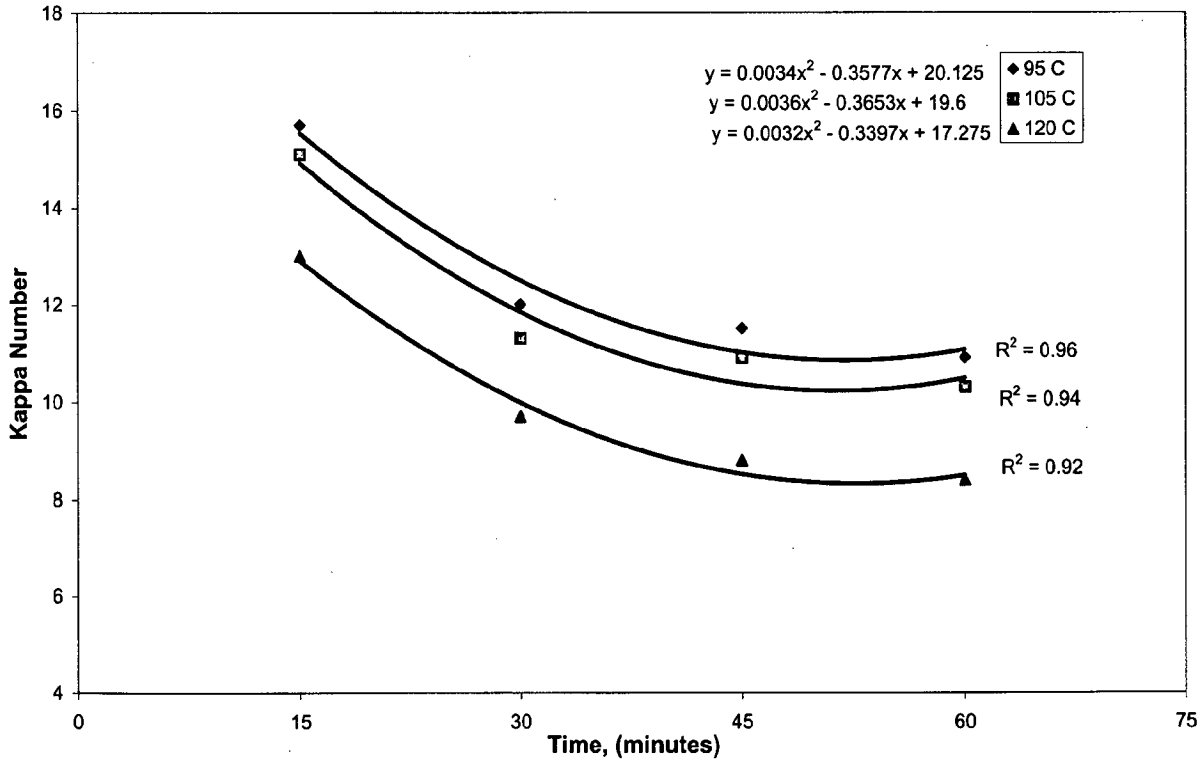


Fig 4.2A: effect of time on kappa number at different temperature,using 2% NaOH.

CHAPTER 4 B

STUDIES ON CONVENTIONAL BLEACHING SEQUENCES

4.1B Introduction :

The main raw material used in the Indian paper mills are, hardwood (eucalyptus), bamboo, agroresidues like bagasse, straws and secondary fibers mainly waste paper. Large capacity mills are based on hardwood, bamboo and bagasse and producing pulp with conventional kraft process, and are well equipped with conventional chemical recovery system. In most of the mills in India, bleachable grade pulp of kappa number around 24 is being produced from hardwoods and pulp of kappa number 16 is produced from bagasse. In India most of the mill use conventional bleaching sequences, the pulps are being bleached by conventional either CEH or CEHH bleaching sequences, to the brightness level of around 80% ISO for most of the end uses. Little doses of hydrogen peroxide in alkaline extraction stage or in final bleaching stage is being used in some of the mills.

The AOX generated in conventional CEH/CEHH bleaching sequences of a 24 kappa number pulp to a brightness of 80% ISO is about 4-5 kg per tons of pulp. The large amount of energy and chemicals are wasted for the treatment of the effluent to bring down its value to the acceptable level of 2 kg per ton of pulp as recommended by central pollution control board.

The chlorination and first alkaline extraction stage are generally considered as the delignification stage of bleaching operations. The chlorine reacts with pulp rapidly and selectively over a narrow range of pH values of about 1 to 3 at ambient temperature and at a low consistency of about 3%. Chlorine is also effective in removing dirt and shives during bleaching. The drawbacks in using chlorine include the formation of chlorinated organic by-products

(highly toxic in nature) formation of chloride ions, which renders the filtrate highly corrosive in nature towards conventional carbon and stainless steel.

Chlorine is partially soluble in water and exists in various molecular forms at different pH. Molecular chlorine (Cl_2) and hypochlorous acid (HOCl) are in equilibrium at pH 2.0 at 25 ^{0}C

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \text{ ---------- (1)}$$

Both hypochlorous and hydrochloric acids dissociate in water to release a hydrogen ion (H+). Hydrochloric acid is completely dissociated at the normal chlorination stage pH level, but hypochlorous acid is only slightly dissociated according to the equation mentioned (145) below :

$$HOCl \longrightarrow H^+ + OCl^- \text{ ---------- (2)}$$

The most important process variable controlling the form of chlorine present in the C-stage is pH. The equation 1 and 2 indicates that as the hydrogen ion concentration increases, the equilibrium is shifted to left, facilitating molecular chlorine. Increasing the pH shifts the equilibrium to the right hand side and enhance the formation of hypochlorous acid and finally hypochlorite.

The type of reactive species present in the chlorination stage is significant, because hypochlorous acid reacts with pulp components by different mechanisms than does chlorine. Hypochlorous acid reacts less selectively with lignin than chlorine and degrade pulp quality and low yield may result from attack on carbohydrates. Reactions of hypochlorous acid with lignin are mainly oxidative, but reactions with chlorine involve oxidation, substitution and addition, contributing to the break down of the lignin macromolecules into small soluble fragments or modify the lignin so that it become soluble in following alkaline extraction stage. The substitution and addition lead to the formation of highly toxic chlorinated organics compounds. However chlorine is the most versatile bleaching agent, the efficiency of the bleaching is very

high. Chlorine attacks lignin and can cause loss of strength properties if used improperly (144). However the use of chlorine is decreasing rapidly due to environmental concerns.

The main function of chlorination stages is to remove the lignin from unbleached pulp in more selective manner than pulping. The various types of reaction such as oxidation, substitution and addition reactions takes place with various reactive species leads to the breakdown and removal of most of the residual lignin from the pulps. Some of the lignin is dissolved in acidic chlorination filtrate. The dissolved lignin consists of relatively low molecular weight carboxylic acid containing organic compounds. Various chlorine-containing compounds such as phenols and fatty and resins acids (107,209). The lignin which is not dissolved in acidic C-stage is modified extensively by reaction with chlorine (97). Oxidation reaction destroys aromatic ring structure generating hydrophilic acid, substitution and addition reactions lead to the incorporation of the chlorine atoms into the structure of residual lignin. Most of these chlorine substituted lignin substituted lignin is solubilized and removed by alkaline hydrolysis reactions. It has been shown that the products of the substitution reaction, highly chlorinated phenolic and chlorinated dioxin and furans can be decreased by operating the chlorination stage at higher pH and splitting the total charge of chlorine among multiple addition (65,66). The effects of other selected process variables on chlorine reaction are given in table 4.1B. However the reaction of molecular chlorine with cellulose are much slower than those with lignin. Cellulose chain can be broken by oxidation reaction involving hypochlorous acid or chlorine and also by attack of chlorine radical. Carbonyl groups are generated which render the carbohydrate chain cleavage in latter alkaline extraction stages.

The use of hypochlorite is decreasing rapidly now-a-days. Hypochlorite should be used at the proper pH, hypo is capable of reducing the viscosity of the pulp significantly. The pH of any hypo stage is especially important. If the pH is allowed to drop much below a level of 1(

around pH 9 or even less, the hypo changes into hypochlorous acid. This chemical attacks cellulose thereby both viscosity and pulp strength will drop. Excessive hypo charge also results in cellulose attack.

4.2B Experimental Methodology:

The bleaching experiments were carried out in polythene bags, except chlorination which was performed in polyethene bottles air tight with lid. The bleaching experiments were conducted with 50 gm. (o.d) pulp. After each stage, the pulps were washed with water properly. The effluent generated from each stage was mixed together to a consistency of 1% and the combined pollution load from a specific sequence was determined. The conditions maintained during bleaching at various stages have been reported in table 4.2B.

4.3B Conventional Bleaching Sequences Studied:

In India, most of the mills uses either CEH or CEHH conventional bleaching sequences. Some of the mills use little dose of hydrogen peroxide in alkaline extraction stage or in the final bleaching stage. Use of oxygen bleaching have been adopted by only very few mills. The various conventional bleaching sequences studied for the soda and kraft poplar pulps includes the CEH, CEHH, and CEHP bleaching sequences with and without oxygen delignification.

The soda, soda-AQ, kraft and kraft-AQ pulps were studied for the conventional CEH, CEHH, and CEHP bleaching sequences. These pulp were also oxygen delignified and then bleached by the above mentioned bleaching sequences to observe the effect of oxygen during bleaching operations. During bleaching, a kappa factor of 0.2 was applied for all the pulps. During the chlorination stage, 70% of total chlorine demand was applied to the pulp and the remaining 30% chlorine demand was applied in the Hypochlorite (H) stage. In the case of two hypochlorite stages, the chlorine demand of 20% was applied in the first hypochlorite stage and

the remaining 10% was applied in the final H-stage. In the case of CEHP sequence, 0.2% hydrogen peroxide was applied in the final P stage. It has been observed that poplar pulps respond very well towards the conventional bleaching sequences, producing pulps with a brightness level of 80% ISO. The results of soda, soda-AQ, kraft and kraft-AQ pulps with and without oxygen for CEH bleaching sequence have been reported in tables-4.3B and 4.4B respectively. The results of soda, soda-AQ, kraft and kraft-AQ pulps with and without oxygen for CEHH bleaching sequence have also been reported in tables- 4.5B and 4.6B respectively.

4.4B Bleach Effluent Characteristics:

The effluent generated from each stage was mixed together to a consistency of 1% and combined pollution load from a specific sequence was determined. The BOD and COD values were determined as per standard method. AOX has been calculated theoretically and the results has been reported in table-4.8B.

4.5B Pulp Evaluation:

The pulps bleached with CEH, CEHH, CEHP, OCEH, OCEHH were beaten to a freeness level of around 300 ml. CSF. The standard hand sheets were made on British sheet former as per TAPPI standard method. These hand sheets were conditioned at 65%±2 relative humidity, $27\pm1^{0}C$ temperature and evaluated for the various physical strength properties. The results have been reported in table-4.7B.

4.6B Results and Discussion:

The soda, soda-AQ, kraft and kraft-AQ pulps were bleached with the conventional, CEH, OCEH, CEHH, OCEHH and CEHP bleaching sequences. The results has been reported in table-4.3B, 4.4B, 4.5B, and 4.6B. It has been observed that the pulp of poplar deltoides could be easily bleached using conventional bleaching sequences at the lower chlorine demand (0.2 × kappa no.) to the brightness level of around 80% ISO and above. These experiments indicated that popla

pulp has good bleachability and they respond very well towards conventional bleaching sequences. The soda, soda-AQ, kraft and kraft-AQ pulps with kappa no. 24.1, 21.8, 17.6 and 16.7 respectively consumes all the chlorine applied i.e. 4.75, 4.3, 3.45, 3.15% chlorine respectively during bleaching, while the kappa number of these pulps as a result of oxygen delignification reduced to 13.2, 9.8, 9.1 and 8.5 respectively and consumes 2.68, 1.80, 1.75 and 1.65% chlorine respectively during bleaching. Due to the reduction in kappa number (the lignin content in the pulps) during oxygen delignification, the bleach chemicals consumption has also reduced drastically to the same tune. The reduction in kappa number also enhances pulp bleachability by allowing high brightness pulp during bleaching. The chlorine consumption has been reduced to about 50% from its original level. The bleaching data on evaluation revealed that the OCEH and OCEHH bleached pulp have better viscosity as compared to CEH and CEHH bleached pulps due to comparatively lower degradation of carbohydrate material. In the case of CEHP bleaching sequence, the use of 0.2% hydrogen peroxide increases the brightness of the pulp by 0.8 ISO. It has been seen that the oxygen delignified pulp have better viscosity. The strength properties of these bleaching sequence are quite comparable. The oxygen-delignified pulp shows a very slight decrease in the strength properties. The result of analysis of the bleach effluent shows that there is drastic, decrease in the values of BOD and COD with the oxygen-delignified pulps. This effluent on secondary treatment gives acceptable values within the tolerance limits as prescribed by central pollution control board.

The unbleached pulp of around 20 kappa contains about 3% of the lignin. This shows that in the perfectly selective delignification, the yield loss should be 3% but the actual yield loss is estimated 5-6% depending on the final brightness of the pulp and bleaching process.

Most of the residual lignin is degraded and removed in the chlorination stage, so the chlorinated stage filtrate is the major contributor of organic loading. The lignin remaining in the

fiber after pulping still contain aromatic structures but different from more the native lignin in that it contains more carbon-carbon inter linkages and fewer inter unit ether linkages (113). During chlorination, carboxylic acid groups are formed and chlorine atoms are introduced with de-polymerization of lignin. Most of the aromatic rings are destroyed by oxidative cleavage reaction. Some of the degraded material is dissolved and removed in acidic chlorination stage filterate, but most of the degraded lignin and carbohydrate fragments are solubilized in the hot extraction stage.

A number of structures including carbohydrate and lignin found in pulp that can react with chlorine to yield chloroform (71) although largest amount of chloroform is formed in hypochlorite bleaching stage in a multiple bleaching stages accounting for 5-15 times of the total amount produced by C, E and D stages (34). Hypochlorite consumption is the dominant factor affecting the amount of chloroform produced in the H stage (34). It is also affected by the CE kappa number, which determines the hypochlorite charge. It has been reported in literature that the hard woods produce much less chloroform during hypochlorite stage compared to soft woods (34).the developed countries have stoped using hypochlorite during bleaching, however in the developing countries like India the use of hypochlorite in bleaching of pulp is still in practice.

4.7B Conclusions:

The soda and kraft pulps of poplar deltoides respond very well towards good bleachability and could be easily bleached to the brightness level of 80% ISO at 0.2 kappa factor. The oxygen delignified pulps followed by further bleaching sequences gives the pulp of higher brightness and higher viscosity. Oxygen delignification of pulps has resulted in drastic drop in pollution load particularly in conventional bleaching sequences. The strength properties of these bleaching sequences are comparable.

Table 4.1B: Effects of other selected process variables on chlorine reaction

Pulp composition	Effect on bleaching Reaction
High temperature	More Oxidation
Longer reaction time	More Oxidation
High pH	More Oxidation
High chlorine content	More Substitution
High lignin content	More Substitution
More condensed lignin	More Oxidation

Table 4.2B: Bleaching conditions

Particulars	C	E	H	O	P
Consistency,%	3-4	10	10	10	10
PH	>2	11-12	11-12	<11	10-11
Temperature , C	Ambient	70	60-70	100-105	70
Timc ,minutes	45	120-180	45	45	90-180

Table 4.3B: Conventional CEH bleaching sequence of soda and soda AQ pulps with and without oxygen delignification .

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda AQ pulp	16% soda AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.2
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
Total chlorine demand, %	4.82	2.64	4.36	1.86
Chlorination stage				
Chlorine applied, %	3.4	1.85	3.05	1.33
E-stage				
NaOH, %	2.0	1.0	2.0	1.0
pH	12.3	12.3	12.3	12.0
Hypochlorite stage				
Calcium hypochlorite as available chlorine ,%	1.42	0.6	1.3	0.5
NaOH,%	0.5	0.2	0.5	0.2
Brightness ,%ISO (±0.4)	78.6	80.6	79.2	81.3
Pulp Viscosity, cm^3/g (±10)	330	340	350	390

Table 4.4B: Conventional CEH bleaching sequence of Kraft and Kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16% Kraft oxygen delignified pulp	16% Kraft AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.7	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
Total chlorine demand, %	3.5	1.8	3.3	1.7
Chlorination stage				
Chlorine applied ,%	2.45	1.25	2.4	1.2
E-stage				
NaOH, %	1.45	1.0	1.5	1.0
pH	11.8	11.8	11.9	11.9
Hypoclorite stage				
Calcium hypochlorite as available chlorine ,%	1.05	0.55	0.95	0.5
NaOH,%	0.8	0.3	0.8	0.3
Brightness ,%ISO (±0.4)	79.2	81.6	80.1	82.3
Pulp Viscocity,cm^3/g (±10)	370	410	380	410

Table 4.5B: Conventional CEHH bleaching sequence of soda and soda AQ pulps with and without oxygen delignification .

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda AQ pulp	16% soda AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
Total chlorine demand, %	4.82	2.64	4.36	1.86
Chlorination stage				
Chlorine applied,%	3.4	1.85	3.10	1.25
E-stage				
NaOH, %	2.0	1.0	2.0	1.0
pH	12.3	12.4	12.4	12.4
Hypoclorite stage				
H1 stage				
Calcium hypochlorite as available chlorine ,%	1.0	0.4	0.85	0.40
NaOH,%	0.5	0.3	0.6	0.2
H2 Stage				
Calcium hypochlorite available as chlorine ,%	0.4	0.2	0.4	0.2
NaOH,%	0.4	0.3	0.4	0.2
Brightness ,%ISO (±0.4)	79.2	81.0	80.1	81.9
Pulp Viscosity, cm^3/g (±10)	340	410	350	420

Table 4.6B: Conventional CEHH bleaching sequence of Kraft and Kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft AQ pulp	16% Kraft AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.7	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
Total chlorine demand, %	3.5	1.8	3.3	1.7
Chlorination stage				
Chlorine applied,%	2.45	1.25	2.3	1.2
E-stage				
NaOH, %	1.5	1.0	1.5	1.0
pH	12.3	12.3	12.3	12.3
Hypoclorite stage				
H1 stage				
Calcium hypochlorite as available chlorine ,%	0.7	0.37	0.63	0.33
NaOH,%	0.8	0.5	0.8	0.5
H2 Stage				
Calcium hypochlorite as available chlorine ,%	0.35	0.18	0.32	0.17
NaOH,%	0.5	0.5	0.5	0.5
Brightness,%ISO (±0.4)	80.3	82.0	81.2	83.1
Pulp Viscosity, cm^3/g(±10)	380	430	390	440

Table 4.7B: Strength Properties of bleached Poplar pulps at 300 ml CSF

Table 4.7B: Strength Properties of bleached Poplar pulps at 300 ml CSF

Pulps	Bleaching Sequence	Tensile Index (N.m/g) (±1.2)	Tear Index (mNm^2/g) (±0.4)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Viscosity, cm^3/g (±10)
Soda Pulp	CEH	56.8	5.2	3.7	330
	CEHH	56.7	5.2	3.8	340
	CEHP	57.2	5.3	3.8	330
	OCEH	55.2	5.5	4.0	370
	OCEHH	56.0	5.3	4.0	410
Soda –AQ Pulp	CEH	57.2	5.5	3.8	340
	CEHH	57.6	5.5	3.9	350
	CEHP	57.2	5.6	3.9	330
	OCEH	56.0	5.8	4.0	390
	OCEHH	57.1	5.4	4.0	410
Kraft pulp	CEH	61.6	6.0	4.1	370
	CEHH	62.2	6.2	4.2	380
	CEHP	61.4	6.2	4.3	370
	OCEH	62.0	6.3	4.3	410
	OCEHH	61.4	5.9	4.1	430
Kraft-AQ Pulp	CEH	62.0	6.2	4.0	380
	CEHH	62.4	6.5	4.2	390
	CEHP	61.3	6.6	4.2	380
	OCEH	61.4	6.5	4.1	410
	OCEHH	61.8	6.5	4.1	440

Table 4.8B: Characteristics of bleach effluents at 1% consistency.

