CANDIDATE (Ph.D) THESIS

OPTIMIZATION APPROACH OF DISSOLVING PULP AND ITS ESTERIFIED DERIVATIVE PREPARATION FROM NEW RESOURCES

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BIOGRAPHY

Laith A. Abdul-Karim was born in Baghdad, Iraq on April 12, 1956. He received his high school education in baghdad, Iraq. He graduated in 1978 from the chemical engineering department, college of engineering, university of baghdad with a Bachelor of Science degree in chemical engineering.

After six years employment in industry and research laboratories, he joined his postgraduate studies at the same university and in 1986 he graduated with a Master of Science degree in chemical engineering and his thesis entitled "Process Optimization of Soda-Anthraquinone Pulping of Local Reeds".

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ABSTRACT

The objective of the present work was to determine optimum conditions for production of dissolving pulp from reed, eucalyptus, wheat straw, and hemp. Moreover to produce cellulose nitrate using statistical methods of experimental planning.

Approximate chemical analysis of the studied materials have been done, showing the difference between their main constituents.

Experimental planning followed the second order central composite rotatable design of three independent variables:

X_1: maximum pulping temperature, °C.

X_2: time at maximum temperature, minute for reed and eucalyptus and hour for wheat straw and hemp.

X_3: active alkali charge (as Na_2O) percent on dry chips, %.

A chlorine-free multistage process (PPEA) was used for bleaching of wheat straw and hemp pulps, meanwhile (CEHDEA) and (CEHD) multistage processes were used for bleaching of reed and eucalyptus pulps, respectively for preparation of dissolving pulps.

Second order polynomial regression of bleached pulp yield, degree of polymerization, and alpha-cellulose content of dissolving pulps and nitrogen content of cellulose nitrate gave a quadratic functions which adequatly describe the system behaviour.

Good fits were obtained between calculated and experimental values for bleached pulp yield and some polynomial models were obtained. Using optimum processing conditions dissolving pulps from reed, eucalyptus, wheat straw, and hemp are suitable raw materials for production of cellulose nitrate.

Oxygen bleaching of the kraft wheat straw cellulose was performed in order to achieve optimum conditions of delignification. A well performed study showing promising

results was done. Clearlly can be seen that when the oxygen bleaching is prolonged to kappa numbers below 10 the yield starts to drop faster (higher yield loss per kappa number unit), which means that the process is getting more and more unselective. This is in line with the previous experience showing that from yield and selectivity point of view, the oxygen bleaching stage should be performed with about 40-45% degree of delignification. At this levels the specific yield values are about 94-96% at kappa number 10. When oxygen bleaching is prolonged to lower kappa numbers (below 7), the specific yield values are too low. Therefore an optimal kappa number level is around 10.

Bleached wheat straw kraft pulps of 80% brightness with good pulp strength properties, viscosity above 730 dm^3/kg, and alpha-cellulose content about 92% were obtained without the use of chlorine bleaching compounds. Oxygen delignification, (EOP), and hydrogen peroxide bleaching stages were used, producing only 0.004 kg/odt of AOX.

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CHAPTER ONE

LITERATURE REVIEW

1.1 COMPOSITION OF WOOD

Wood is exceedingly difficult to define chemically because of its complex nature$^{(1)}$. It is, a heterogenous product of high molecular mass. The principal components generally are classified as cellulose, lignin, hemicellulose, and solvent-soluble substances (extractives). These chemical components are normally impossible to separate as quantitative yield without degradating its structure. This difficulty of separation is due to [1] the high molecular mass of the components, [2] the close similarity between many components, [3] the physical bonding between components, and [4] the high crystallinity of the wood structure which reduces the accessibility of some components.

1.1.1 α-CELLULOSE

α-Cellulose represents 40-50% of wood. It is a major component of cell walls of wood fibres and yields finally ß-D-glucose by hydrolysis (it is a polymer of ß-D-glucoseanhydride)$^{(2)}$. The structure of a α-cellulose molecule is shown in Figure (1.1).

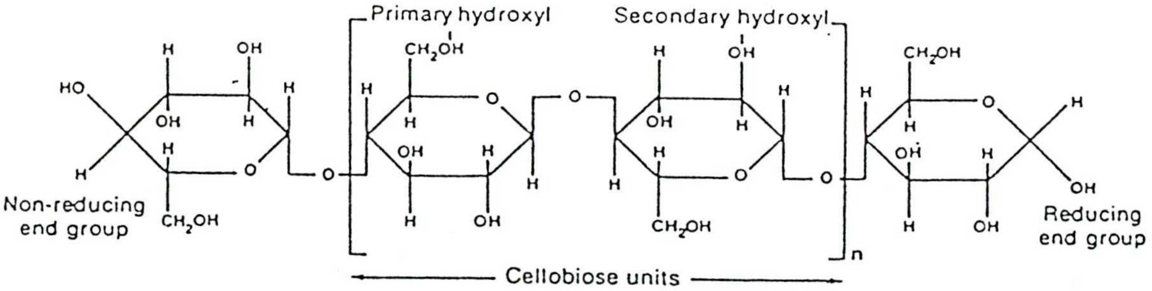


Figure 1.1 : Cellulose structure.