Pulps	Bleaching Sequence	COD mg/l	BOD mg/l	AOX kg/ton
Soda	CEH	390	130	4.8
	CEHH	400	140	4.8
	CEHP	390	120	4.4
	OCEH	240	70	2.6
	OCEHH	260	70	2.6
Kraft	CEH	370	110	3.5
	CEHH	390	120	3.5
	CEHP	370	110	3.2
	OCEH	230	70	1.8
	OCEHH	240	80	1.8

4.1.C: Introduction:

Rapson in 1956 reported the use of ClO_2 in the bleaching of sulfite pulps to achieve low resin content (172). By the time the use of chlorine dioxide in kraft bleaching was developed rapidly. In 1960s Feller and Jack discovered the synergistic effect of using chlorine dioxide ahead of chlorine in chlorination stage (87). Other workers described the use of chlorine and chlorine dioxide in various modes and combinations (32). The use of mixtures of chlorine dioxide and chlorine to bleach the pulp has been described in the literature on numerous occasions (82,156,161,164,167,217). When chlorine dioxide was substituted for chlorine delignification efficiency increases significantly (170). Further it was discovered that when the chlorine dioxide and chlorine were added to the pulp sequentially and the chlorine dioxide added first the benefit was greater (55,87). Maximum delignification efficiency was achieved when the fraction of chlorine was between 40 to 60% (62). When the chlorine dioxide added first delignification efficiency found to be decreased when 100% chlorine dioxide is used in chlorination stage; it is much less effective, often resulting a higher lignin content after the Cl stage and lower final brightness. Therefore, higher chlorine multiple is used in 100% chlorine dioxide bleaching sequences. At 10-30 ^{0}C, chlorine dioxide reacts more slowly than chlorine or a mixture of chlorine and chlorine dioxide although at 50 ^{0}C, the rates are indistinguishable. The use of 100% chlorine dioxide has the advantages of causing little damage to pulp, lowering the resin content and decreasing the NaOH consumption in the first extraction stage (32).

In the early 1980s, another surge of interest was brought by environmental concerns leading to numerous publications. Germgard conducted definitive studies on the kinetics an

stoichiometry of delignification with ClO_2 and Cl_2/ClO_2 combinations (54-59). The ClO_2 delignification rate doubles with every increase in temperature of approximately 10 ^0C (59). Germgard found the Stoichiometry of delignification of kraft pulps was same with ClO_2 as with combination of chlorine and chlorine dioxide. That the same amount of equivalent chlorine is required to decrease the kappa number by a given amount. However on oxygen delignified pulps, ClO_2 was found to be less efficient than chlorine.

Modification of bleaching process is generally the least costly and simplest means of reducing environmental load of bleach plants. The growing concerns about chlorinated organic compounds have resulted in a decreased use of chlorine in the first stage. It is being replaced by more and more chlorine dioxide and eliminating the use of hypochlorite in the first stage (137).

- In mixtures with chlorine.
- In a sequential order with the chlorine dioxide usually preceding the chlorine treatment.
- As a total replacement of chlorine.

When a moderate amount of chlorine dioxide is applied in a sequential ClO_2/Cl_2 treatment, most of the chlorine dioxide is consumed prior to the addition of chlorine. As a consequence, little chlorine dioxide may remain to exert its protective influence on the carbohydrates in the ensuing chlorination phase of the treatment, as compared to the case when chlorine dioxide and chlorine are mixed. The sequential addition of chlorine dioxide and chlorine is preferred when delignification is the prime consideration.

In the case of oxygen delignified pulps, the final kappa number is higher for 100% chlorine dioxide as compared to 100% chlorine, illustrating the relative difficulty in delignifying these pulps with chlorine dioxide (7,8,54,57), due to the decrease in the free phenolic groups in the pulp; thereby increasing the difficulty and delignification with chlorine dioxide alone.

The use of chlorine dioxide in the first stage decreases the color of the bleach plant effluent (185). This effect becomes more pronounced with an increase in the proportion of chlorine dioxide used in this stage. The addition of chlorine dioxide in the first stage also helps in reducing the toxicity of the effluent. Therefore, the environmental regulations have made the use of chlorine dioxide important and more over it is economical too, even if total replacement of chlorine by chlorine dioxide is done (126).

Moreover, the addition of hydrogen peroxide or oxygen or both is reported to have further cut down the steam consumption of chlorine dioxide. The TOCl formation has also been reduced due to oxidative extraction. The formation of chlorinated compounds have been decreased by prebleaching the pulp with oxygen. By employing oxygen prebleaching, the kappa number of the pulp can be reduced by 40-50%, without affecting much, the viscosity of pulp and thereby decreasing the consumption of bleaching chemicals in the following stages (1,21,22,41,122).

4.2.C: Experimental Methodology:

The soda and kraft pulps were oxygen delignified in the Weverk rotatory digester fitted with lids, incorporating valves to introduce oxygen into the vessel. Pulp samples were mixed with $MgSO_4$ (0.1% pulp basis) and NaOH (1.5-2.0%) and water to a pulp consistency of 10% and placed in the vessel which were pressurized with oxygen at a pressure of 5 kg/cm^2 and at of 70 ^0C and heated at 105 ^0C for 45 minutes.

The chlorine and chlorine dioxide/chlorine stages were done at 4% pulp consistency in the sealed plastic bottles at 70 ^0C for 60 minutes. In chlorine dioxide/chlorine stages, the ClO_2 was added 60 seconds ahead of the chlorine. The E-stage bleaching was done at 10% consistency at 60 ^0C for 1 hour. The initial pH maintained at around 10.5. The alkali charge was 0.75 – 1.0% and the final pH was around 9.5-10.0. The EO and EOP stages were done at 10% pulp

consistency in stainless steel vessel at a temperature of 105 ^{0}C for 30 minutes, at a oxygen pressure of 5 kg./cm^2 with 1.5% NaOH charge on pulp basis. The amount of H_2O_2 added in EOP stages was 0.2 to 0.3%. The final D-stages were done in plastic bags at 10% pulp consistency at a temperature of 70 ^{0}C for 240 minutes.

4.3C: Bleaching Sequences Studied:

Due to the strict regulations of the pollution control boards of India. The mills are trying to force some changes in their bleaching process. Many mills have started using hydrogen peroxide. A few of them has started using chlorine dioxide in conventional bleaching sequences and intend to introduce oxygen delignification also.

The soda and kraft pulps of poplar were bleached using CEHED, CEDED and D/C EDED bleaching sequences. These pulps were also oxygen delignified and bleached by the above mentioned bleaching sequences. In the case of D/C EDED, the chlorine dioxide and chlorine were used sequentially to bleach the pulps. The chlorine dioxide was added first and then chlorine was added to get the maximum benefits (15). During the substitution chlorine dioxide and chlorine were used 50-50%.

4.4C: Bleach Effluent Characteristics :

The bleach effluent generated from each stage was collected and mixed together to a consistency of 1%, and combined pollution load from specific sequences was determined. The BOD and COD values were determined as per ASTM standard methods. AOX has been calculated theoretical with a formula devised by Germgard (58,59), to estimate the amount of chlorinated organics formed during bleaching of kraft pulp, from the quantities of chlorine, chlorine dioxide and sodium hypochlorite consumed in various bleaching stages. The original equations has been modified (42,108) for Cl_2 and ClO_2 bleaching as given below:

$$AOX = 0.1 (Cl_2 + ClO_2/5)$$

Where AOX is the amount of adsorbable organic halide expressed as kg/t of pulp.

Cl_2 is the total amount of molecular chlorine used in bleaching sequence expressed as kg/t of pulp.

ClO_2 is the total amount of ClO_2 used in bleaching sequence, expressed as kg of active chlorine/t of pulp.

The factor 0.1 can vary with the type of pulp, but this value is used in most cases.

The results have been reported in table 4.10C

As reported in the literature, the values of AOX for the first two staged effluent accounts for about 70% of the chlorinated organics generated in the bleach plants. In fact, the pulp after CE,(C/D)E or DE stages contains very low amount of lignin hence in the last stages most of the bleaching chemical is used for brightening only.

4.5C: Pulp Evaluation:

The kraft pulps of poplar with and without oxygen delignification were bleached using CEHED, bleaching sequences. These pulps were beaten in the PFI mill, to the freeness level of around 300 ml CSF. The hand sheets were formed on British sheet former as per TAPPI standard method. These hand sheets were conditioned at 65±2% relative humidity, 27±1 ^{0}C temperature and evaluated for the various strength properties. The results have been reported in table 4.9C.

4.6C: Results and Discussions:

The results of CEHED, CEDED, C/D EDED and D/C (EOP) DED bleaching sequences of soda and kraft pulps with and without oxygen delignification are reported in table 4.1C to 4.8C. In the case of CEHED bleaching sequence of soda and kraft pulps with and without oxygen delignification, the chlorine applied in C stage was 0.14 x kappa number and ClO_2 applied was 1%. The results are reported in table 4.1C and 4.2C. It could be observed that the use of chlorine dioxide increases the brightness and the viscosity of the pulp as compared to CEHH bleaching

sequence as the chlorine dioxide provides pulp with higher brightness and lower brightness reversion and effective in particle elimination. It does not react extensively with carbohydrates although some oxidation of cellulose takes place. If the chlorine di oxide stage is very acidic, some acidic hydrolysis of cellulose takes place. The viscosity loss in chlorine di oxide bleaching is very low. However, in aggressive conditions such as pH 2 and temperature greater than 80°C some carbohydrate degration takes place which effect the strength properties of the pulp. The oxygen delignified pulps tend to increase the brightness by 1.5-1.8 units. The oxygen delignified pulps have better viscosities, however the improvement in viscosity was not clearly reflected in terms of better physical strength properties of the refined bleached pulps at 300 ml. CSF. The pulps bleached with CEHED bleaching sequences trended to have lower tensile and tear index with comparable burst as compared to the without oxygen delignified bleached pulps. The loss in strength properties of oxygen delignified pulps is about 10-15%. The results have been reported in table-4.1C and 4.2C. In table 4.3C and 4.4C the results of the CEDED bleaching of soda and kraft pulps of poplar with and without oxygen delignification have been reported. In this case the kappa factor of 0.14 was applied in the C stage and 1% ClO_2 was applied in D_1 stage and 0.6% ClO_2 were applied in D2 for pulps delignified with and without oxygen.. The results indicates that the pulps bleached with CEDED bleaching sequence have the higher brightness with better viscosity as compared to CEHED bleaching sequence. The results of the strength properties, as tabulated in table – 4.9C, also indicate a improvement in physical strength properties.

In the case of D/C EDED bleaching sequence, chlorine dioxide is applied in a sequential ClO_2/Cl_2 treatment. In chlorine dioxide/chlorine bleaching, the ClO_2 was added about 1 minute ahead of the chlorine. In C/D stage a kappa factor of 0.14 was applied in D_1 and D_2 stage which is similar as in the case of CEDED bleaching sequence. The results are reported in table-4.5C and 4.6C. The results of D/C EDED bleaching shows that there is significant increase in the

brightness and viscosity of the fully bleached pulp. The D/C stage also responded well in the case of oxygen delignified and AQ pulps with a definitive increase in the brightness and viscosity D/C EDED bleached pulp was found to have better strength properties as compared to CEDED bleached pulps.

In the case of D/C (EOP) DED bleaching sequence, the chlorine and chlorine dioxide applied was similar as in the case of D/C EDED bleaching, only E-stage has been replaced by EOP using 0.2% hydrogen peroxide. The results have been reported in table 4.7C and 4.8C. The pulp bleached with D/C (EOP) DED sequence were found to have ultra high brightness of 86% to 90.3% ISO. The strength properties of D/C (EOP) DED bleached pulps were found to be slightly lower than the D/C EDED bleached pulps.

The soda and soda-AQ and kraft and kraft-AQ pulps were bleached by either using the same kappa factor and/or the same chlorine dioxide charges in D_1 and D_2 stages. It has been found that the fully bleached soda-AQ and kraft-AQ pulps were have 1.6 ISO brightness more than the conventional soda and kraft pulps. In appears that AQ, presumably inhibit the lignin condensation and/or bonding to carbohydrate during the course of cooking operation, rendering the residual lignin more easily removable during the chlorination stage to produce the brighter pulps (123).

The results of the effluent characteristics reported in table-4.10C shows that the oxygen delignification has been an important tool in reducing the pollution load by lowering the bleach chemicals demand. In the case of oxygen delignified pulps, there has been a drastic decrease in the COD and BOD characteristics of effluent. The use of chlorine dioxide further helps in decreasing the pollution load of the effluent. The substitution of chlorine dioxide also shows higher reduction of the effluent characteristics.

The economic consideration in the use of chlorine di oxide in delignification is the chemical cost. Many studies have been conducted regarding econonic cosideration. A study showed lowest

cost is obtained in the range of 30-50% substitution with the cost being relatively insensitive over this range. As 100% substitution is approached the chemical cost increased sharply. A trial in hard wood kraft pulp indicated that increasing chlorine di oxide substitution to about 50% does not influence cost (211). A study showed that 25% substitution, chemical cost were decreased by 10% in one mill but remained unchanged inanother (39). Recent millstudies and mill survey have examined 100% chlorine di oxide substitution have reported significant increase in bleaching chemical cost (89,153,216)

4.7C: Conclusion:

The use of chlorine dioxide improves the delignification efficiencies by increasing the brightness and the viscosity of the pulps. To obtain pulps with higher brightness, little higher chlorine dioxide charge is required. The substitution of chlorine with chlorine dioxide increases the delignification efficiency and results in the brighter bleached pulps. The use of chlorine dioxide protects the carbohydrates from the degradation as it does not react extensively with carbohydrates although some oxidation of cellulose takes place. If the chlorine di oxide stage is very acidic, some acidic hydrolysis of cellulose takes place. The viscosity loss in chlorine di oxide bleaching is very low. However, in aggressive conditions such as pH 2 and temperature greater than 80°C some carbohydrate degration takes place which effect the strength properties of the pulp and results in the higher viscosity and better physical strength properties.

Oxygen delignified pulps responsd well towards chlorine dioxide bleaching. The effluent characteristics of the oxygen-delignified pulp bleached with chlorine dioxide drastically reduce the BOD and COD values, which values are within the limits of the central pollution control board.

The AQ pulps also respond well towards the chlorine dioxide bleaching. The soda AQ and kraft AQ pulps bleached with ClO_2, produce pulps with almost 1% higher ISO brightness values than the conventional soda and kraft pulps.

Table 4.1C: CEHED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification .

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda AQ pulp	16% soda AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
Total chlorine demand, %	4.82	2.64	4.36	1.86
Chlorination stage				
Chlorine applied, %	3.4	1.85	3.10	1.25
Consumed,%	3.25	1.83	3.08	1.23
Final pH	2.1	2.2	2.1	2.2
E-stage				
NaOH, %	2.0	1.0	2.0	1.0
pH	12.3	12.4	12.4	12.4
CE Kappa No.	2.9	2.4	2.6	2.1
H1 Stage				
Hypochlorite, % as Cl_2	1.0	0.6	0.9	0.4
pH	10.5	10.4	10.5	10.4
E-Stage				
NaOH, %	1.0	0.75	1.0	0.75
pH	12.0	11.8	12.0	11.8
D –Stage				
ClO_2,%				
Applied, %	0.8	0.8	0.8	0.8
Consumed, %	0.67	0.62	0.65	0.62
Brightness, %ISO (±0.4)	80.3	82.2	81.4	83.1
Pulp Viscosity, cm^3/g (±10)	330	370	350	380

Table 4.2C: CEHED bleaching sequence of Kraft and Kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft AQ pulp	16% Kraft AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.2	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
Total chlorine demand, %	3.5	1.8	3.2	1.7
Chlorination stage				
Chlorine applied, %	2.45	1.25	2.25	1.2
Consumed, %	2.39	1.20	2.22	1.15
Final pH				
E-stage				
NaOH, %	1.5	1.0	1.5	1.0
pH	12.3	12.3	12.3	12.3
CE Kappa No.	2.7	2.3	2.4	2.1
H1 Stage				
Hypochlorite, % as Cl_2	0.7	0.37	0.63	0.33
pH	10.8	10.5	10.8	10.5
E –Stage				
NaOH, %	1.0	0.75	1.0	0.75
pH	11.8	11.6	11.8	11.6
D –Stage				
ClO_2,%				
Applied, %	0.8	0.8	0.8	0.8
Consumed, %	0.7	0.67	0.69	0.66
Brightness, %ISO (±0.5)	80.7	83.1	82.1	84.2
Pulp Viscosity ,cm^3/g(±10)	380	400	430	4500

Table 4.3C: CEDED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification .

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda-AQ pulp	16% soda -A oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
Chlorination stage				
Chlorine applied, %	3.4	1.85	3.05	1.33
E – stage				
NaOH, %	2.0	1.5	2.0	1.5
PH	12.3	12.4	12.4	12.3
D 1 – Stage				
ClO_2,%	1.0	1.0	1.0	1.0
Applied, %	0.91	0.88	0.9	0.86
Consumed, %				
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
PH	12.1	11.9	12.2	11.8
D 2 – Stage				
ClO_2,%	0.6	0.6	0.6	0.6
Applied, %	0.54	0.52	0.51	0.50
Consumed, %				
Brightness,%ISO (±0.4)	81.6	83.8	83.0	84.7
Pulp Viscocity,cm^3/g (±10)	350	400	370	400

Table 4.4C: CEDED bleaching sequence of Kraft and Kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16% Kraft oxygen delignified pulp	16% Kraft AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	14.8	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	520	580	530
Chlorination stage				
Chlorine applied, %	2.45	1.25	2.25	1.2
E – stage				
NaOH, %	1.5	1.0	1.5	1.0
PH	11.8	11.8	11.9	11.9
D 1 – Stage				
ClO_2,%	1.0	1.0	1.0	1.0
Applied, %	0.88	0.83	0.84	0.82
Consumed, %				
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
PH	12.0	12.1	12.2	11.9
D 2 – Stage				
ClO_2,%	0.6	0.6	0.6	0.6
Applied, %	0.56	0.52	0.56	0.5
Consumed, %				
Brightness,%ISO(±0.4)	82.1	84.7	83.6	85.4
Pulp Viscocity,cm^3/g (±10)	400	430	410	430

Table 4.5C: D/ CEDED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification .

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda AQ pulp	16% soda AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
D/C Stage				
ClO_2,% as Cl_2,%				
Applied, %	1.75	1.0	1.5	0.75
Chlorine as Cl_2 applied, %	1.75	1.0	1.5	0.75
Final pH	2.2	2.3	2.2	2.1
E – stage				
NaOH, %	2.0	1.5	2.0	1.5
PH	12.3	12.1	12.2	12.4
D 1 – Stage				
ClO_2,%				
Applied, %	1.0	1.0	1.0	1.0
Consumed, %	0.9	0.87	0.89	0.87
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
PH	12.2	11.8	12.0	11.9
D 2 – Stage				
ClO_2,%				
Applied, %	0.6	0.6	0.6	0.6
Consumed, %	0.56	0.55	0.56	0.54
Brightness, %ISO (±0.4)	84.3	86.1	85.4	87.1
Pulp Viscosity, cm^3/g (±10)	400	420	400	420

Table 4.6C: D/ CEDED bleaching sequence of Kraft and kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft -AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.2	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
D/C Stage				
ClO_2,% as Cl_2,%	1.25	0.8	1.15	0.7
Applied, %	1.25	0.8	1.15	0.7
Chlorine as Cl_2 applied, %	2.2	2.3	2.1	2.2
Final pH				
E – stage	1.5	1.0	1.5	1.0
NaOH, %	12.0	11.9	11.9	12.0
PH				
D 1 – Stage	1.0	1.0	1.0	1.0
ClO_2,%	0.88	0.85	0.87	0.84
Applied, %				
Consumed, %				
E 2-Stage	1.0	0.75	1.0	0.75
NaOH, %	12.0	11.9	12.1	11.8
PH				
D 2 – Stage	0.6	0.6	0.6	0.6
ClO_2,%	0.56	0.54	0.54	0.52
Applied, %				
Consumed, %				
Brightness, %ISO (± 0.4)	85.4	87.2	86.9	88.0
Pulp Viscosity,cm^3/g (±10)	450	440	450	470

Table 4.7C: D/ C(EOP)DED bleaching sequence of Kraft and kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft -AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.2	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
D/C Stage				
ClO2,% as Cl_2,%	1.25	0.8	1.15	0.7
Applied, %	1.25	0.8	1.15	0.7
Chlorine as Cl_2 applied, %	2.2	2.3	2.1	2.2
Final pH				
E OP stage :				
NaOH, %	1.5	1.0	1.5	1.0
H_2O_2,%	0.2	0.2	0.2	0.2
Temperature, (°C)	70	70	70	70
Time,(min)	45	45	45	45
Consistency,(%)	10	10	10	10
O_2 Pressure,Kg/cm^2	5	5	5	5
D 1 – Stage				
ClO_2,%	1.0	1.0	1.0	1.0
Applied, %	0.88	0.86	0.88	0.85
Consumed, %				
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
PH	12.0	11.9	12.1	11.8
D 2 – Stage				
ClO_2,%	0.6	0.6	0.6	0.6
Applied, %	0.57	0.54	0.55	0.52
Consumed, %				
Brightness, %ISO (±0.4)	88.5	90.3	89.9	91.7
Pulp Viscosity,cm^3/g (±10)	430	460	460	460

Table 4.8C: D/ C(EOP)DED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification.