The recurring unit is composed of two consecutive glucose anhydride units, known as cellobiose unit. Pure cellulose can be rather easily hydrolyzed to glucose ($C_6H_{12}O_6$) under controlled chemical (acidic) conditions $^{(3)}$. Native cellulose is a highly crystalline material with the average molecular mass of about 1/2 million , and shows good resistance to the dissolving effect of pulping chemicals and to the oxidizing action of bleaching agents. The properties of cellulosic materials are related to the average degree of polymerization of the cellulose molecules. Decreasing the molecular mass below a certain level will cause deterioration in strength. When a cellulosic fibrous material is treated with a stronge aqueous solution of sodium hydroxide, the alkali-resistant portion of it, which remains undissolved is known as α-cellulose. The filtrate contains dissolving materials of two kinds : that portion which precipitates when the filtrate becomes neutral is called ß-cellulose, whereas the portion remaining in the solution is τ-cellulose(4).

The nature of the building units and their linking, together with the average molecular length and its range, are of primary importance in the establishment of the structure of macromolecule. These aspects have been thoroughly studied for cellulose. Each anhydroglucose unit of the cellulose molecule has three hydroxyl groups, which can undergo etherification and esterification (5,6). Methylation studies showed that the three hydroxyl groups are located in positions 2,3 and 6. The groups have decreasing acidic properties due to the electron effects in the order 2,3 and 6. The primary hydroxyl at position 6 is sterically the most unhindered. The chain molecules in natural cellulose are not of the same length.The number of glucose units in different chains varies. This is revealed by different samples of cellulose of no detectable chemical difference giving different alkali solubilities and viscosities. A given sample represents a molecular homologous series in which there is no molecular heterogeneity. We have to deal with averages, such as average molecular mass and average chain length. The degree of polymerization (DP) of unopened cotton has been reported at 15,300; this value decreases rapidly to 8,100 on exposure to the atmosphere(7). Whenever the distance between the various oxygen and hydrogen atoms within and among the cellulose molecules reaches 0.3 nm or less, they interact with each other to form intramolecular and intermolecular hydrogen bonds. The intramolecular hydrogen bridges anchor the anhydroglucose units to a very limited region of free play around the acetal linkage. Thus, they impart a certain stiffness to the cellulose molecule.

1.1.2 **HEMICELLULOSE**

This fraction represents 15-30% of wood(2). When delignified extractive free wood is treated at room temperature with dilute aqueous alkali (for example, 17.5% sodium hydroxide or 24% potassium hydroxide), the equivalent of 15 to 30% of the initial wood mass gets dissolved. These alkali soluble, essentially noncellulosic fractions of wood polysaccharides are termed hemicelluloses. It is a complex mixture of different polysaccarides of lower molecular mass and crystallinity than those of α-cellulose.

The major polymers present are slightly branched xylans and glucomannans. Acid hydrolysis of hemicellulose yields monosacharides as glucose, mannose, galactose, xylose, arabinose, and uronic acids. The relationships between the major cell-wall constituents are indicated, highly diagrammatically in Figure (1.2) .

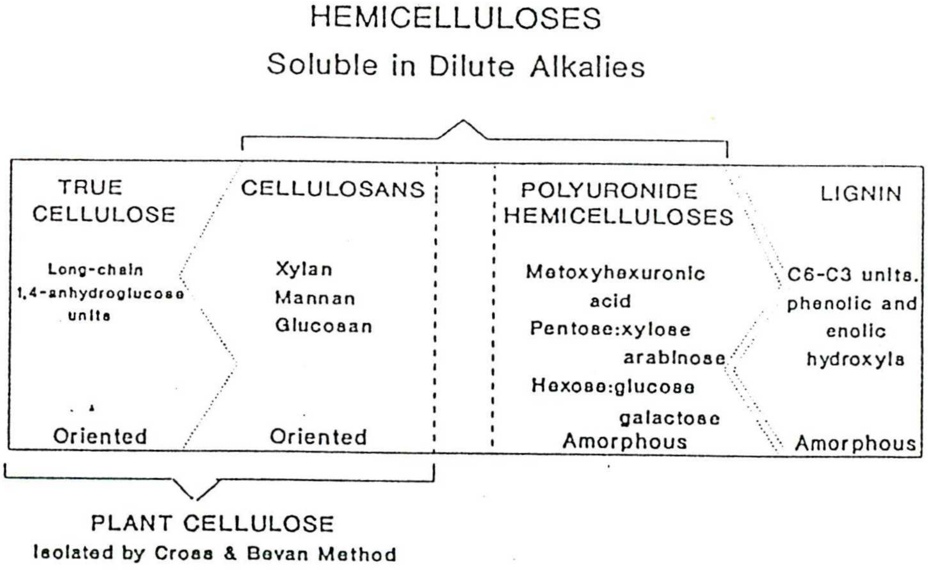
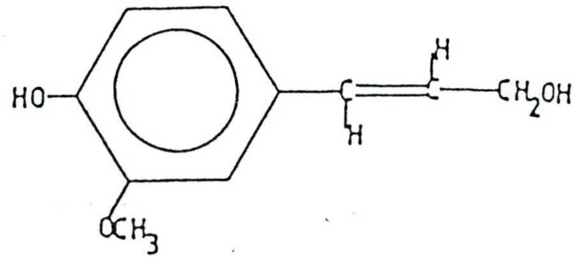


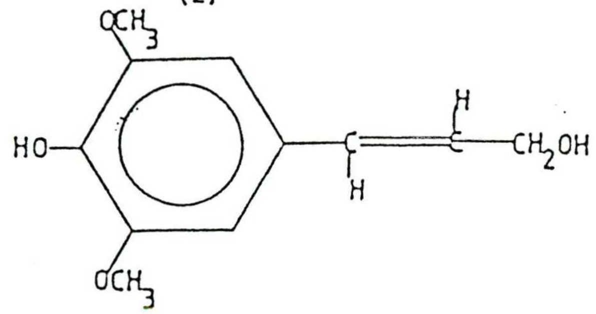
Figure 1.2 : Schematic representation of the major cell-wall constituens

Hemicelluloses, which constituted up to 80% of the non-cellulosic substances, predominantly played the role of intercellular binders, whereas the role of lignin as binder was insignificant. The role of hemicelluloses in influencing the mechanical strength was closely related, however, to the protective action of lignin. The removal of lignin resulted in essential changes in the properties of hemicelluloses, and hence of the fibre(8).

(1)



(2)



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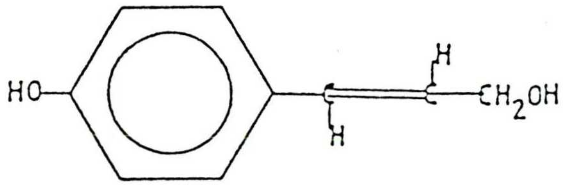

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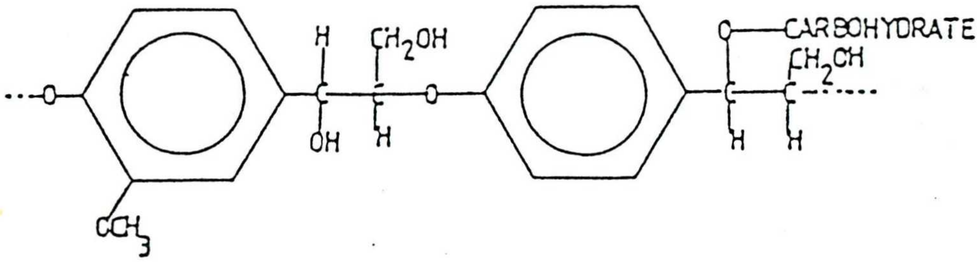


1: trans-coniferyl

2: trans-sinapyl

3: trans-coumaryl

4: The bonding between lignin and the carbohydrate in the softwood.

Figure 1.3 : Structure of lignins.

1.1.3 LIGNIN FORMATION AND REACTIONS

Lignin is properly the most complicated and least well characterized group of substances in nature. It comprises 20 to 35% of the wood substance and consists of the total noncarbohydrate fraction of extractive-free wood. Lignin network is concentrated between the outer layers of the fibres, it causes the wood structural rigidity by stiffening and holding the fibres together(2). It is a polymeric natural product arising from an enzyme-initiated dehydrogenative polymerization of three primary precursors : trans-coniferyl (1), trans-sinapyl (2), and trans p-coumaryl (3) alcohol(9), (see Figure 1.3).

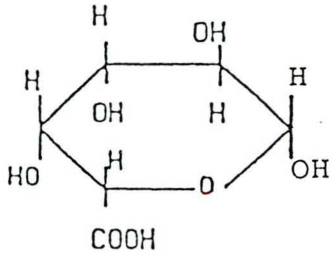
Lignin reactions are important in order to understand pulping and bleaching. The kraft process involves mercaptation, alkaline hydrolysis, and alkaline condensation of lignin. The sulphite and neutral sulphite processes involve lignin sulphonation, acid hydrolysis, and acid condensation.