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda AQ pulp	16% soda AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
D/C Stage				
ClO_2,% as Cl_2,%	1.75	1.0	1.5	0.75
Applied, %	1.75	1.0	1.5	0.75
Chlorine as Cl_2 applied, %	2.2	2.3	2.2	2.1
Final pH				
E OP stage :	1.5	1.0	1.5	1.0
NaOH, %	0.2	0.2	0.2	0.2
H_2O_2,%	70	70	70	70
Temperature, (°C)	45	45	45	45
Time,(min)	10	10	10	10
Consistency,(%)	5	5	5	5
O_2 Pressure,Kg/cm^2				
D 1 – Stage				
ClO_2,%	1.0	1.0	1.0	1.0
Applied, %	0.88	0.86	0.88	0.82
Consumed, %				
E 2-Stage	1.0	0.75	1.0	0.75
NaOH, %	12.2	11.8	12.0	11.9
pH				
D 2 – Stage	0.6	0.6	0.6	0.6
ClO2,% ,applied	0.57	0.57	0.56	0.58
Consumed, %				
	84.3	86.1	85.4	87.1
Brightness, %ISO (±0.4)	380	410	390	410
Pulp Viscosity,cm^3/g (±10)				

Table 4.9C: Characteristics of bleach effluents at 1% consistency.

Pulps	Bleaching Sequence	COD mg/l	BOD mg/l	AOX kg/ton
Soda	CEHED	380	130	4.5
	D/CEDED	390	110	2.4
	OCEHED	240	90	2.6
	OD/CEDED	230	80	1.5
Kraft	CEHED	340	120	3.3
	D/CEDED	290	100	1.5
	OCEHED	220	80	1.8
	OD/CEDED	210	80	1.4

Table 4.10C: Strength Properties of bleached Poplar pulps at 300 ml CSF

Pulps	Bleaching Sequences	Tensile Index (N.m/g) (±0.8)	Tear Index (mNm^2/g) (±0.4)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Viscosity, $cm^3/$ (±10)
Soda Pulp	CEHED	56.0	5.3	3.8	330
	CEDED	57.7	5.4	3.9	360
	D/CEDED	59.6	5.6	4.2	400
	D/C(EOP)DED	58.9	5.5	4.1	380
	OCEHED	55.1	5.1	3.6	390
	OCEDED	57.2	5.2	3.7	400
	OD/CEDED	58.6	5.6	3.9	430
	OD/C(EOP)DED	58.2	5.5	4.0	410
Soda –AQ Pulp	CEHED	56.5	5.9	3.9	350
	CEDED	57.3	6.1	4.1	370
	D/CEDED	60.0	6.2	4.3	400
	D/C(EOP)DED	59.5	6.1	4.1	380
	OCEHED	55.4	5.7	3.8	380
	OCEDED	56.5	5.9	4.0	400
	OD/CEDED	58.7	6.0	4.2	420
	OD/C(EOP)DED	57.7	5.8	4.1	410
Kraft pulp	CEHED	62.9	6.2	4.0	380
	CEDED	64.0	6.5	4.2	410
	D/CEDED	65.7	6.7	4.5	450
	D/C(EOP)DED	64.9	6.7	4.4	430
	OCEHED	62.0	6.0	4.0	400
	OCEDED	62.8	6.2	4.1	430
	OD/CEDED	65.0	6.4	4.3	440
	OD/C(EOP)DED	64.5	6.3	4.4	460
Kraft-AQ Pulp	CEHED	63.2	6.3	4.0	430
	CEDED	64.7	6.5	4.1	400
	D/CEDED	66.8	6.7	4.4	450
	D/C(EOP)DED	66.2	6.8	4.4	460
	OCEHED	62.4	5.9	3.9	450
	OCEDED	63.8	6.2	3.9	430
	OD/CEDED	65.3	6.4	4.2	470
	OD/C(EOP)DED	65.2	6.4	4.2	460

4.1D: Introduction

The common definition for elemental chlorine free (ECF) bleaching of pulp means bleaching of pulp without chlorine gas. This definition implies that the pulp bleached with chlorine dioxide, hypochlorite, oxygen, peroxide etc. comes under the category of ECF bleaching. The demand for elemental chlorine free (ECF) bleached pulps and total chlorine-free (TCF) bleached pulps have really forced the pulp and paper producers to stretch the desired technology to meet these tough demands in terms of environmental pollution load.. In USA and Europe, most of the mills are producing ECF pulps (148). The main reason for ECF pulp demand is market pressure for an environmentally friendly pulp. most of the ECF sequences, used chlorine dioxide, usually in the first stage alongwith reinforced oxidative extraction stage. The main methods used alone or in combination to produce ECF pulps, are xylanase enzyme pretreatment (155,201), 100% chlorine dioxide substitution, and reinforced extraction. The extended delignification, oxygen or ozone delignification makes ECF pulp production more readily achievable because of the lower lignin content entering the bleach plant. However, chlorine dioxide in the first D stage of ECF bleaching sequence increases the DE kappa number indicating the less delignification taking place in the DE stage, therefore, lower brightness of the pulps have been obtained which can be compensated by increasing the chlorine dioxide charge in the first D stage and subsequent D_1 and D_2 stages. This increases the ClO_2 generation load. Moreover, it decrease the discharge of chlorinated organic compounds in the effluent (156). The use of hydrogen peroxide aids a lot, by increasing the brightness and brightness stability in the ECF bleaching sequences.

There has been an extensive work on the utilization of chlorine dioxide prebleaching of the pulps (61,138,150,151,156,164,172,201). Chlorine dioxide prebleaching, is essentially a delignification treatment and therefore requires operating conditions different from those requires normally for chlorine dioxide brightening stage. Nils-Erik studied the role of chlorine dioxide in the chlorination of the pulp (138,139). However optimum conditions for ClO_2 prebleaching are not clear and appears to be influenced by several factors including wood species (55). Overseas workers studied a range of process conditions that affect chlorine dioxide prebleaching (35,55,56,171,213). These studies revealed that pH, pulp consistency and the presence of chloride ion are particularly important for effective chlorine dioxide delignification. The pH, affects the chemical interactions between chlorine dioxide and the various chlorine species produced i.e. chlorite, chlorate, hypochlorite and chlorine (53,213,214). It has been reported that for efficient chlorine dioxide brightening, during final bleaching, the formation of chlorite and unreactive chlorate anions must be minimized and this typically occurs at a final pH of about 3.5-4.5 (57,61). There is less agreement in the literature as to the optimum pH for chlorine dioxide delignification (9,35,55,56,171,213). Germgard, Tedder (55,56) reported that the optimum pH for ClO_2 prebleaching of kraft oxygen pulp from Scandinarian pine was pH 2.0 or even less, this would require pre-acidification of the kraft oxygen pulp prior to the application of chlorine dioxide. Other studies have shown that the effective chlorine dioxide charge is reasonably high and alkaline carry over is minimized. The studies have report that the increase in chloride ions concentration during chlorine dioxide prebleaching have been shown to improve the delignification presumably through the formation of addition chlorine (55). Van Heiniger (14) has shown that much of the observed delignification during ClO_2 bleaching is due to the action of chlorine, and its hydrolysed form, hypochlorous acid. Other studies however, have shown that increased chloride concentration decreases the formation of chlorate ion at the same

time as it enhances bleaching effectiveness (32,33). Reeves (32, 35) have shown that chlorine dioxide delignification at medium pulp consistency around 10% is more effective than similar treatment at lower pulp concentration (around 3%). This effect has been found to be species dependent with hardwood pulps showing greater response to concentration changes than softwood kraft pulps.This type of study was also done by Allison (161,162). However Germgard (55,56) reported that consistency has no effect on the effectiveness of chlorine dioxide delignification.

Many studies shown that hydrogen peroxide has been an effective media in increasing the brightness of the pulp and in decreasing the amount of ClO_2 usage in the bleaching sequence (154). Meng et al, showed the application of peroxide in second extraction stage (E_2P), reduces the ClO_2 consumption using, by 0.2% H_2O_2. These savings could be obtained using the bleaching sequences with 100% ClO_2(164).

ECF bleaching with 100% chlorine dioxide requires a higher kappa factor. In a Canadian mill trail (219), it was reported that kappa factor of 0.23 was required for ECF, as compared to 0.19 for 45% substitution. Allison (5) verified this for oxygen delignified radiata pine, pulps which required a third more equivalent chlorine. This increased charge also applied to modified kraft pulps as well as oxygen delignified pulps (73). One key to optimizing an ECF sequence is not to over charge ClO_2 in the first stage rather to use a balance over all subsequent stages. This will minimize chemical consumption and cost.

The objective of the present work was to study the effect of ECF bleaching sequences on the improvement in the brightness levels of pulps obtained alongwith reduction in environmental pollution load. The effect of hydrogen peroxide in the ECF bleaching sequences alongwith the efficiency of H_2O_2 in reducing the ClO_2 usage at different H_2O_2 application points, have also been studied.

4.2D: Bleaching Sequences Studied:

The soda, soda AQ, kraft, and kraft-AQ pulps of poplar deltoides with and without oxygen delignification were bleached using DEDED, D(EOP)DP and D(EOP)DED bleaching sequences. The kappa factor applied to the soda, soda-AQ kraft, and kraft-AQ pulps for the first D stage was 0.14. In the D_1 and D_2 stages 1% and 0.8% chlorine dioxide was applied respectively, and the results of these experiments have been reported in tables 4.1Dto 4.6D.

4.3D: Results and Discussion:

Results of DEDED and ODEDED bleaching sequence of soda and kraft pulps of poplar have been reported in table 4.1D and 4.2D.The kappa factor applied in the first D stages of with and without oxygen delignified was 0.14 respectively. In the D_1 and D_2 stages the chlorine dioxide applied was 1.0 and 0.8% respectively, in the all cases. The soda, soda-AQ kraft, and kraft-AQ pulps bleached with DEDED and ODEDED bleaching sequences, attained a brightness values of 82.2, 81.8, 86.2, 86.0 and 81.5, 81,3, 85.1 and 86.1% ISO, respectively. These results indicates that the oxygen delignified pulps were found to have slightly lower brightness compared to conventional pulps. These results indicates the slightly lower efficiency of AQ and oxygen delignified pulps towards ECF bleaching.

The soda, soda-AQ kraft, and kraft-AQ pulps with and without oxygen delignification was bleached with D(EOP)DP bleaching sequences. Soda, soda-AQ, kraft, and kraft-AQ pulps bleached, using D (EOP) DP bleaching sequence have a brightness values of 84.4, 85.5, 86.6 and 87.7% ISO respectively. While the oxygen delignified pulps obtained the brightness of 86.1, 88.3, 87.9, 89.6% ISO respectively. The results of these experiments have been reported in Table 4.5D and 4.6D. These results revealed that the conventional soda and kraft pulps responded well towards ECF bleaching sequences as compared to the AQ and oxygen delignified pulps, however the kappa numbers are lower in the case of AQ and oxygen delignified pulps. The reason may be

that the oxygen delignified pulp may not have enough available phenolic propane units in the lignin molecules to make these molecules respond favourably to chlorine dioxide delignification. Moreover hardwoods have fewer free phenolic groups than softwoods. During the oxygen delignification large number of phenolic groups are removed leaving the deficiency in reactive free phenolic groups. This leaves the lesser reactive sight for the chlorine dioxide. This may be the reason for the lower brightness of the oxygen-delingified pulps.

The soda, soda-AQ, kraft, and kraft-AQ pulps were also bleached using D (EOP) DED bleaching sequence. These pulps have a brightness range of 87.4, 89.2, 88.5, and 90.3% ISO. These pulps, bleached by using OD(EOP)DED bleaching sequence, produce the pulps with highest brightness range of 88.1, 89.8, 89.4, and 91.6% ISO. The results of these bleaching sequences have been reported in Table 4.3D and 4.4D. These results indicates that the use of hydrogen peroxide in the reinforced oxidative extraction stage improves the efficiency of chlorine dioxide delignification. The results of these experiments revealed that the D(EOP) kappa number is about 40% lower than the DE kappa number. In the case of DEDED bleaching sequence for obtaining the pulps with higher brightness values, higher kappa factor for the first D-stage is required. The use of higher kappa factor in turns increases the effluent load and the chlorine dioxide consumption, which affects the advantages of ECF bleaching. The decrease in the chlorine dioxide in first D-stage and subsequent D-stages, the use of hydrogen peroxide has been proved effective in increasing the rate of delignification and improving the pulp brightness. Moreover the use of hydrogen peroxide in the reinforce oxidative extraction stage, has been found to be more effective and beneficial in decreasing the chlorine dioxide demands for the first D-stage and the subsequent D-stages for the same brightness levels of the pulps. Liebergott and Lachapelle has also shown that the bleaching in 100% chlorine dioxide sequences can be

compensated by adding hydrogen peroxide in the EO or E_2 stages or in high density storages of the pulps. (108,164).

4.4D: Effluent Characteristics:

The effluent from the each stage was collected and diluted to the 1% consistency and tested for the COD, BOD characteristics. AOX has been calculated theoretically using the following equation devised by Germgard (42,50,55,56) AOX=0.1 (Cl_2+ ClO_2/5). The results of the effluent characteristics have been reported in the Table 4.7D. Compared to the conventional bleaching sequences, these results indicate that the use of chlorine dioxide decreases the pollution load drastically. The pollution load of oxygen delignified pulps bleached with 100% chlorine dioxide and reinforced oxidative extraction is significantly low.

Further the results shows that the substitution of chlorine with chlorine di oxide reduces the environmental pollution load. When oxygen delignification is employed prior to bleaching, the COD is reduced by 50-60% for soda pulps and 60-65% for soda-AQ and kraft pulps. Therefore. The combination of oxygen delignification and DED bleaching of soda and kraft pulps has a potential of reducing environmental load (COD&BOD) by almost 75% as in the case of CEHH bleaching of these pulps.

3.4D: Pulp Evaluation:

The results of the soda, soda AQ, kraft, and kraft-AQ pulps bleached with various sequences using chlorine dioxide have been reported in Table 4.8D . These results indicates that the strength properties of the pulp are preserved using ClO_2. Since the chlorine dioxide reacts more selectively with lignin as compared to cellulose, there is very little degradation of carbohydrate material. Therefore, the pulps bleached with chlorine dioxide has better strength properties as compared to conventional bleached pulps.

However, the strength properties of the oxygen delignified pulps were found to be slightly lower than the pulps bleached without oxygen delignification. The strength may be slightly lower due to the little degradation of carbohydrates in the oxygen stage. The pulps bleached with reinforced oxidative extraction stages found to have about 5% drop in strength properties but the pulps were found to be brighter with low environmental pollution load. However, chlorine dioxide retains the strength properties and the pulps bleached using chlorinedioxide were found to be comparatively stronger.

4.5D :Conclusion:

The soda and kraft pulps of poplar deltoides can be easily bleached with chlorine dioxide using lesser kappa factors as compared to other hardwoods. The soda and Kraft oxygen delignified pulps of poplar although having lower kappa number found to have slightly lower brightness than the conventional pulps. The reason may be that the oxygen-delignified pulp may not have enough phenolic propane units in the lignin molecules to make these molecules respond favorably to chlorine dioxide delignification.

The use of hydrogen peroxide in EOP or EP stage increases the delignification ability of the chlorine dioxide resulting in the production of the brighter pulp and helps in reducing ClO_2 consumption. The use of hydrogen peroxide in EOP or EP stage can reduce the chlorine dioxide for the same brightness. It has been observed that the bleaching efficiency of AQ and oxygen delignified pulps is increased by using EOP or EP stages to obtains the pulps of ultra high brightness. The use of hydrogen peroxide in the last stage increases the brightness stability. The substitutions of chlorine with 100% chlorine dioxide in first D-stage is an effective way of decreasing effluent load, to meet the legislative limits of pollution load and the market requirements.

Table 4.1D: Results of DEDED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification.

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda-AQ pulp	16% soda-AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
D Stage :				
Kappa Factor applied	0.14	0.14	0.14	0.14
ClO_2 as Cl_2, applied, %	3.5	2.0	3.0	1.5
Final pH	3.8	3.8	3.6	3.7
E stage :				
NaOH, %	2.0	1.5	2.0	1.5
PH	12.3	12.1	12.2	12.4
DE Kappa Number :	3.8	3.6	3.8	3.5
D 1 Stage :				
ClO_2,applied, %	1.0	1.0	1.0	1.0
Consumed, %	0.94	0.88	0.94	0.82
E 2-Stage :				
NaOH, %	1.0	0.75	1.0	0.75
pH	12.2	11.8	12.0	11.9
D 2 – Stage :				
ClO_2 applied, %	0.6	0.6	0.6	0.6
Consumed, %	0.57	0.54	0.55	0.52
Brightness, %ISO (± 0.5)	82.2	81.5	81.8	85.3
Pulp Viscosity,cm^3/g (± 10)	400	410	410	400

Table 4.2D: Results of DEDED bleaching sequence of Kraft and kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft-AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.2	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Pulp Intrinsic viscosity, cm^3/g	570	510	580	530
D Stage				
Kappa factor applied,	0.14	0.14	0.14	0.14
ClO_2,% asCl_2,%applied	2.5	1.6	2.3	1.4
Final pH	2.2	2.3	2.1	2.2
E – stage				
NaOH, %	1.5	1.0	1.5	1.0
pH	12.0	11.9	11.9	12.0
DE Kappa number	3.6	3.4	3.6	3.3
D 1 – Stage				1.0
ClO_2 applied, %	1.0	1.0	1.0	0.93
Consumed, %	0.95	0.92	0.94	
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
pH	12.0	11.9	12.1	11.8
D 2 – Stage				
ClO_2 applied, %	0.6	0.6	0.6	0.6
Consumed, %	0.56	0.52	0.53	0.52
Brightness, %ISO (±0.5)	86.2	85.1	86.0	86.1
Pulp Viscosity,cm^3/g(±10)	450	440	460	450

Table 4.3D: Results of D(EOP)DED bleaching sequence of soda and soda AQ pulps with and without oxygen delignification.

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda-AQ pulp	16% soda-AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Pulp Intrinsic viscosity, cm^3/g	530	470	550	480
D Stage				
Kappa Factor Applied	0.14	0.14	0.14	0.14
ClO_2, applied as Cl_2,%	3.5	2.0	3.0	1.5
Final pH	3.8	3.8	3.6	3.7
E OP stage :				
NaOH, %	1.5	1.5	1.5	1.5
H2O2,%	0.2	0.2	0.2	0.2
Temperature, (°C)	70	70	70	70
Time,(min)	45	45	45	45
Consistency,(%)	10	10	10	10
O_2 Pressure,Kg/cm^2	5	5	5	5
D(EOP) Kappa number	2.8	2.6	2.7	2.5
D 1 – Stage				
ClO_2,applied, %	1.0	1.0	1.0	1.0
Consumed, %	.92	0.9	0.92	0.9
E 2-Stage				
NaOH, %	0.75	0.75	0.75	0.75
pH	11.9	11.9	11.9	11.9
D 2 – Stage				
ClO_2 applied, %	0.6	0.6	0.6	0.6
Consumed, %	0.56	0.55	0.56	0.53
Brightness, %ISO (± 0.5)	87.4	88.1	89.2	89.8
Pulp Viscosity,cm^3/g (± 10)	410	400	430	420

Table 4.4D: Results of D(EOP)DED bleaching sequence of Kraft and kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft-AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	17.6	9.1	16.2	8.5
Pulp Brightness, % ISO	35.6	41.2	36.0	42.1
Intrinsic viscosity,cm^3/g	570	510	580	530
First D Stage :				
Kappa Factor Applied	1.4	1.4	1.4	1.4
ClO_2,% asCl_2,%Applied	2.46	1.27	2.25	1.24
pH	2.2	2.2	2.1	2.2
E OP stage :				
NaOH, %	1.5	1.0	1.5	1.0
H_2O_2,%	0.2	0.2	0.2	0.2
Temperature, (^oC)	70	70	70	70
Time,(min)	45	45	45	45
Consistency,(%)	10	10	10	10
O_2 Pressure,Kg/cm^2	5	5	5	5
D(EOP) Kappa number	2.3	2.1	2.2	2.0
D 1 Stage :				
ClO_2,% Applied, %	1.0	1.0	1.0	1.0
Consumed, %	0.90	0.89	0.88	0.87
E 2-Stage				
NaOH, %	1.0	0.75	1.0	0.75
pH	12.0	11.9	12.1	11.8
D 2 – Stage				
ClO_2 % applied	0.6	0.6	0.6	0.6
Consumed, %	0.55	0.54	0.55	0.52
Brightness, %ISO	88.5	89.4	90.3	91.0
Pulp Viscosity,cm^3/g	430	420	440	440

Table 4.5D: Results of [D(EOP)DP] bleaching sequence of soda and soda AQ pulps with and without oxygen delignification.

Particulars	16% soda pulp	16% soda oxygen delignified pulp	16% soda-AQ pulp	16% soda-AQ oxygen delignified pulp
Kappa Number	24.1	13.2	21.8	9.8
Pulp Brightness, % ISO	31.1	39.7	33.2	40.3
Intrinsic viscosity,cm^3/g	530	470	550	480
First D Stage :				
Kappa Factor applied	0.14	0.14	0.14	0.14
ClO_2 % as Cl_2,%applied	3.5	1.8	3.0	1.4
Temperature, (°C)	60	60	60	60
Time,(min)	45	45	45	45
pH	3.6	3.6	3.6	3.6
Consistency,(%)	4	4	4	4
ClO_2 consumed,%	3.3	1.7	2.8	1.3
E OP stage :				
NaOH, %	2.0	1.7	2.0	1.7
H_2O_2,%	0.2	0.2	0.2	0.2
Temperature, (°C)	80	80	80	80
Time,(min)	45	45	45	45
Consistency,(%)	10	10	10	10
O_2 Pressure,Kg/cm^2	5	5	5	5
D(EOP) Kappa number	2.9	2.5	2.7	2.5
Final D Stage :				
ClO_2% Applied, %	1.2	1.2	1.2	1.2
Temperature, (°C)	75	75	75	75
Time,(min)	120	120	120	120
Consistency,(%)	10	10	10	10
pH	3.8	3.8	3.8	3.8
ClO_2 consumed,%	1.15	0.95	1.10	0.95
Yield,(%)	95.4	96.4	95.8	96.8
Brightness, %ISO	84.0	84.7	84.5	85.8
Reverted,%ISO	81.6	82.8	82.6	83.1
Post Peroxide Stage :				
H_2O_2,%				
Temperature, (°C)	0.2	0.2	0.2	0.2
Time,(min)	45	45	45	45
Consistency,(%)	120	120	120	120
Brightness, %ISO	85.9	87.3	86.8	89.8
Reverted,%ISO	84.4	86.1	85.5	88.3

Table 4.6D: Results of D(EOP)DP bleaching sequence of Kraft and kraft AQ pulps with and without oxygen delignification .

Particulars	16% Kraft pulp	16 % Kraft oxygen delignified pulp	16% Kraft-AQ pulp	16% Kraft- AQ oxygen delignified pulp
Kappa Number	24.1	9.1	24.1	8.5
Pulp Brightness, % ISO	31.1	41.2	31.1	42.1
Intrinsic viscosity,cm^3/g	530	510	530	530
First D Stage :				
Kappa Factor applied	.14	.14	.14	.14
ClO_2,% asCl_2,%applied	3.5	1.6	3.5	1.4
Temperature, (°C)	60	60	60	60
Time,(min)	45	45	45	45
pH	3.6	3.6	3.6	3.6
Consistency,(%)	4	4	4	4
ClO_2 consumed,%	3.3	1.4	3.3	1.2
E OP stage :				
NaOH, %	2.0	1.7	2.0	1.7
H_2O_2,%	0.2	0.2	0.2	0.2
Temperature, (°C)	80	80	80	80
Time,(min)	45	45	45	45
Consistency,(%)	10	10	10	10
O_2 Pressure,Kg/cm^2	5	5	5	5
D(EOP) Kappa number	2.4	2.0	2.2	1.9
Final D Stage :				
ClO_2,% Applied, %	1.2	1.2	1.2	1.2
Temperature, (°C)	75	75	75	75
Time,(min)	120	120	120	120
Consistency,(%)	10	10	10	10
pH	3.8	3.8	3.8	3.8
ClO_2 consumed,%	1.15	0.95	1.15	0.95
Yield,(%)	96.4	96.9	96.6	96.4
Brightness, %ISO	86.3	87.6	86.6	89.2
Reverted,%ISO	84.1	85.4	84.3	86.6
Post Peroxide Stage :				
H_2O_2,%				
Temperature, (°C)	0.2	0.2	0.2	2.0
Time,(min)	45	45	45	45
Consistency,(%)	120	120	120	120
Brightness, %ISO	88.1	89.3	88.5	91.1
Reverted,%ISO	86.6	87.9	87.7	89.6

Table 4.7D: Characteristics of bleach effluents at 1% consistency.

Pulps	Bleaching Sequence	COD mg/l	BOD mg/l	AOX kg/ton
Soda	DEDED	260	100	1.1
	D(EOP)DP	240	90	0.94
	ODEDED	200	80	0.75
	OD(EOP)DP	190	80	0.60
Kraft	DEDED	240	90	0.82
	D(EOP)DP	220	80	0.75
	ODEDED	190	70	0.64
	OD(EOP)DP	180	70	0.56

Table 4.8D: Strength Properties of bleached Poplar pulps at 300 ml CSF

Pulps	Bleaching Sequences	Tensile Index (N.m/g) (±0.8)	Tear Index (mNm^2/g) (±0.4)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Viscosity, cm^3/g (±10)
Soda Pulp	DEDED	61.3	5.9	4.5	400
	D(EOP)DED	60.2	5.8	4.3	390
	D(EOP)DP	60.4	5.9	4.4	400
	ODEDED	60.0	5.7	4.3	390
	OD(EOP)DED	58.3	5.6	4.1	420
	OD(EOP)DP	57.9	5.8	4.0	430
Soda –AQ Pulp	DEDED	61.8	6.5	4.6	410
	D(EOP)DED	60.9	6.3	4.3	430
	D(EOP)DP	61.0	6.3	4.4	430
	ODEDED	61.1	6.3	4.4	410
	OD(EOP)DED	59.9	6.1	4.0	430
	OD(EOP)DP	60.3	6.0	4.2	440
Kraft pulp	DEDED	68.9	7.0	4.8	480
	D(EOP)DED	68.1	6.8	4.6	460
	D(EOP)DP	68.3	6.8	4.7	470
	ODEDED	67.0	6.7	4.5	480
	OD(EOP)DED	66.8	6.6	4.4	470
	OD(EOP)DP	66.4	6.6	4.3	480
Kraft-AQ Pulp	DEDED	69.4	7.0	4.7	490
	D(EOP)DED	68.2	6.7	4.7	470
	D(EOP)DP	68.3	6.8	4.6	480
	ODEDED	67.9	6.9	4.4	490
	OD(EOP)DED	66.7	6.7	4.3	470
	OD(EOP)DP	66.6	6.7	4.3	470

CHAPTER 4E

ENZYMATIC BLEACHING

4.1E Introduction:

In response to the energy crisis of early 1980's, the biotechnology programs went through a period of rapid growth and much of the attention were focussed on converting the waste biomass to value added fuels and chemicals. Wood inhabiting microbes produce a variety of enzymes that degrade all components of wood. Attempts were made to separate and isolate the enzymes produced by these microbes (30). One type of hemicellulose degrading enzyme xylanase was .Actually, the xylanases are the xylan-degrading enzymes. Xylan is precipitated on the surfaces of fibres during kraft pulping, forming a barrier against the extraction of residual lignin from cellulose fibers. The xylanase enzyme removes this barrier. Xylanase is actually not a bleaching agent, but it facilitates the removal of xylan in the following chemical bleaching stages. Now a significant number of Scandinavian, European and North American Mills are using xylanases for bleaching pretreatment.

Xylanase enhance pulp bleaching by reducing the amount of chlorine required and organochlorine compounds generated (28). Xylan, a polysaccharide containing a backbone of β-1, 4 linked xylano pyranose residues, is a major component of the hemicellulose found in plant cell walls and of hardwoods. Xylanases are xylan-specific enzymes. They catalyze the hydrolysis of xylose-xylose bonds within the xylan chain and only solubilize a fraction of the total xylan present (98,99).

Compared to soft wood kraft pulp, hardwood kraft pulp contains more xylan, more carboxylic acid groups and surface charge (24,91,220) and smaller xylan macromolecule. Relatively more lignin xylan complexes, where lignin and xylan are covalently linked, seems to

occur in hardwood pulps whereas more lignin-cellulose complexes occur in softwood pulps (28,79). There is a tendency for hardwood kraft pulp to show higher benefits with regard to chlorine savings, during xylanase aided bleaching. These differences may be partly attributed to differences in xylan solubilization from pulp. Which may in turn be related to the amounts of accessible xylan present and ion composition and buffering capacity of pulp that could moderate enzyme-fibre interactions or the woods response to kraft pulping. Xylanase aided bleaching appears more effective on pulp produced by a conventional process.

During conventional kraft cooking part of the hemicellulose is first solubilized in the cooking liquor. In the later phases of cooking, when the alkalinity of the cooking liquor decreases, part of the solubilized xylan is precipitated on the cellulose fibers (24,91). The effects of the enzyme may be smaller observed in continuous modified cooking, extended modified continuous cooking (EMCC) and in other low kappa pulps such as RDH super and batch kraft-AQ pulp. In the modified cooking methods, the alkali profile of the cooking is usually different. The alkalinity of the cooking liquor is maintained at a constant level throughout the cook by liquor displacement for example as in super batch cooking, or by addition of alkali to the cooking liquor in small doses as in the modified continuous cooking method (24,220). Only minor reprecipitation of hemicelluloses is expected to occur in pulps cooked by these methods. In the production of ECF and TCF pulps, oxygen treatment is commonly used as a prebleaching stage, before the actual bleaching sequence. A reduction in kappa number of about 50% can be achieved using oxygen with relatively lower loss of carbohydrate yield and without impairing strength properties.

Originally the main aim in the enzyme aided bleaching, is to reduce the chlorine chemical consumption in bleaching to reduce environmental discharge and to increase the brightness of pulps. When combined with TCF bleaching sequences, enzymes can be used to increase the final

brightness of pulps. The improved bleachability of conventional kraft pulps is suggested to be mainly due to limited hydrolysis of reprecipitated xylan or enhanced extractability of lignin-carbohydrate complexes after enzymatic treatment (24,91,220). In addition to xylanase, mannanases also have been reported to enhance the bleachability of softwood kraft pulps. Reduction in chlorine equivalents has been reported from laboratory work and mill trials by using enzyme pretreatment (201). Subsequently the AOX load of the bleaching effluent has been reduced by nearly the same percentage (28). The chemical oxygen demand of the effluent is due to higher yield loss Enzymes also in improving the drainability of pulps(135).

4.2E Laboratory Preparation of Xylanase:

Phanerochacte chrysosporium, one of the species of thermophillic fungi exhibiting higher xylanase activity with greater stability at high temperatures and at near about neutral pH values were used for standardization of biobleach process (48,49,208).

Phanerochacte chrysosporium was isolated in laboratory from decaying wood samples and tested for hyperxylanase production. This stain of fungi was subculture on wheat bran agar medium at 40 ^{0}C for 5-7 days and then stored at 4 ^{0}C until used. These stains were stabilized by inoculating mycelia residues separately onto the solid medium containing fine powder of 2% wheat bran in sterile 9 cm petriplates. The culture was grown three times on the same medium at 40 ^{0}C and was finally considered as stabilized.

Production of enzyme under liquid state fermentation conditions.

Liquid culture medium was prepared having 1.5 g/l KH_2PO_4, 4g/l NH_4Cl, 0.5g/l $MgSO_4$, 0.5 g/l KCl and 1g/l yeast, in distilled water with 0.04 ml/l trace elements solution and pH was adjusted to 6.0 (According to Vishnia and Samter 1957). 25 ml of liquid culture medium was added to 100 ml Erlenmeyer borosil flasks having partially delignified and finely powdered 2% wheat barn as substrate in each flask. These flasks were auto claved at 15 lb/in^2 for 15-20 min. at

120 ^{0}C. Vesicles prepared from 5-7 days old solid state culture were inoculated by adding one vesicle per flask aseptically. The inoculum flasks were incubated at 40 ^{0}C in BOD incubator and harvested as required. The results of preparation of xylanase at different conditions have been reported in Table-4.1E to 4.5E.

Harvesting and Storage of Enzyme.

After desired growth of last species, culture flasks were kept on orbital shaker at 100 rpm for 30 min. at room temperature and contents were filtered through 4 layers cheesecloth. The filtrate was centrifuged first at 3000xg (Remi centrifuge model RBC) for 10 min. and finally at 15000xg (sigma centrifuge model 2K15) for 1 hr. at 4 ^{0}C temperature. The supernatant liquid was treated as crude enzyme. The enzyme preparation was stored frozen at –10 ^{0}C temperature until use.

4.3E Effects of different parameters involved in xylanase production,

Different parameters such as effects of temperature on enzyme production, pH for enzyme production, enzyme activity and effect of incubation period of xylanase production were studied.

4.3.1E Effects of temperature on enzyme production and enzyme activity :

Phanerochaete chrysosporium was tested for the xylanase production at different temperatures in B.O.D. incubator ranging from 35 ^{0}C to 50 ^{0}C with a difference of 5 ^{0}C. The enzyme secreted by this fungus was also tested for xylanase activity at different temperatures of water bath incubation ranging from 50 ^{0}C – 70 ^{0}C with same difference. The optimum xylanase activity was observed at 5 ^{0}C. The results have been reported in Table 4.1E. The results of the xylanase production by P. Chrysosporium at different temperature have been reported in Table-4.1E. These results indicates that the maximum activity has been observed at the temperature of

45 ^{0}C for incubation in liquid state fermentation using the culture medium conditioned as mentioned in table 4.1E.

4.3.2E Optimisation of pH for enzyme production and enzyme activity:

P. chrysosporium stain was tested for xylanase production at different pH of culture medium ranging from 4.5-7.5 with difference of 0.5 pH. The enzyme preparation secreted by this fungus was also tested for xylanase activity at different pH of potassium phosphate buffer over a range of 6.0 and 7.5 with same difference. The effect of pH on xylanase activity using enzyme secreted by phanerochaete chrysosporium have been studied and the results have been reported in Table 4.3E. The activity of the enzyme secreted by P. chrysosporium has been analysed at pH 6.0, 6.5, 7.0 and 7.5 was found to be 3.19, 5.27, 4.30 and 4.16 IU/ml. These results show that the activity increases upto pH 6.5 and decreases on increasing the pH. Thus the pH 6.5 may be considered optimum for analysing the xylanase activity of the enzyme produced by P. chrysosporium. The results of the effect of pH on xylanase production by phanerochaete chrysosporium under liquid state fermentation after 6th day of incubation at 40 ^{0}C have been reported in Table-4.2E. These results shows that the xylanase activity produced by P.chrysosporium increases the pH of incubating medium increases from 5 to 7.0 and sharply declines at pH 8.0. The maximum activity of 6.66 IU/ml has been found, in the enzyme produced at pH 7.0 by P.chrysosporium. These results shows that P. chrysosporium produces the enzyme of maximum activity at neutral pH.

4.3.3E Effect of incubation period of xylanase production:

Effect of incubation period on xylanase production by P.chrysosporium using liquid state fermentation has been studied upto 20 days of incubation. The xylanase activity has been calculated after every day of incubation. The results of xylanase activity are reported in table

4.4E. The results of the effect of incubation period on xylanase production by phanerochaete chrysosporium wider liquid state fermentation shows the xylanase activity of the enzyme produced by P. Chrysosporium increase on increasing the incubation period (in days). The maximum activity of 199.87 IU/ml has been observed on 17th day of incubation. If the incubation period is further increased the xylanase activity decreases. Thus the optimum incubation period of 17 days may be considered as optimum for the xylanase productivity of P. chrysosporium.

The cellulose activity in term of CMCase of the enzyme secreted by phanerochaete chrysosporium has been calculated from a period of 14^{th} day to 20^{th} day of incubation and the results have been reported in Table-4.5E. The results from table 4.4E and 4.5E shows that on 17^{th} day of incubation the enzyme produced by P. chrysosporium has the maximum activity of 199.87 IU/ml and CMCase activity of 0.12 IU/ml. The CMCase activity increases with increase in incubation period. Therefore, the 17^{th} day of incubation may be considered as optimum giving the highest xylanase activity and the lower CMCase activity. Therefore this enzyme has the maximum effect on the pulp treatment and lower cellulose degradation.

Enzyme assays:

Xylanase activity was estimated by determining the release of reducing sugars from birch wood xylan (sigma). The reaction mixture contained, 1 ml enzyme preparation diluted in0.1M potassium phosphate buffer, pH 7.0 and 1 ml substrate suspension (10 mg/ml xylan in phosphate buffer) controls, in which enzyme preparation or substrate has been omitted, were routinely included. Assay mixtures were incubated for 15 min with shaking at 55 ^{0}C. Reducing sugar released was determined by the dinitrosalicylic acid (DNS) method (127) and enzyme activity expressed as micromoles of D-xylose equivalents released per min at 55 ^{0}C (127).

Endoglucanase activity was tested by replacing xylan in the above, with 2% carboxymethyl cellulose (CMC) at pH 4.8 in .05 m citrate buffer, the reaction mixture incubated for 30 min at 50 ^{0}C. Reducing sugar released from CMC was determined as described for xylan and endoglucanase activity expressed as micromoles of D-glucose equivalent released per min at 50 ^{0}C.

4.4E: Enzymatic Treatment of Pulps and Experimental Methodology:

For standardization of various parameters, the release of reducing sugar (mg/g dry wt of pulp) was measured at 5% pulp consistency. Different incubation temperature (45 to 70 ^{0}C), pH values (pH 6-8), phosphate buffer concentrations (0.1-0.5M) were compared. Different enzyme concentrations and pulp mixing regimes were also assessed. A set of standard parameters was chosen to study the effect of xylanase on paper properties under optimum conditions.

4.5E Results and Discussion:

4.5.1E Effect of time on xylanase treatment:

A suitable amount of 5 gm pulp, was taken in 250 ml Erlenmeyer flask. The reaction mixture contained 10 IU of xylanase activity/g pulp and potassium phosphate buffer (.1M, pH 7.0) containing 0.03% sodium azide is used to maintain the pulp consistency of 5%. They were incubated at 55 ^{0}C for 6 hrs. with shaking at 100 rpm. The experiments were carried out in triplicate. The controls were prepared similarly but the enzyme preparations that had been autoclaved at 121 ^{0}C for 15 min. The pulps were incubated with enzyme for 1,2,3 and 24 hours. The pulps were squeezed and the filtrate was retained for reducing sugars determination. Reducing sugars were determined from the enzyme treated pulp filtrate by the DNS method. Absorption spectra of enzyme treated pulp filtrates were measured at 237, 254, 280 and 465 *nm* against the respective controls using auto claved enzyme, as blank. The results have been reported in table 4.6E and 4.7E.

4.5.2E Effect of the Enzyme Dose:

A suitable amount of pulp was taken in 250 ml Erlenmeyer flask and a charge of control, 2 IU, 5 IU, 10 IU, 20 IU, 50 IU/g of pulp doses of enzymes were added to the pulp. 5% consistency was maintained by potassium phosphate buffer. These flasks were incubated at 55 ^{0}C for 2 hours with constant shaking. The filtrate was collected for reducing sugar determination by DNS method. Optical density of enzyme treated pulp filtrates were measured at 237, 254, 280 and 465 *nm* against the respective control using autoclaved enzyme as blank. The results of these experiments are reported in table 4.6E. At the enzyme concentration of 10 IU and above most of the chromophore release takes place in 1 hour and was almost completed in 2 hour treatment, although reducing sugar release continued at a reduced rate. Release of chromophore is probably a better indicator of the kinetics of enzyme attack on the pulp. As reducing sugar will continue to be generated by xylanase hydrolysis of the soluble oligosaccharides released by the initial depolimerizationof the xylan coating of the fiber surface. This data indicates that there may be scope for reducing the treatment time from 2 to 1 hour. Similarly, the fact that increasing the enzyme concentration above 10 IU /g of pulp does not significantly increase chromophore release but does yield more reducing sugar may due to further degration of soluble products rather than the enhancement of primary xylan removal. From the results of the reducing sugar release (table 4.8E) it can be concluded that the enzyme dose of 10 IU/g of pulp is sufficient for treatment. The use of higher enzyme dose may degrade more xylan and effect the strength properties of the pulps.

4.5.3E Effect of Pulp Consistency:

For the enzymatic pretreatment of pulps, various investigators have used pulp consistencies in the range of 1-10%. The enzyme to substrate ratio is the most important factor, but the accessibility of the substrate to enzyme will be influenced by the pulp consistency. In this

context, pulps at different consistencies (1 – 10%) were treated under conditions of fixed enzyme to substrate ratio at 10 IU xylanase per 1g pulp. At 1% pulp consistency, it has been observed the reducing sugar release was linear for 6 hrs at 55 ^{0}C, while all other values release continued in an approximately linear manner upto 10 hrs.(fig.4.1E). At 1% consistency after 24 hrs, approximately 13 mg xylose equivalents per 1g pulp has been released at 1% pulp consistency, in contrast to 30-40 mg xylose equivalents at the higher pulp consistencies. A pulp consistency of 5% gave the highest yield of reducing sugar released by 10 IU/g pulp. Moreover at pulp consistencies >3%, significant release of reducing sugars continued for the duration of (24 hrs.) the experiment, while at 1% pulp consistency no further release of reducing sugar was observed after 6 hr. (fig.4.1E). These observations can be explained by close interaction between enzyme and substrate for the promotion of xylan hydrolysis. These data demonstrate the importance of optimizing the enzyme substrate/volume relationship to obtain maximum hydrolysis of xylan in pulp. Figure 4.1E may also explain the nature of the xylan present in poplar pulp. During alkaline pulping, xylan is dissolved and some of it is re-deposited on the surface of cellulose fibres.

4.5.4E Release of Chromophoric Material during enzymatic treatment:

The results of spectrophotometric analysis of enzyme treated filtrates of soda and kraft pulps of poplars are reported in table-4.6E and 4.7E. Most of the chromophores and the color is released within 4 hrs.

The release of color, was estimated by absorption at 237, 254, 280 and 465 *nm*. The absorption as 465 *nm* indicates that a small amount of lignin is also degraded during enzymatic treatment. This pattern was similar at different pulp consistencies, and pulps treated with autoclaved enzyme preparations did not release significant amounts of material, which absorbed at any of these wavelengths. Thus chromophoric materials is released as the result of the action

of xylanase, these data suggest that there is a significant decrease in the aromaticity of residual lignin, which is confirmed by the determination of kappa number. Enzyme treatment of pulp reduced the kappa no. of soda, soda-AQ, kraft and kraft-AQ pulps by 5-10%. The magnitude of the effect on enzymatic treatments depends upon the pulping process and the kappa no. of the pulp. In general higher the initial kappa no. greater would be the effect of a xylanase treatment in bleaching sequences. It is well known that the function of xylanase is not to degrade lignin, xylanase degrades the xylan hemicellulose in this action the lignin gets wear off and is solubilized which shows a slight decrease in kappa number of treated pulp.

4.5.5E: Reducing Sugar Release:

Table 4.8E report the results of the reducing sugar mg/100 ml released during enzymatic treatment. The pulp was treated with control, 10 20, and 50 IU/gm of pulp at 5% consistency for 1, 2 and 3 hours. The reducing sugar was estimated after 1,2,3 hrs. On evaluation of the results of table 4.8E, we can conclude that the xylanase dose of 10 IU/g is sufficient and 1 hr. treatment gives good results. Poplar hemicellulose have about 24% xylose. The enzyme treatment degrades 6 mg xylose per gram of pulp, which shows positive results for enzymatic treatment.

4.6E: Comparison of xylanase produce of P.chrysosporium and commercial enzyme preparations.

To see the efficiency of the enzyme produced by P.chrysosporium, it has been compared with the commercial enzyme preparation. The enzyme was procured from M/s sigma chemicals, pulpzyme, cartazyme and these enzyme preparations were applied to pulp at 50 ^{0}C in accordance with manufacturers instructions. The enzyme dose of 10 IU/g of pulp was applied for 1 hr. The enzyme were tested for the reducing sugar release and the enzyme treated pulps were bleached

using convention CEHH bleaching sequences using 0.2 kappa factor. These results have been reported in table-4.16E. The results indicates that cartazyme exhibited the largest bleach boosting effect, indicating the higher brightness of the bleached pulp. However, it has been found that, there is detrimental effect on the strength properties. The results of the enzyme pulpzyme was found to have similar effect. Therefore it can be concluded that the enzyme produced by P. chrysosporium was found to be as good as commercial enzymes and can give comparable results. It is becoming apparent that sufficient hemicellulose removal from the pulps to produce comparable boosting effects can be achieved by xylanasein general, and since they are produced by variety of micro organisms, further selection criteria need to be employed.

4.7E: Conventional Bleaching Sequences of Enzyme Treated Pulp:

The soda and kraft pulps of poplar deltoides has been bleached using conventional bleaching sequence. For the enzymatic treatment, the soda and kraft pulps has been treated with 10 IU/g of pulp at the conditioned mentioned earlier. The results of the enzymatic treatment of soda and soda AQ pulps has been reported in table-4.9E and the results of enzymatic treatment of kraft and kraft AQ pulps has been reported in table-4.11E. The enzymatic treatment of pulp reduces the kappa number and accordingly increases the brightness of the pulp subjected to conventional CEHH bleaching sequence. The kappa number reduction shows the enzyme treatment had both removed chromophoric material and rendered the remaining lignin more amenable to removal during extraction (E) stage. Further these enzymatic treated pulps have been bleached using the conventional CEHH bleaching sequence at a kappa factor of 0.2 for the total chlorine demand and by using the 70% of total chlorine demand, to see the effect of enzyme. The results of the bleaching of soda and soda AQ pulp has been reported in table-4.10E and kraft and kraft AQ pulp has been reported in table-4.12E.

Results and Discussion:

The soda and kraft pulps has been bleached by CEHH, XCEHH bleaching sequences using the chlorine multiple of 0.2× kappa factor. It has been observed that the enzymatic treated pulp gains the brightness of around 4 units. When the enzyme treated pulp has been bleached using 30% less chlorine the brightness obtained is comparatively equal. The results have been reported in table-4.10E and table-4.12E.

These results shows that 16% soda pulp bleached with CEHH bleaching sequence using chlorine 0.2× kappa no. and XCEHH bleaching sequence using 30% lesser chlorine, the brightness obtained were 78.6 and 77.4% ISO respectively and using the same chlorine multiple, the brightness obtained is 83..% ISO. These results shows that xylanase has an effective role in the boosting of bleaching. The hemicellulose of poplar has the higher xylan content, xylanase dissolves the xylan which weakens the lignin and cellulose bonding. Therefore the xylanase treated pulp can be easily bleached using lesser amount of chlorine or the brightness is increased. Moreover the xylanase produced from P. Chrysosporium has been found very effective in the bleaching of the pulp. The results of the strength properties have been reported in table-4.10E and 4.12E. The results of strength properties shows a slight decrease in the strength properties. The advantage of xylanase treatment is to reduce the bleaching chemicals upto 30% to obtain the similar brightness which reduces the use of chlorine and the cost of bleaching. The process for the reduction of chlorine through the use of xylanase treatment was first patented by Enzo-Gutzeit. (130).

4.8E Elemental Chlorine Free (ECF) Bleaching Sequence of Enzyme Treated Pulps:

Now a days the ECF bleaching sequences are gaining prominence due to the environmental concerns and the market demand. The soda and kraft pulps have been bleached using XDEDP, XDEDED, XD(EOP)DP, XD(EOP)DED. OXDEDP. OXDEDED,

OXD(EOP)DP, OXD(EOP)DED and OXD (EOP)DP bleaching sequences. The xylanase dose of 10 IU/g was applied on the pulp. The results have been reported in table-4.13E.

Results and Discussion:

The soda and kraft oxygen delignified pulps were treated with xylanase and the chlorine multiple of 0.14× kappa number was applied in the first D-stage. 1.0% and 0.6% chlorine dioxide was applied in D_1 and D_2 stages. In the EOP and P stage, 0.2% hydrogen peroxide was applied. Moreover these pulps were bleached by using 30% less chlorine chemicals. The results have been reported in table-4.13E and 4.14E.

The results shows that the xylanase treated pulp shows an improvement in the bleachability of the pulp, increasing the brightness to the tune of around 4 units. When these pulps were also bleached by using 30% less chemicals using XDEDED and XD(EOP)DED bleaching sequence, the brightness are almost similar to the brightness of pulp bleached by bleached using DEDED and OD(EOP)DEP bleaching sequence. The results indicates that the xylanase boost the effect of bleaching to obtain the higher brightness. The use of hydrogen peroxide has been proved to be significant in increasing the brightness of the pulp. However the result shows the slight loss in the strength properties. The pulps bleached using about 30% less chemicals shows good brightness. It saves the consumption of bleach chemicals, lowers effluent load and saves bleaching cost.

4.9E: TCF Bleaching Sequences

TCF stands for totally chlorine free and is fairly used to describe pulp bleached without any chlorine-based compounds, including chlorine dioxide. TCF guarantees no chlorinated compounds whatsoever from bleaching. However, rapidly evolving experience with various non-chlorine bleaching chemicals such as extended delignification by extended cooking, oxygen, ozone, the use of enzyme, peroxides is driving increases efforts to develop total chlorine free

(TCF) bleaching. The TCF bleaching eliminates the corrosion problem since no chlorine is present. In the interest of reducing the environmental impact of pulp mill effluents, stress has been paid to examine ways to modify effluents composition and reduce effluent volumes (21). Regulatory issues were once the driving force behind the bleaching developments but now the market place has superceded the regulations and demanded ECF pulps. Using peroxide alone in TCF pulps causes the main problem to achieve full brightness and good pulp properties. Achieving even reasonable brightness require, high temperature and a longer reaction time. To preserve pulp strength and to keep peroxide consumption within reasonable limits, transition metals have to be removed carefully before the pulp is bleached. The key to good results in ECF/TCF bleaching is the elimination of transition metal ions from the pulp because these interfere with the bleaching action of per oxygen compounds. In kraft pulping the metal ions are not water-soluble after the pulping process. During pulping, metal ions get reduced to a low state of oxidation and are precipitated as sulphides. These sulphides are very insoluble under alkaline and neutral conditions, so normal washing does not remove them. Oxygen delignification might oxidize them to a higher oxidation state, but the resulting oxides are still insoluble under the conditions of oxygen stage washing. They become water soluble under mild to strong acidic conditions (72). However, to obtain higher brightness more bleaching chemicals are required. However TCF sequences does not require capital expenditure and for this reasons it will worth developing. Ozone has been the most important oxidizing chemical for TCF bleaching. Due to the problem of high reactivity of ozone, ozone bleaching is, therefore, not sufficiently selective and results in lower viscosity and poorer pulp yield (159).

The role of hydrogen peroxide has expended in TCF bleaching, because of the drop of the use of chlorine based chemicals (164,165). The role of hydrogen peroxide extend reinforce extraction stage, boost final brightness, and in ECF sequences, to extend chlorine dioxide

delignification, and to improve pulp quality. All this was achieved without any major capital expenditure; peroxide has been used as key ingredient in the ECF and TCF bleaching sequences. Key variables for control of peroxide are pH, temperature, transition metal ions content and the equilibria of reaction intermediates (164,202). High pH is a key factor for both delignification and brightening with peroxide.

4.10E TCF Bleaching sequences studied:

The soda and kraft pulps of poplar were bleached using X(EP)P, X(EOP)P, OX(EP)P, OX(EOP)P bleaching sequences, a 0.2% hydrogen peroxide on o.d. pulp has been used in the each stage. Transition metals were removed from the pulp by chelation under the following conditions.

Consistency	-	3-4 %
Temperature	-	about 50 ^{0}C
EDTA charge	-	0.2%
pH	-	4.5-5
Retention time	-	60 minutes.

Results and discussion:

The results of soda and kraft pulps of poplar bleached with X(EP)P and OX(EP)P bleaching sequences has been reported in table-4.15E. The brightness obtained by the soda and kraft pulps using X(EP)P sequences were 69.8 and 71.3% ISO and by OX (EP)P bleaching sequence were 72.9 and 75.4% ISO respectively. However these brightness could be further increased by using ozone. These results indicates that the brightness obtained using TCF bleaching sequences depends upon the incoming kappa number of the pulps. Hydrogen peroxide is the primary chemical responsible for bleaching in TCF sequence. It has been shown that brightness and brightness stability are optimum when hydrogen peroxide is effective in

eliminating carboxyl groups, which are responsible for the brightness reversion of the pulps. Therefore, final D-stage leads to excellent brightness stability in TCF sequences. TCF pulps have however relatively higher residual lignin content.

4.10E: Pulp evaluations:

The pulps on bleaching using xylanase treatment shows improve drainability and lesser energy requirements during beating. The Enzyme treated pulps shows a slight loss in the pulp strength properties. The loss in the pulp strength may be due to the small amount of cellulose present with xylanase or due to the degradation of xylan type hemicellulose during its action. However the enzyme produced by P. chrysosporium shows almost negligible cellulose activity. These results shows that there is little loss in the strength properties of the enzyme treated pulps, however the enzymatic bleaching increases the brightness of the pulp or decreases the oxidizing chemicals upto 30% for the similar brightness. The conventional, ECF and TCF bleached pulps were beaten to around 300 CSF and the strength properties have been reported in table 4.9E, 4.10E, 4.13E, 4.15E. These results indicates that the loss in strength properties is higher in case of pulps bleached with conventional bleaching sequences, however the pulps bleached with ECF and TCF bleaching sequences shows better properties.

4.11E Conclusion:

The xylanase produced from P.chrysosporium are almost as effective in bleach boosting and reducing chlorine consumption as compared to commercial products. At the enzyme concentration of 10 IU and above most of the chromophore release takes place in 1 hour and was almost completed in 2 hour treatment, although reducing sugar release continued at a reduced rate. This data indicates that there may be scope for reducing the treatment time from 2 to 1 hour. On the basis of results of the present investigation, it could be concluded that sufficient xylan type hemicellulose is removed from the pulp to boost bleaching effects as compared to

commercial xylanase preparation. Further the temperature stability of enzyme preparation and their activity at neutral to alkaline pH values offers significant advantages for applications for pulp and paper industry. Moreover, it could be prepared at the site by the industry itself and can be used for the pulp treatments. One of the interesting things is that its cost of production is very low than the expected cost. The enzyme was found to be effective on poplar pulps. Since the poplar hemicellulose has about 22 to 24% xylan so these pulps were found very effective on enzymatic treatment. The 1-hour treatment of this enzyme is sufficient which is also very economical. The pulps bleached with xylanase shows an improvement of brightness upto 3-4 units. The use of xylanase could save about 30% oxidizing chemicals for obtaining the similar brightness. The use of lesser oxidizing chemicals decreases the effluent characteristic. The pulps bleached using enzymatic treatment shows a slight loss in the physical strength properties, this may be due to very small amount of cellulose present in enzyme or due to the degradation of the xylan type of hemicellulose. However the slight loss in strength properties can be compensated by benefits of the saving of oxidizing chemicals.

Table 4.1E: Effect of temperature on xylanase production by Phanerochaete chrysoporium under liquid state fermentation after 11th day of incubation.

Temperature ^{0}C	Xylanase activity IU/ml (± 0.1)
35	11.6
40	16.1
45	19.98
50	17.21

Fermentation conditions 2% wheat barn as substrate
pH of enzyme production 7.0
pH of enzyme activity 6.5
Temperature of enzyme activity 65 ^{0}C

Table 4.2E: Effect of pH on xylanase production by Phanerochaete chrysoporium under liquid state fermentation after 6th day of incubation at 40 ^{0}C.

PH	Xylanase activity IU/ml (±0.1)
5.0	1.11
5.5	1.39
6.0	3.05
6.5	4.72
7.0	6.66
7.5	2.82

Fermentation conditions 2% wheat barn as substrate
pH of enzyme activity 6.5
Temperature of enzyme activity 55 ^{0}C
Substrate concentration of enzyme activity 25mg xylan/ml potassium phosphate buffer

Table 4.3E: Effect of pH on xylanase activity using enzyme secreted by Phanerochaete chrysoporium after 6th day of incubation at 40 ^{0}C.

PH	Xylanase activity IU/ml (±0.05)
6.0	3.19
6.5	5.27
7.0	4.30
7.5	4.16

Fermentation conditions	2 % wheat barn as substrate
pH of enzyme production	7.0
pH of enzyme activity	6.5
Temperature of enzyme activity	55 ^{0}C
Substrate concentration of enzyme activity	25mg xylan/ml potassium
phosphate buffer	

Table 4.4E: Effect of incubation period on xylanase production by Phanerochaete chrysoporium under liquid state fermentation.

Incubation period (Days)	Xylanase activity IU/ml (±0.05)
14	59.96
15	79.95
16	146.57
17	199.87
18	184.39
19	128.80
20	115.48

Fermentation conditions	2% wheat barn as substrate
pH of enzyme activity	6.5
Temperature of enzyme activity	55 ^{0}C
Temperature of enzyme production	45 ^{0}C
Substrate concentration of enzyme activity	25mg xylan/ml potassium
phosphate buffer	

Table 4.5E: Estimation of celluase activity in terms of CMCase using enzyme secreted by Phanerochaete chrysoporium in order to increasing Incubation period.

Incubation period (Days)	CMCase activity IU/ml (±0.02)
14	.14
15	.09
16	.13
17	.12
18	.30
19	.20
20	.18

Fermentation conditions	2% wheat barn as substrate
pH of enzyme production	7.0
pH of enzyme activity	6.5
Temperature of enzyme production	45 ^{0}C

Table 4.6E: Spectrophotometric Analysis of Enzyme treated Pulp filtrates after 1, 2 and 3 hours of treatment of Soda, Soda-AQ , Kraft , Kraft-AQ pulps of poplar

Pulps	Time of treatment	Absorbence at 465nm	280nm	254nm	237nm
A		0.244	3.32	4.32	7.64
B		0.228	3.00	3.52	6.00
C	1hr	0.208	3.00	3.60	5.76
D		0.200	3.04	3.64	5.96
E		0.184	2.16	3.56	4.12
A		0.320	3.72	4.84	8.92
B		0.300	3.44	4.04	6.40
C	2hr	0.260	3.60	4.24	7.08
D		0.240	3.88	4.64	7.68
E		0.200	2.82	3.20	5.36
A		0.324	3.76	4.88	9.52
B		0.312	3.68	4.32	6.80
C	3hr	0.264	3.60	4.42	7.36
D		0.248	3.92	4.80	7.80
E		0.208	2.88	3.68	5.44

A- 16 % Soda pulp Kappa No. 24.1
B- 18 % Soda pulp Kappa No. 19.0
C- 16% Soda -AQ pulp Kappa No. 21.8
D- 14 % Kraft pulp Kappa No. 21.4
E- 16 % Kraft- AQ pulp Kappa No. 17.6

Table 4.7E: Spectrophotometric Analysis of Enzyme treated Pulp filtrates after every hour of treatment of Soda pulp of poplar
Kappa No. 24.1

Enzyme dose IU/gm of pulp	Time of treatment	Absorbence at 465nm	280nm	254nm	237nm
Control		0.120	1.44	1.72	2.80
10 IU	1hr	0.228	2.96	3.56	5.76
20 IU		0.236	3.12	3.64	6.00
50 IU		0.244	3.60	7.20	7.68
Control		0.160	2.24	2.56	4.32
10 IU	2hr	0.300	3.44	4.04	6.72
20 IU		0.320	3.60	4.28	7.08
50 IU		0.324	4.20	4.80	8.92
Control		0.184	2.40	2.96	4.36
10 IU		0.308	3.68	4.32	6.80
20 IU	3hr	0.320	3.72	4.44	7.36
50 IU		0.332	4.24	5.20	9.24
Control		0.224	2.84	3.40	4.80
10 IU	24hr	0.324	3.92	4.48	7.24
20 IU		0.344	4.08	4.60	7.84
50 IU		0.356	4.52	5.80	9.52

Table-4.8E Reducing Sugar release mg/ g pulp

Enzyme (xylanase) Dose IU/g of pulp	1 hour	2 hour	3 hour
Control	0	0	0
10 IU	35 ± 2	43 ± 2	47 ± 2
20 IU	47 ± 2	52 ± 2	56 ± 2
50 IU	60 ± 3	80 ± 4	84 ± 4

Table 4.9E: Enzymatic treatment of Soda and Soda-AQ pulp

Particulars	16% Soda pulp	16% Soda pulp	18% Soda pulp	16% Soda AQ pulp
Kappa No.	24.1	24.1	19.0	21.8
Brightness %	31.1	31.1	35.6	33.1
Enzyme charge IU/gm of pulp	-	10	10	10
Reducing sugar release, %	-	0.38	0.32	0.34
Kappa No. after treatment	24.1	22.0	17.5	20.2
% decrease in Kappa No.	-	9	8	7

Table 4.10E: Conventonal CEHH Bleaching of Enzyme treated Soda and Soda-AQ pulp

Particulars	16% Soda pulp	16% Soda pulp		18% Soda pulp		16% Soda AQ pulp	
Total Cl_2 demand,0.2 x Kappa No.	4.82	4.82		3.8		4.36	
Cl_2 applied, %	4.82	4.82	3.4	3.8	2.3	4.36	3.1
% Cl_2 applied to total chlorine demand	100	100	70	100	70	100	70
Brightness, % (±0.4)	78.6	83.0	77.4	84.4	78.2	83.2	77.2
Opacity, %(±0.5)	83	82.1	83.8	81.3	82.0	81.9	82.3
Tensile Index, Nm/g (±1.0)	59.0	54.5	56.4	55.8	56.7	56.2	57.8
Tear Index, mNm^2/g(±0.4)	5.6	5.2	5.3	5.1	5.1	5.5	5.5
Burst Index, $kPa.m^2/g$ (±0.2)	3.8	3.6	3.6	3.5	3.5	3.7	3.7

Table 4.11E : Enzymatic treatment of kraft and kraft-AQ pulp

Particulars	16% kraft pulp	16% kraft pulp	16% kraft-AQ pulp
Kappa No..	17.6	17.6	14.8
Brightness %	35.6	35.6	36
Enzyme charge IU/gm of pulp	-	10	10
Reducing sugar release %	-	0.33	0.31
Kappa No. after treatment	17.6	16.3	14.1
% decrease in Kappa No.	-	7	5

Table 4.12E: Conventonal CEHH Bleaching of Enzyme treated Kraft and Kraft-AQ pulp

Particulars	16% Kraft pulp	16% Kraft pulp		16% Kraft-AQ pulp	
Total Cl_2 Demand,0.2 x Kappa No.	3.5	3.5		3.2	
Cl_2 applied, %	3.5	3.5	2.5	3.2	2.3
% Cl_2 applied to total chlorine demand	100	100	70	100	70
Brightness, % (±0.4)	79.2	83.6	77.8	84.7	78.2
Opacity, % (±0.5)	82.8	82.2	83	82.1	83.1
Tensile Index, Nm/g (±1.0)	63.0	59.1	59.8	58.6	59.0
Tear Index, mNm^2/g (±0.4)	6.5	6.4	6.5	6.7	6.7
Burst Index, k $Pa.m^2/g$ (±0.2)	4.2	4.0	4.0	4.0	4.1

Table 4.13E: Results of the ECF bleached pulps

Pulps	Bleaching Sequences	Tensile Index (N.m/g) (±1.2)	Tear Index (mNm^2/g) (±0.4)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Brightness , % ISO (±0.5)
Soda Pulp	XDEDP	54.2	5.2	3.6	85.2
	XDEDED	55.4	5.5	4.0	86.7
	XD(EOP)DP	58.3	5.5	3.8	87.1
	XD(EOP)DED	58.0	5.6	3.8	89.9
	OXDEDP	53.1	5.1	3.7	86.0
	OXDEDED	54.4	5.3	4.0	86.9
	OXD(EOP)DP	56.3	5.5	3.9	89.9
	OXD(EOP)DED	56.2	5.4	3.7	90.6
Kraft pulp	XDEDP	61.8	6.6	4.1	86.3
	XDEDED	63.3	6.7	4.2	88.9
	XD(EOP)DP	62.1	6.5	4.1	89.1
	XD(EOP)DED	62.9	6.7	4.0	90.4
	OXDEDP	59.1	6.3	4.1	86.5
	OXDEDED	61.3	6.5	4.0	88.5
	OXD(EOP)DP	60.2	6.4	4.2	89.7
	OXD(EOP)DED	60.6	6.4	4.2	91.4

Table 4.14E: Pulps Bleached using 30% less oxidizing chemicals.

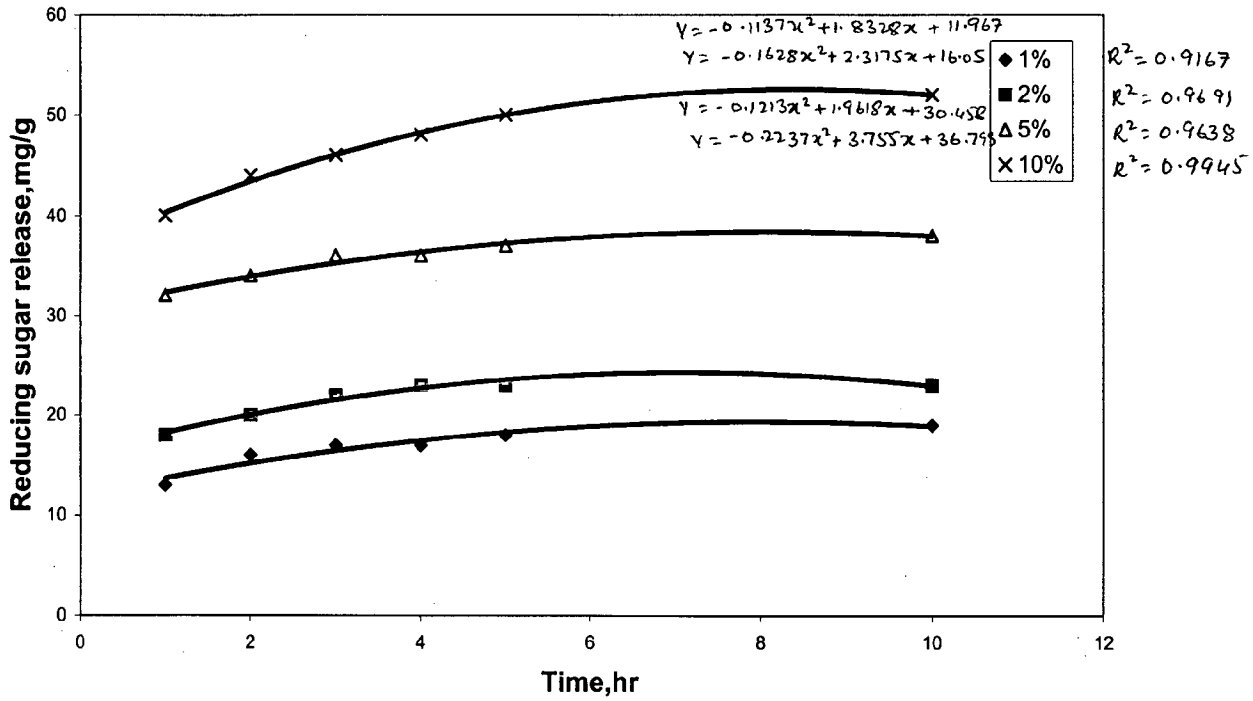
Pulps	Bleaching sequences	Brightness,%ISO (±0.5)
Soda	XDEDED	77.2
	XD(EOP)DED	78.8
Kraft	XDEDED	78.1
	XD(EOP)DED	79.4

Table 4.15E: Results of the TCF bleached pulps

Pulps	Bleaching Sequences	Tensile Index (N.m/g) (±1.0)	Tear Index (mNm^2/g) (±0.4)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Brightness , % ISO (±0.5)
Soda Pulp	X(EP)P	59.7	6.1	3.7	69.8
	OX(EP)P	58.2	6.0	3.8	71.3
	X(EOP)P	59.3	6.0	3.9	73.9
	OX(EOP)P	58.0	5.8	3.7	76.3
Kraft pulp	X(EP)P	64.1	6.8	4.2	72.9
	OX(EP)P	63.4	6.7	3.9	75.4
	X(EOP)P	64.3	6.8	4.1	74.6
	OX(EOP)P	63.2	6.7	3.9	78.3

Table 4.16E: Comparison of Xylanase Produced by P. chrysosporium,Sigma chemicals Xylanase, Pulpzyme and Cartazyme on Pulp Treatment with XCEHH bleaching sequence

Enzyme	Reducing Sugar release, mg/g of Pulp (±2)	Brightness %ISO (±0.5)	Tensile Index (N.m/g) (±1.0)	Burst Index ($k.Pa.m^2/g$) (±0.2)	Tear Index (mNm^2/g) (±0.4)
P. chrysosporium	35	83.6	57.1	3.8	6.1
Sigma Xylanase	37	84.1	58.4	4.0	6.6
Pulpzyme	39	84.7	60.0	4.1	6.6
Cartazyme	37	90.4	54.1	3.8	5.8



4.1E: Effect of pulp consistency on enzyme bleaching

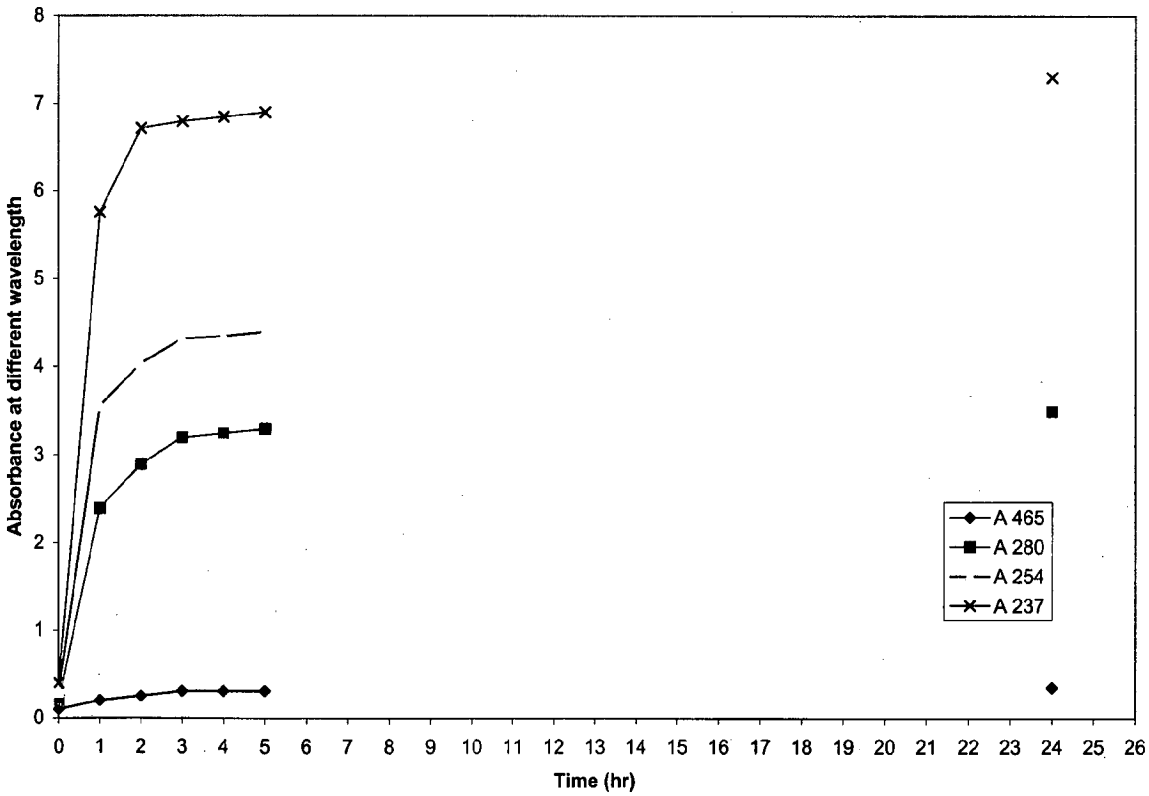


Fig. 4.2E Plot of absorbance vs time (hr) using 10 IU enzyme doses on soda pulp of poplar

CHAPTER 5

STUDIES ON WET WEB STRENGTH PROPERTIES

5.1 Introduction

The wet web strength of pulp in paper making has been studied by many researchers (19,90,114,115,116,147,158), however literature survey indicated that limited work has been done on indigenous pulps (158,190). Wet web properties of pulps directly effect the paper machine runnability which has direct impact on the final production of the paper. The machine speed and the frequency of wet- end breaks are related to the wet web strength characteristics of the furnish. The efficiency of paper machines significantly reduced by sheet breaks at the machine wet end (114,116). Breaks at the couch are considered as a serious problem in paper machine operations. After the couch, the newly formed paper webs which is moist, heavy and weak, is transferred to the press section. At this point the wet web must have sufficient tensile strength to carry its own weight, across the machine in supported areas. Certain amount of tension is applied to the web to transfer it from couch to press and desired force is obtained by driving the press section faster than the couch. The stress increases directly to the weight of the wet web and the square of the paper machine speed (115). Wet web strength is an important property of the sheet at the point of transfer to the press section and the probability of sheet breaks increases as the tension on the sheet approaches the wet web strength. The strength of the wet web increases with increasing solid contents. The development of the initial wet web strength properties can be explained by the fact that, at low solid contents, the wet sheet is held together by surface tension and by frictional forces created between the fibers. The formation of hydrogen bonds between the fibers increases with removal of water and the consolidation of the web and this leads to a considerable increase in the initial wet web strength.

Robertson has comprehensively and theoretically studied the relative relations between fiber properties and wet web behaviour. He considered that fiber flexibility is the basic factor in determining wet web strength. The another most important factor is the volume change of the fiber during water removal and it is characterized by collapsibility index. Flexibility and collapsibility may or may not correlate with each other. With undried unbeaten pulps, collapsibility is correlated to the flexibility. In the case of beaten fibers, the resulting fibrillation increases the collapsibility index, hence the wet web strength. In this case, the strength of the wet web is determined by the resultant of the two effects acting in opposite direction. The third factor affecting wet web strength is the hydrodynamic specific surface of the fibers, which provides an indicationof the extent of fibrilation.

Wet web quality can be expressed by wet tensile strength, stretch at break or wet rupture energy, all obtained from the load elongation curve of the wet web. Page et al. (184) suggested that all three characteristics should be collectively accepted as criteria of wet web quality. However mill practices and other experimental evidences (13,19,184) indicated that high stretch governs the ability of the wet web to withstand stresses on the paper machine. Long fibered pulps have excellent machine runnability followed by various hard woods species, the agriculture residue pulps like bagasse, cereal straws still have inferior runnability.

5.2 Experimental

The unbleached pulp of poplar and poplar blends with imported softwood and bamboo were chosen for studies. These pulps were beaten in PFI mill as per ISO-5264 method to a freeness level of 350± 10 ml CSF. For the blend pulp, the constituent pulp were seperately beaten and blended. The pulps were diluted to 0.2% consistency. The wet web measuring strips 20mm wide and 150mm length were made by placing stainless steel mould on the top of the wire mesh of British sheet former during hand sheets preparation. The strips were pressed by placing

3kg weight for 60 seconds and transferred on the blotter. For obtaining wide range of dryness values, the strips were further subjected to pressing. The strips after pressing were tested for wet web tensile index, wet web elongation and tensile energy absorption (TEA) using L&W wet web tensile strength tester as per scan C:31:77 method. The dryness values of the strips were determined subsequently by drying at 105+2 °C for 3 hours.

5.3 Results and Discussion

5.3.1 Wet web strength of Poplar

The wet web strength properties, wet web tensile index (WWTI), wet web elongation and TEA of poplar pulp (at 20% dryness) at different freeness levels have been reported in table 6.1. The results indicate that the wet web strength properties increases with decrease in freeness values of the pulp. The increase in the wet web properties on refining is due to the fact that refining improves the bonding properties of pulp fibers. The bonding ability of pulp is related to the degree of swelling of fiber, increase in fibrillation, increase in collapsibility index and the hydrodynamic specific surface area of the fiber which holds the fibers together by surface tension, hydrogen bonds and frictional forces created between the fibers. The formation of hydrogen bonds between the fibers increases with the removal of water and leads to increase in initial wet web strength. The wet web strength and the wet web elongation of poplar at around 20% dryness were found to be around 0.75 Nm/g and 11.0% respectively. The wet web tensile is not sufficient to withstand the stress of paper machine. This stress is redistributed, which is related to the elongation of the wet web and TEA. However WWTI and wet web elongation is the function of dryness. WWTI increases with increase in the dryness of the pulp while wet web decreases.

5.3.2 Wet web strength of different Pulps

The wet web properties i.e wet web tensile, wet web elongation, tensile energy absorption (TEA) of different pulps have been reported in table 6.2. At 20% dryness, wet web tensile of the bagasse pulp was found to be lowest i.e. 0.62Nm/g. The wet web tensile of the soft wood pulp was found to be 1.52 Nm/g which is highest. The wet web strength of bamboo, eucalyptus and poplar were 1.10, 0.72, 0.75 respectively. The WWTI of hard woods Eucalyptus and poplar are comparable.

The wet web elongation in the case of soft wood pulp and bamboo were found to be 17.2 and 19.8 respectively. These results showed that the soft wood pulp have lower wet web elongation compared to bamboo. The wet web elongation in the case of eucalyptus and poplar were found to be 11.4 and 11.0 respectively which are comparable.

5.3.3 Wet Strength of pulp blends

The poplar pulp was blended with bamboo and soft wood pulps. The results of the pulp blends of poplar and bamboo (90:10) and poplar and softwood (90:10) have been reported in table 6.3 and 6.4. The blending consisting of 90% poplar and 10% softwood, has the wet web tensile index 0.83Nm/g, wet web elongation 12.2% and TEA 75.3J/kg, while in the case of blending of 90% poplar with 10% bamboo, the WWTI was found to be 0.80 Nm/g and wet web elongation 12.4% and TEA 72.1Nm/g. These results indicates that as the blending with long fibered pulp increases, the wet web strength properties improved continuously, which will certainly improve the paper machine runnability. The effect of blending with long fibered pulps namely softwood or bamboo on various properties has been shown in fig 5.1 and 5.2. The increasing the proportion of long fibered pulps, the gain in wet web tensile is more in the case of soft wood pulp compared to bamboo pulp. However the gain in the wet web elongation has been found to be more in the case of bamboo pulp as compared to soft wood pulp.

5.4 Conclusion

- The wet web strength properties of poplar were found to be comparable with other raw materials such as eucalyptus
- The results of the wet web strength indicates that the wet web strength increases linearly on blending with long fibered pulps.
- The wet web strength properties such as wet web elongation and TEA can be improved considerably by blending with long fibered pulp, which help in improving the paper machine runnability

Table 5.1: Wet web strength of Poplar at different Freeness

Freeness	TEA J/kgm (±0.5)	WWTI Nm/g (±0.02)	Wet web elongation, % (±0.3)
680	28.1	0.31	6.2
590	32.8	0.42	8.1
430	42.3	0.58	9.7
320	64.3	0.75	11.0
190	70.2	0.82	11.5

Table 5.2: Wet web strength of different pulps at 20% dryness (Freeness of pulps 320+10ml CSF at different Freeness

Pulps	TEA J/kg (±0.5)	WWTI Nm/g (±0.02)	Wet web elongation, % (±0.3)
Bagasse	50.1	0.61	9.4
Wheat straw	56.4	0.78	12.6
Eucalyptus	62.5	0.72	11.4
Poplar	64.3	0.75	11.0
Bamboo	143.2	1.10	19.8
Softwood	170.2	1.52	17.2

Table 5.3: Wet web strength of Poplar and Softwood blends

Pulp Furnish	TEA J/kg (±0.5)	WWTI Nm/g (±0.02)	Wet web elongation, % (±0.3)
100% Poplar	64.3	0.75	11.0
90% Poplar + 10% Softwood	75.3	0.83	12.2
80% Poplar + 20% Softwood	83.2	0.89	13.1
70% Poplar + 30% Softwood	98.4	0.97	13.8

Table 5.4: Wet web strength of Poplar and bamboo blends

Pulp Furnish	TEA J/kg (±0.5)	WWTI Nm/g(±0.02)	Wet web elongation, % (±0.3)
100% Poplar	64.3	0.75	11.0
90% Poplar + 10% Bamboo	72.1	0.80	12.4
80% Poplar + 20% Bamboo	79.4	0.85	13.5
70% Poplar + 30% Bamboo	89.9	0.91	14.1

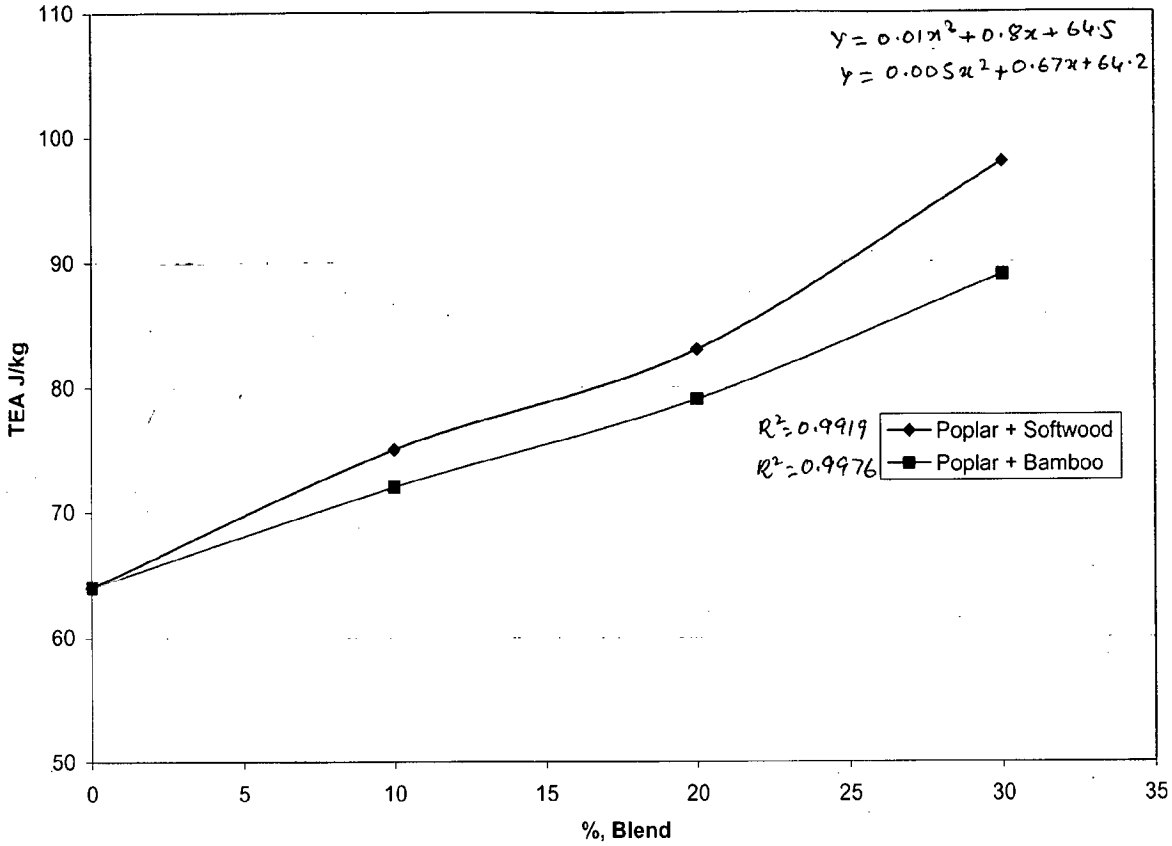


Fig. 5.1 Effect on the improvement of TEA during blending Poplar pulp with Softwood and Bamboo pulps in different proportions

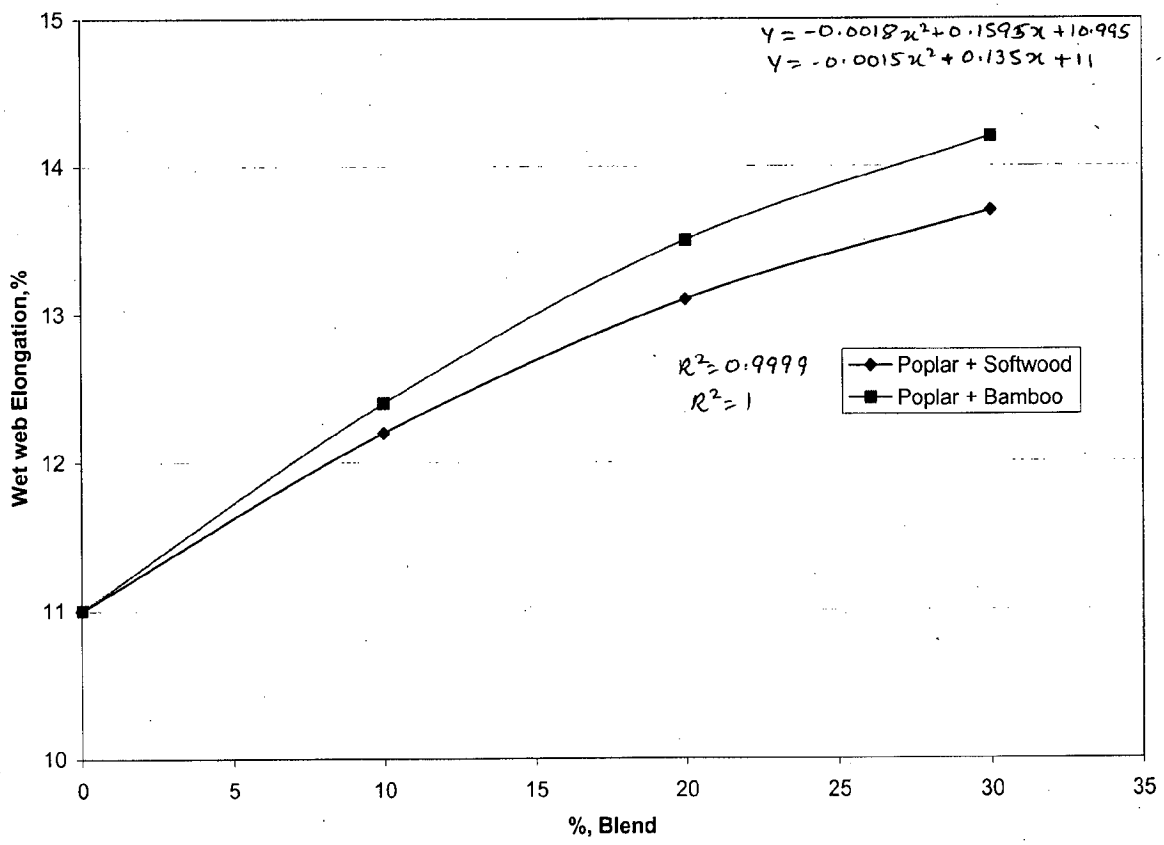


Fig. 5.2 Effect on the wet web elongation during blending Poplar pulp with Softwood and Bamboo pulps in different proportions

CHAPTER 6

STUDIES ON PULP BLENDING

6.1 Introduction:

Even in technically and culturally advance countries, the notable and steady development of the paper industry has raised serious problems of raw material supply. Conifers (softwoods) are the chief raw material for paper making for a long period, due to climatic, topographic and other reasons; are not available at all in sufficient quantity in most of the tropical countries like India. Besides conifers, the hardwoods are also suitable for paper making, the hardwoods are almost exclusively short fibered, with an average fiber length of about 1 mm. Obviously, in their own interest, all countries have to exploit to the greatest possible extent of their different existing resources of fibrous raw materials, including agro residues and other potential non-woody fibrous raw materials. In Indian context, one has in own case, that we have to examine thoroughly species of hardwoods, agricultural residues along with recycling of waste paper, for conversion into suitable pulp and paper products. It has been well known that the short-fibered raw materials, lowers the quality of the paper to be produced and various difficulties arise during the manufacturing process. The aim of the present studies is to make the effective utilization of short fibered hard woody raw materials in blends with long fibered materials, satisfactory both for the manufacturing process and for their paper making characteristics. The pulps made of hardwood trees differs in many respects from the coniferous pulps in terms of paper making, fibre dimensions, fiber-morphology and their behaviour on the paper machine and in the properties of the paper sheet itself.

If such short fibered raw materials are to be used in large quantities, it is not only their characteristics properties that must be thoroughly known, but they have to be applied in

mixtures, in such a manner that the inferior characteristics of one material are counter balanced by the advantages of other components; moreover, the machinery has to be correspondingly adjusted to eliminate difficulties in processing. The short fibered pulps create troubles during drainage (low runnability), lower wet web strength, and the tendency to pick at the press roles. These problems are more pronounced with agricultural residue pulps. Furthermore other difficulties have been observed with certain qualities of the paper, primarily with its dynamic strength properties. Further on, in the manufacturing process, breaks may occur between presses and dryers, or in the drier part itself. These defects may appear also in finishing the paper or during their end use. The first group of difficulties is relatively easy to combat-by the insertion of a longer wire, by increasing the suction areas, by using lower vacuum, but the behavior of the paper in finishing and its better wider application can be influenced by proper selection of raw materials and their appropriate refining, leaving aside the treatment with different synthetic and other materials during or after the beating or refining operation.

The fall in strength characteristics, increases the risk of breaks in the web, on the wet end and also between the dryers. In paper industry, there is a pronounced trend towards the blending of different types of long fibered and short fibered pulps, during the manufacture of most of paper qualities, in order to achieve the certain minimum requirement of various physical strength properties. The main reason for blending long fibered with short-fibered pulps is the resulting increased possibility of improving the existing paper qualities.

Most commercially produced papers, contain more than one fibrous components and non fibrous materials (fillers) to improve the properties given by the pulp furnish. The pulp blends are chosen in such a way that the resultant pulp and paper properties are more acceptable when considered as a whole than those of the individual components. The over all assessments of the choice of material for a given furnish is influenced by such factors as the relative costs of the

various pulps and their availability, their ease of beating and over all wet end performance, e.g runnability and formation. Since the addition of fillers reduces the strength of the sheet whilst commensurately improving the opacity and brightness. The qualities that can be added in order to attain satisfactory optical properties are limited. Hence the final paper will often contain various pulps and fillers blended together in such a way as to produce the desired product economically and that satisfies the customer's specifications.

The three principal factors controlling paper strength are cell wall thickness (which influences both fiber flexibility and bonding), fiber length and fiber strength. Studies of softwood chemical pulps have shown that thin-walled, slender fibers forms sheet with high tensile strength, elastic modulus, burst and fold, and at the same time tends to collapse during the sheet forming process, to give paper of high density; while on the other hand the thick-walled fibers produce paper with high bulk, tear and porosity but lower burst, tensile and fold (149,173).

The mechanical treatment or refining of pulp is an important step in the development of pulp furnishes for paper making (102). The extent to which pulps are refined significantly influences the resultant fiber properties, and consequently the end product. Moreover, refining processes has a critical effect on the formation and runnability of the paper machine. The refining process produces a number of modifications to fiber morphology. Such as fiber cutting, external fibrillation, secondary wall delamination, and altered collapsibility and flexibility. Several other processing factors such as drying history, slushing regimes, stock concentration, pH, temperature and pulping and bleaching significant influence the degree of modification induced by mechanical refining, as do inherent fiber including wood species, origin, age and chemical composition (103,104). It has been well recognized that paper properties are highly correlated to inherent fiber morphology, such as fiber length, fiber diameter and wall thickness. The refining process effectively causes fibers of relatively low coarseness, consisting of thin cell

walls, to readily collapse during pressing and drying and are consequently highly suitable for the production of fine paper. In contrast, thick walled fibers, of higher coarseness are more difficult to develop and consequently retain their intrinsic strength and are more appropriate for packing grade materials and speciality products. It has been observed that some hard wood pulps are readily refined to given strength and freeness while others not. The refining requirement and fiber quality if hardwood pulps can vary significantly which may be the consequence of rapid growth of the wood.

Peckham and May (143) worked with blends of pine and gum bleached kraft pulps and concluded that the strength of a pulp can be predicted very closely if the two pulps are beaten before combining simply by obtaining a weighted average of the strength properties at the two freeness level. Brecht (18) concluded that when the two pulps differ only slightly in their physical properties, the blend follows a linear relationship. More extended work on this subject has been carried out by the Institute of Paper Chemistry (78). In experiments with blends of aspen and western softwood pulps, they found that blends were inhibited consistently higher tearing resistance that could be predicted by assuming linear relationship. Nordemen (149) concluded that the properties of a blend of two pulps can be predicted by weighing the properties of the respective blend components in proportion to their fraction of the blend, was investigated by testing blends of upto 30% high yield unbleached hardwood pulps with high yield bleached pine pulps.

Short thin walled fiber pulps are currently used for the manufacture of many varied grades of paper (129,149,136) have pointed out the usefulness of incorporating such fibers in papermaking furnishes. Short thick walled fibers from the genus eucalyptus have not been generally accepted because paper made from this type of fiber have relatively low strength (102,103,181) and since most of the previous work done on this material was in relation to high

strength wrapping paper, this source of pulp wood has often been regard as being unsuitable for paper making. Hardwood and annual plants fibers differs from conifers fibers in fiber dimensions and fiber morphology etc. produce paper of different properties. Most commercial papers contains more than one fiber. The choice of material for a given furnish influenced by factors such as the relative costs, availability, beatability and over all wet end performance, runnability, formation etc.

Kelogg and Wangaard (72) found highly significant correlation's between fiber strength and sheet properties, through multiple regression analysis, showing that sheet tensile strength and burst are highly correlated with individual fiber strength and sheet density. At low sheet density, the contribution of fiber strength to paper tensile strength is negligible, but becomes significant at higher densities. In the case of tear, Kellogg and Wangaard concluded that their property increases with increased strength of individual fibers.

6.2: Experimental Methodology :

The blending studies of long fibered raw material pulps (bamboo and soft wood) with

The pulp of poplar deltoides has been conducted by the following methods.

(A) Pulping of individual raw materials.

(B) Chip blending i.e. the blending of different raw material chips in appropriate quantity before pulping.

(C) Mixing the different pulps of these raw materials before beating.

(D) Beating each pulp separately to a particular freeness level and then mixing the two pulps in different proportions before sheet making.

6.3: Pulping of Individual Raw Materials :

Since kraft process is the dominant pulping process, therefore the screened chips of acceptable quality of poplar deltoides, bamboo, and pine were individually pulped in the

electrically heated Weverk rotatory digester by the kraft process. All these different raw materials were delignified at different active alkali doses. The pulping conditions and the results of kraft and soda pulping of bamboo and pine have been reported in table-6.1 and 6.2. At the end of the cook these pulp were washed screened and evaluated for kappa number, screened pulp yield, and rejects.

The results of these pulping studies revealed that the screened pulp yield and kappa number of poplar and bamboo were 53.6 and 46.2% and 17.6 and 21.8 respectively at 16% active alkali and 20% sulphidity. The pine chips were cooked at a higher active alkali of 18% and at 20% sulphidity, the screened pulp yield of 43.6% with a kappa number of 19.6 was obtained. These results indicates that pine is delignified at a higher alkali dose while the poplar delignified at lower alkali dose with much ease to a lower kappa pulp. The two woods in mixture influence each other and this fact probably generates imbalancing of lignin and hemicellulose dissolved. The strength properties of the pulp so obtained was found to be lower. During the soda delignification, the bamboo chips were delignified by using 18% alkali and pine chips with 20% active alkali. The pulp yield and kappa numbers were found to be 46.1, 44.2 % and 23.7 and 24.6 respectively.

6.4: Chips Blending (Mixed Cooking) :

Poplar is a short fibered raw material, therefore it essentially requires some mixing of long fibered raw materials such as bamboo or pine in order to improve the runnability as well as to improve quality of furnish. In these set of experiments, the chips of poplar deltoides were mixed with the chips of bamboo and pine in various proportion viz. 10:0, 9:1, 8:2, 7:3, 6:4 and 5:5. These chip blends were delignified by kraft process using 16% active alkali and 20% sulphidity and by soda process with 18% active alkali. The results of these experiments have been reported in table-6.3 to 6.6.

The results of the chip blending with bamboo has been reported in table 6.3 and 6.5. These results indicates that there is a relative decrease in the pulp yield with an increase in the bamboo proportion. It has been observed that the kappa number relatively increases. The results of blending with softwood chips shows that the pulp yield decreases drastically with an increase in the pine chip proportions. It may be due to the easily delignification characteristics of poplar deltoides in comparison to pine delignification, thereby producing a blended pulp with increased kappa number.

6.5: Blending of Pulps :

The pulp of Poplar deltoides was blended with the pulps of bamboo and softwood (pine) in different proportions viz. 10:0, 9:1, 8:2, 7:3, 6:4, 5:5 in the following two ways.

(a) The pulp samples were blended in unbeaten form and then beaten to a freeness levels of 300 + 10 CSF.

(b) The pulps were beaten separately to the freeness of 300±10 CSF and then blended in different proportions.

The results have been reported in table-6.9 to 6.12.

6.6: Pulp Evaluation :

These pulps were beaten in a PFI mill separately or jointly, as the case may be, upto a freeness level of about 300 CSF. The standard handsheets of 60 gsm were made on British sheet forming machine. The sheets were pressed and dried as per TAPPI standard method. T-205, OM-80. These sheets were conditioned at a temperature of 27±1 °C and at 65±2 % relative humidity and evaluated for various physical strength properties and the results of pulp evaluation are tabulated in table-6.9 to 6.12. The results of the pulp evaluation of softwood and bamboo pulps have been reported in table-6.7 and 6.8. The results of the softwood pulp evaluation indicates that tensile index, and burst index increases with beating, however the tear index suffers,

therefore, the softwood pulps used for blending purposes should be beaten to a freeness level of around 350 CSF; so that it can facilitate the tear improvement. However the results of the evaluation of bamboo pulp indicates that the strength properties increases on beating up to a freeness level of 300 CSF and beyond this the strength properties suffers a set back.

6.7: Results and Discussions :

Hardwood fibers are shorter and finer than those from softwood fibers. This significant feature imparted better sheet formation, smoother printing surfaces and excellent optical properties of paper, but blending with softwood pulps is necessary to improve over all sheet strength.

The results of blending studies conducted on the blending of the chips of poplar deltoides with the chips of bamboo and pine are reported in table-6.3 to 6.6. These results indicates that in general, the strength properties of chip blending are poorer than that would be expected. The reason would may be the selectivity of the delignification process, as the different raw materials have different alkali requirement, delignification time, temperature and different process parameters.

On comparing the results of these experiments as shown in tables-6.9 to 6.12, revealed that when poplar deltoides pulp was blended with the pulp of bamboo and pine, and followed by joint beating, there is an improvement in strength properties as compared to the blending of chips prior to cooking operation. On the basis of the experimental data of pulp blending, it has been observed that the tearing strength of poplar and softwood blend is seen to be greater than the arithmetic mean of the components. Under the experimental conditions of the present investigation, the tensile index of the blends is seen to have a tendency to be greater than the calculated values on the average, however these effects are rather smaller. The results of blending experiments of separately beaten pulp of poplar blended with bamboo and pine pulps,

shows that the over all strength properties are further improved in comparison to the pulp blending prior to beating operation. Blending of long fibered pulps with short fibered pulps after beating the pulps separately, showed an improvement in strength properties as compared to mixed cooking as well as separate cooking followed by mixed beating operation. However the results of strength properties of the mixed beating of pulps were found to be marginally inferior. These results must be due to the protecting action of softwood on hardwood fibers, thus giving slightly better tear. It might be said that a blending of fibers of different characteristics seems to offer increased possibilities of producing paper as per quality requirements. In the case of pine pulp the tear index decreases with extensive beating, therefore, the softwood pulp should not be beaten beyond a freeness level of around 350ml CSF, before blending to give the better results.

Tear tensile relationship of the blend pulps is an important property to predict the strength of the pulp. Several researchers have demonstrated that tear-tensile relationships are indicative of pulp strength and its reinforcement potential and web runnability on paper machines (25,105,181,183). Therefore the interrelationship of the tear-tensile has been studied as reinforcement characteristics and over all sheet strength characteristics of poplar pulp blended with softwood and bamboo in different proportions. The tear-tensile relationship of the different pulp blends of poplar softwood and bamboo have been shown in figure 6.1 and 6.2. As expected the tear strength at a given tensile strength increases as long fiber fraction increases from 0-50% both in separate and co-refining. However with increase in refining the tear index of softwood pulp decreases from 24mNm^2/g to a minimal value of 13 mNm^2/g, while in the case of poplar pulp tear increases on refining up to the maximum value 7mNm2/g then decreases on prolonged beating. Figure 6.1and 6.2 shows typical tear peaks at tensile level 50-60 in the softwood and bamboo blends. The tear-tensile properties are directly related to the nature of the softwood component, while the tensile properties is the function of both poplar and softwood components.

The tear tensile relationships are generally the same for the separate and co-refined pulps. In the case of the blends of separate refined pulps the tear is markedly higher compared to co-refined pulps.

The analysis of data also indicate that the linear blending formula could be applied to predict the strength properties as well as the freeness of the blends. The difference between the observed strength properties and their predicted values were found to be very small. The burst index and tear index of the blends having higher proportions of long fibered pulp tended to be greater while the tensile index tended to be lower than the predicted values and the blend freeness was found to be lower than expected value.

6.8: Conclusion :

In general, the influence of long fiber quality differences on hand sheet property interrelationships decreases with decreasing proportions of poplar : long fiber (softwood and bamboo) blends.

Pulp refined swparately before blending has a tendency to exihibit slightly higher reinforcement strengths than those that were blended before co-refining as has been previously observed by the different workers. Based on experimental observation, it can be concluded that the blending of long fibered pulps with short fibered pulps, after beating the pulps separately, showed an improvement in strength properties as compared to mixed cooking as well as separate cooking followed by mixed beating operations. The results of the chip blending indicates the heavy loss in the pulp yield and the strength properties and this may be due to the different pulping characteristics of the two raw materials. Hardwood fibers are shorter and finer than those from softwood. This significant feature imparted better sheet formation, smoother printing surfaces and excellent optical properties of paper, but blending with softwood pulps is necessary to improve over all sheet strength.

5.1

Table 6.1: Results of Kraft pulping of bamboo and pine at 20% sulphidity , using following conditions.
Maximum Temperature: 165°C
Time at Maximum Temperature : 120 minutes.
Wood to liquor ratio : 1:3

Particulars	Bamboo	Pine
Active alkali ,% (as Na_2O)	16	18
Sulphidity ,%	20	20
Screened pulp yield ,% (±0.8)	46.2	43.6
Rejects ,% (±0.1)	0.6	0.8
Total pulp yield ,% (±1.0)	21.8	43.4
Kappa Number (±0.7)	18.2	19.6

Table 6.2: Results of soda pulping of bamboo and pine, using following conditions .
Maximum Temperature: 170°C
Time at Maximum Temperature : 150 minutes.
Wood to liquor ratio : 1:3

Particulars	Bamboo	Pine
Active alkali ,% (as Na_2O)	18	20
Screened pulp yield ,% (±0.8)	46.1	44.2
Rejects ,% (±0.1)	1.2	1.0
Total pulp yield ,% (±1.0)	47.6	45.2
Kappa Number (±0.6)	23.7	24.6

Table 6.3: Mixed chip blending of Poplar and Pine at 16% active alkali and 20% sulphidity , using following conditions .
Maximum Temperature: 165°C
Time at Maximum Temperature : 120 minutes.
Wood to liquor ratio : 1:3

Furnish Poplar : Pine	Screened pulp yield , (%)(±0.8)	Kappa No. (±0.6)
100 : 0	53.6	17.6
90 : 10	51.1	18.0
80 : 20	49.7	18.7
70 : 30	48.4	19.3
60 : 40	47.3	20.7
50 : 50	46.1	21.8

Table 6.4: Mixed chip blending of Poplar and Bamboo at 16% active alkali and 20% sulphidity , using following conditions .
Maximum Temperature: 170°C
Time at Maximum Temperature : 120 minutes.
Wood to liquor ratio : 1:3

Furnish Poplar : Bamboo	Screened pulp yield , (%)(±0.8)	Kappa No. (±1.2)
100: 0	53.6	17.6
90 : 10	52.6	17.9
80 : 20	51.0	18.8
70 : 30	50.4	19.4
60 : 40	49.6	20.1
50 : 50	48.8	21.2

Table 6.5: Mixed chip blending of Poplar and Pine at 18% active alkali, using following conditions.
Maximum Temperature: 165°C
Time at Maximum Temperature : 120 minutes.
Wood to liquor ratio : 1:3

Furnish Poplar : Pine	Screened pulp yield , (%)(±0.8)	Kappa No. (±1.2)
100: 0	55.1	24.1
90 : 10	54.3	24.6
80 : 20	53.6	25.2
70 : 30	52.9	25.8
60 : 40	52.0	26.7
50 : 50	51.3	27.3

Table 6.6: Mixed chip blending of Poplar and Bamboo at 18% active alkali , using following conditions .
Maximum Temperature: 170°C
Time at Maximum Temperature : 90 minutes.
Wood to liquor ratio : 1:3

Furnish Poplar : Bamboo	Screened pulp yield , (%) (±0.8)	Kappa No. (±1.2)
100: 0	55.1	24.1
90 : 10	54.5	25.1
80 : 20	53.7	25.9
70 : 30	52.6	26.4
60 : 40	51.1	27.2
50 : 50	49.9	28.4

Table 6.7: Strength properties of soft wood kraft pulp

PFI Revolutions	Freeness CSF (ml) *(±10)*	Apparent Density (gm/cm^3) *(±0.2)*	Tensile Index (N.m/g) *(±1.2)*	Tear Index ($mN.m^2/g$) *(±0.3)*	Burst Index ($kPa.m^2/g$) *(±0.2)*
0	745	0.45	21.4	11.7	0.8
2000	700	0.59	49.2	24.2	3.5
4000	560	0.67	62.6	19.7	4.8
6000	450	0.70	71.1	17.0	5.1
8000	280	0.72	73.9	14.2	5.8
10000	200	0.74	78.2	13.0	6.0

Table 6.8: Strength properties of bamboo kraft pulp

PFI Revolutions	Freeness CSF (ml) *(±10)*	Apparent Density (gm/cm^3) *(±0.2)*	Tensile Index (N.m/g) *(±1.2)*	Tear Index ($mN.m^2/g$) *(±0.3)*	Burst Index ($kPa.m^2/g$) *(±0.2)*
0	680	0.61	22.3	2.4	1.1
2000	530	0.64	39.7	4.4	2.5
4000	410	0.69	52.7	6.7	3.9
6000	290	0.72	61.4	8.9	5.4
8000	180	0.78	66.9	8.2	5.1

Table 6.9: Strength properties of Poplar Kraft Pulp with Pine kraft Pulp.

1. Mixing of wood chips prior to cooking
2. Mixing of pulps before beating
3. Mixing of pulps after beating separately

FURNISH	Blending before cooking			Blending before beating			Blending after beatir	
	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*
100 : 0	70.2	7.2	4.7	70.2	7.2	4.7	70.2	7.2
90 : 10	71.9	7.6	5.0	72.3	7.9	5.2	72.4	8.1
80 : 20	74.1	8.7	5.1	75.0	9.8	5.3	74.8	10.7
70 : 30	76.3	9.5	5.1	76.9	11.0	5.5	76.3	11.0
60 : 40	78.8	10.2	5.3	80.4	11.3	5.6	79.5	11.5
50 : 50	81.2	10.8	5.4	82.3	11.9	5.6	82.0	13.0

Table 6.10: Strength properties of Poplar soda pulp with pine kraft Pulp.

1. Mixing of wood chips prior to cooking
2. Mixing of pulp before beating
3. Mixing of pulp after beating separately

FURNISH	Blending before cooking			Blending before beating			Blending after beatii	
	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile *Index (N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$ (±0.3)*
100 : 0	58.3	5.1	3.6	58.3	5.1	3.6	58.3	5.1
90 : 10	59.4	5.4	3.9	72.3	5.5	3.9	72.4	6.0
80 : 20	60.6	6.3	4.3	75.0	5.9	4.1	74.8	7.2
70 : 30	61.0	6.7	4.6	76.9	6.5	4.4	76.3	8.7
60 : 40	61.7	7.4	4.7	80.4	7.8	4.7	79.5	9.0
50 : 50	63.0	7.8	4.7	82.3	8.9	5.0	82.0	9.6

Table 6.11: Strength properties of Poplar Kraft pulp with bamboo soda pulp.

1. Mixing of wood chips prior to cooking
2. Mixing of pulp before beating
3. Mixing of pulp after beating separately

FURNISH	Blending before cooking			Blending before beating			Blending after beating		
	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile *Index (N.m/g) (±1.2)*	Tear Index *($mN.m^2$ /g) (±0.3)*	Burst Index *($kPa.m^2$/ g) (±0.2)*	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2$/ g(±0.3)*	Burs Inde *(kPa g) (±0..*
100 : 0	70.2	7.2	4.7	70.2	7.2	4.7	70.2	7.2	4.7
90 : 10	71.4	7.3	4.7	71.8	7.4	4.9	71.6	7.4	4.9
80 : 20	72.1	7.5	4.9	72.9	7.5	5.0	72.7	7.5	5.1
70 : 30	73.5	7.7	5.1	74.0	7.7	5.1	74.3	7.8	5.2
60 : 40	75.0	7.9	5.0	75.3	8.3	5.1	75.5	8.5	5.2
50 : 50	76.7	8.0	5.0	77.3	8.5	5.3	77.4	8.9	5.4

Table 6.12: Strength properties of Poplar soda pulp with Bamboo soda Pulp.

1. Mixing of wood chips prior to cooking
2. Mixing of pulp before beating
3. Mixing of pulp after beating separately

FURNISH	Blending before cooking			Blending before beating			Blending after beating		
	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2/g$) (±0.2)*	Tensile *Index (N.m/g) (±1.2)*	Tear Index *($mN.m^2/g$) (±0.3)*	Burst Index *($kPa.m^2$/g) (±0.2)*	Tensile Index *(N.m/g) (±1.2)*	Tear Index *($mN.m^2$/g(±0.3)*	Bu Inc *(kP m^2/ (±(
100 : 0	58.3	5.1	3.9	58.3	5.1	3.6	58.3	5.1	3.6
90 : 10	58.6	5.5	4.1	60.3	5.8	4.4	60.4	6.0	4.6
80 : 20	59.7	5.7	4.3	62.3	6.6	4.5	62.8	6.8	54.
70 : 30	61.5	6.0	4.6	63.9	6.9	4.7	64.3	7.3	4.9
60 : 40	63.0	6.4	4.8	65.2	7.3	4.9	65.8	7.7	5.0
50 : 50	63.5	6.7	4.8	67.0	7.5	5.1	67.9	7.9	5.1

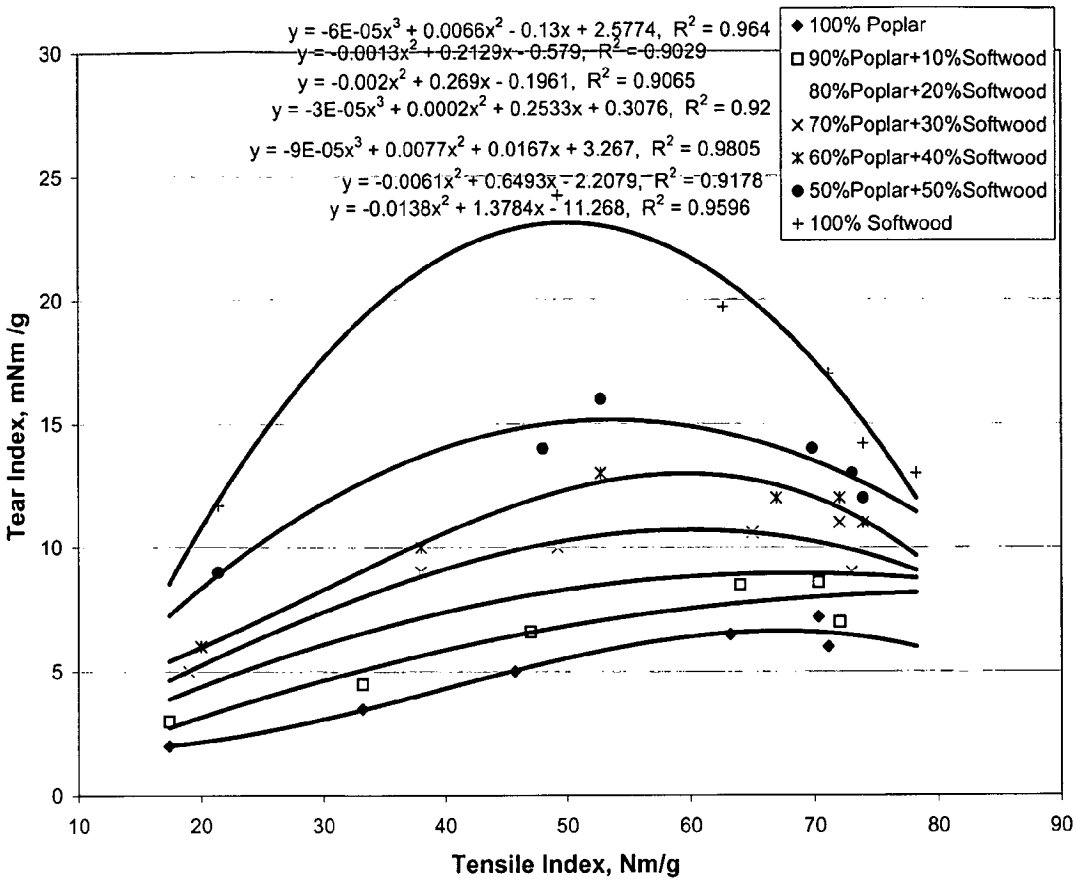


Figure 6.1 Plot of Tear Tensile relationship of Poplar and softwood blends

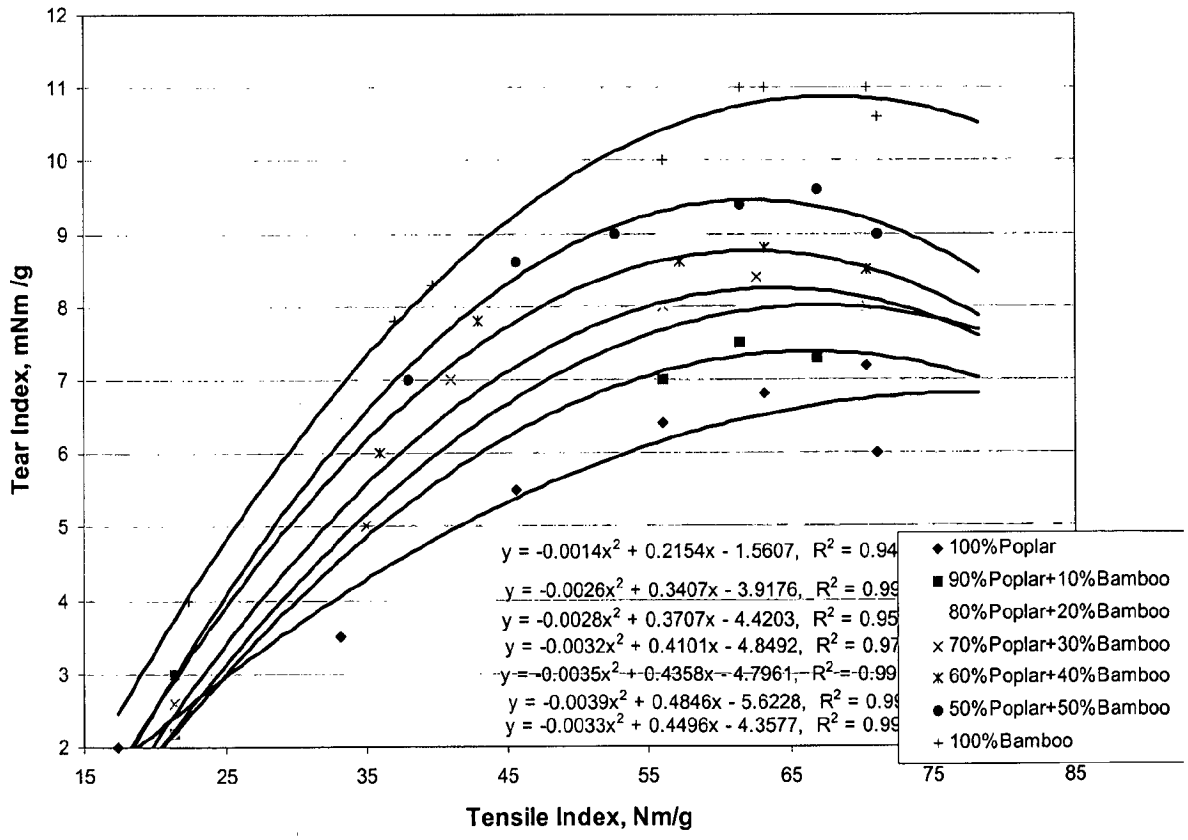


Figure 6.2: Plot of Tear Tensile relationship of Poplar and Bamboo Blends

CHAPTER 7

CONCLUSIONS

The present investigation has been made to do systematic studies on Poplar deltoides with reference to pulp and papermaking. Poplar deltoides is one of the most potential fast growing hardwood plant, and the plantation of poplars has been increasing rapidly in the northern and other parts of India. Poplar plantation has maximum benefits in the agro-forestry and has been succeeded in obtaining higher biomass of the pulp wood. At present among the hardwoods, eucalyptus is the most widely used fibrous promising raw material for pulp and papermaking. The another most potential hardwood (alternative to eucalyptus) for conversion into pulp and paper product is Poplar deltoides. Poplar deltoides has the fiber length comparable to that of eucalyptus, but the fiber diameter is almost two times more, hence the pulps of poplar is expected to have higher bulk. The results of proximate chemical analysis indicated that poplar has less water solubles and alcohol benzene solubles as compared to eucalyptus. All the soluble material comes under the category of extractives and completely undesirable for pulp and papermaking. The lignin content of poplar on lower side compared to eucalyptus, which indicate its the ease in the delignification. The total carbohydrate fraction of poplar is higher than the eucalyptus, which is the most important requirement of pulp and papermaking, thereby producing more pulp as compared to eucalyptus. The pentosans content of poplar is more than eucalyptus indicating the higher degree of fungal decay on storage a longer period. The ash content of both is quite comparable. Hence in view of these investigations poplar deltoides is one of the most potential fibrous raw material for pulp and papermaking.

The pulping studies on poplar deltoides were conducted using soda, kraft, polysulfide and alkaline sulphite processes. The effect of AQ on pulp yield, and kappa number was also studied in all these pulping processes. The present investigation indicated that the poplar deltoides prodeuce good quality pulps with better papermaking characteristics. These pulping studied has shown have the poplar deltoides require lower cooking chemicals, shorter cooking cycle with milder process conditions to achieve the desired degree of delignification during the course of pulping. The results of the pulping studies also revealed that the kraft pulping process is best suited for making high strength paper. However, it has been observed that soda-AQ process produce a pulp comparable to kraft, which is a non sulphur process and eliminates the emission pollutants like mercaptans and dimethyl sulphide etc. The polysulphide pulping process has been proved a very good process in terms of providing higher yield and stronger pulps, but the major draw back is the production of sodium thiosulphate during polysulphide generation, which highly accelerates the corrosion of the process equipments. Alkaline sulphite process found to be beneficial for producing high yield pulps. The addition of AQ during the various pulping processes has been proved to be beneficial in reducing the kappa number substantially alongwith a slight, increase in pulp yield or in reducing the energy and chemical requirements to achieve a pulp with desired degree of delignification.

Oxygen delignification play an important role in reducing the kappa number of the pulp by removing almost half of the residual lignin of the pulp. Thus, the oxygen delignification reduces the amount of the bleach chemical requirement to the same extent. The chlorine used, during bleaching of pulp produces chloro-organic compound, which increases pollution load in the environment. Oxygen delignification reduces the use of hazardous chlorine

chemicals and reduces the environmental pollution load drastically. The oxygen-delignified pulps bleached with conventional bleaching sequences were found to have better viscosity.

The results of conventional bleaching experiments indicated that poplar deltoides pulps are easily bleached to higher brightness level with low chemical requirement as compared to other hardwood pulps. These results shows that poplar deltoides pulps have good bleachability. The poplar deltoides pulps, bleached with CEHH bleaching sequence using a kappa factor of 0.2 attains a brightness level of around 80% ISO. The use of chlorine dioxide in the last stages was found to increase the pulp brightness. The 50% substitution of chlorine dioxide in the first C-stage has been proved to improve the delignification efficiencies of the unbleached pulps. The AQ pulps and oxygen delignified pulps responded very well toward sequential addition of ClO_2 and Cl_2 to obtain a pulps with higher brightness values.

The soda and kraft pulps of poplar responded also very well towards the ECF bleaching sequences. It has been observed that poplar pulps requires lower kappa multiple in the first D-stage as compared to other hardwood pulps to obtain a good brightness level. It has been also observed that the introduction of reinforced oxidative extraction (EOP) stage improves the bleaching efficiency of the pulps alongwith substantial reduction in effluent colour. The use of hydrogen peroxide increases the brightness and brightness stability of poplar pulps. In the case of oxygen delignified pulps, the introduction of reinforced oxidative extraction (EOP) has been proved to be beneficial in obtaining pulps with higher brightness level. However, the oxygen delignified pulps bleached with chlorine dioxide produce pulps with slightly lower brightness than the conventional pulps, but their bleaching efficiency were found to be better by introducing EOP and peroxide stages. Therefore, by utilizing the

advantages of the oxygen delignification followed by ECF bleaching sequences one can produce a bleached pulp have higher brightness level, better physical strength properties alongwith a substantial reaction in environmental pollution load.

The poplar pulps have also been studied with special reference to the effect of enzymatic treatment (by xylanase) on the over all quality of bleached pulps. Since the poplar hemicellulose has about 22-24% xylan, these pulps were found to respond very well during enzymatic bleaching by utilizing xylanase enzyme.

A brief study has been made on the preparation of xylanase from the thermophillic fungi P. chrysosporium. The various process conditions used for the preparation of xylanase enzyme from this fungi have been found to be quite soothing for the industry. The xylanase enzyme produced at a incubation temperature of 45 ^{0}C and at almost neutral pH, has been found to have maximum activity at a temperature of 55-60 ^{0}C. These type of temperature ranges easily prevails in the industry. The enzyme produced by these fungi could be produced by the industry itself, and can be used for the enzymatic treatment of pulps in order to produce a better quality bleached pulp with low pollution load. One thing has been also interesting, that the cost of the production of enzyme is quite lower than the expected cost. For the xylanase, produced by P chryrosporium 1 hour treatment time has been found to be sufficient to get the maximum benefits. This 1 hour treatment is quite economical for the industry. The xylanase produced by the P. Chrysosporium has been found to be quite effective in the bleaching. The enzyme treated pulps were found to consume about 30% less oxidizing chemicals to obtain the similar brightness level. Enzymatic preparation of xylanase from these fungi needs more eloborative research, so that the paper industry may get maximum benefits.

The wet web strength properties of poplar were found to be comparable with other raw materials used for papermaking such as eucalyptus and othe nonwood raw matirial. The results of the wet web strength indicates that the wet web strength increases linearly on blending with long fibered pulps. The wet web strength properties such as wet web elongation and TEA can be improved considerably by blending with long fibered pulp, which help in improving the paper machine runnability

Since poplar is a short fibered raw material therefore it requires a certain proportion of the longer fibers, to improve the strength properties, drainage characteristics and the runnability on the paper machine. The results of chip blending of poplar with pine and bamboo have been found to be poorer than the expected one. The results of the pulp blending, followed by the joint beating showed a little improvement in strength properties as compared to chip blending prior to cooking. The results of blending of separately beaten pulps of poplar, pine and bamboo in different proportion revealed that the strength properties have been further improved as compared to the pulp blending, prior to beating. These results also indicate that the observed freeness was found to be lower than predicted value. The burst and tear index of the blends having higher proportions of long fibered pulp, tended to be greater, while the tensile index tended to be lower than the predicted values.

Hence, from the present investigation, it can be concluded that poplar deltoides is one of the most potential hard wood source of fibrous raw material for pulp and papermaking in India.

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