Both pulping methods cause colour reactions. Halogenation, oxidation of lignin, and alkali degradation of halogenated lignin, and also the colour reactions must be considered in bleaching processes(2). Reactions of sulphur with lignin in the kraft process is not fully understood, but it appears to result in [1] stabilizing phenolic groups to prevent lignin condensation and [2] aiding the cleavage of ether bonds between phenyl propane units. It is suggested that HS^- ions react and protect a part of the condensable phenolic groups which are liberated by alkali cleavage of phenolic ether linkages, thus preventing condensation. The sulphide bonds are splitted readily by alkali to regenerate HS^- and to yield a kraft lignin containing a small amount (2 to 4%) of sulphur. The lignin from the kraft process is low in molecular mass and is rich in phenolic groups owing to ether cleavage and the splitting of methoxyl groups(2).

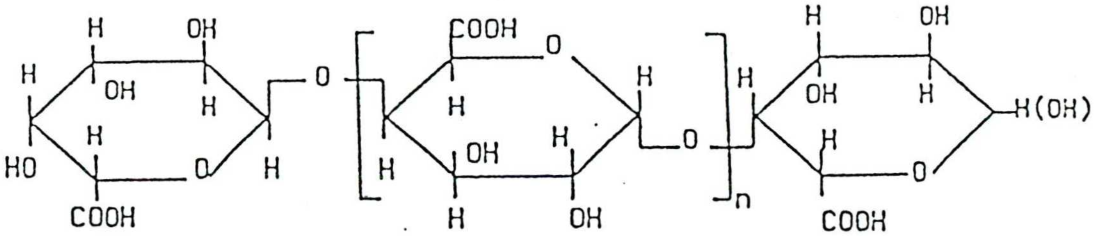
1.1.4 PECTINS

The pectins seem to be connected with the cortex and the cuticle cells of the epidermis. Pectins can be extracted by boiling, however, on boiling in water they will not be completely extracted, whereas when a solution of ammonium oxalate is used, the extraction is more complete(10).

Pectins which are found in great amounts in the vegetable world (contained in the pith and juice of different fruits and roots) form a peculiar group of carbohydrates of very complex composition. Their main and characteristic component is calcium-magnesium pectate. Pectic acid belongs to polyuronides and is a polygalacturonic acid in which part of the carboxyl groups is esterified by methyl alcohol. Thus, the main structural element of polygalacturonic acid is galacturonic acid.



Polygalacturonic acid has a chain structure similar to that of other higher carbohydrates, for instance, the structure of pectic acid macromolecule is represented as follows :



Pectic acid is soluble in a weak solution of caustic soda and ammonium hydroxide. Its lead and calcium salts are insoluble in water and the method of quantitative determination of pectic acid is based on the formation of the insoluble calcium salt(10,11).

1.1.5 EXTRACTIVES

Compounds such as volatile acids, volatile oils, terpentine, tannins, fatty acids, and resin acids are the extractives(1,2).

1.2 PULPING PROCESS

Pulping is the process by which wood is reduced to a fibrous mass using mechanical and or chemical methods. Put another way, it is the means of rupturing the bonds within the wood structure. The pulp consuming industries are based on the use of either the fibres as such, or main constituent, cellulose. In both cases a liberation of the fibre is required prior to further treatment, and this is the primary purpose in the preparation of unbleached pulp. The secondary purpose is to give the fibre optimal properties for its ultimate use, to which it may come directly or after further modification in the bleachery(1). Pulping processes are of three principal types : mechanical, semichemical, and chemical(12).

1.2.1 MECHANICAL PULPING

The mechanical process involves the reduction of wood or other raw material to the fibrous state by mechanical means, generally by grinding wood to a pulp against a large grindstone. The yield of pulp is high by this process (about 95%), but the pulp is of low purity and there is considerable fibre damage(12). This method suffers from the difficulty of separating the fibres without damage to the fibre walls, especially in the case of hardwoods with their content of vessel elements with thin walls.Therefore this process gives low-strength paper, and requires long-fibred softwoods(1).

1.2.2 SEMICHEMICAL PULPING

Semichemical pulping is a two-stage process involving chemical treatment of wood chips to obtain a softening and partial removal of the lignocellulose bonding material, followed by mechanical refining to complete the fibre separation. Chemimechanical pulping is similar, but consists of a milder chemical treatment followed by a stronger mechanical action.

With a 60 to 80% yield range such pulps are classified as semichemical. Pulps with a 85 to 95% yield range are termed mechanical(12).

1.2.3 <u>**CHEMICAL PULPING**</u>

Chemical processes involve a cooking of the wood with chemicals which selectively remove lignin and other impurities, thereby isolating and partially purifying the individual fibres. The yield is, as would be expected, much lower than in mechanical pulping, but the pulp purity is higher, and there is relatively little fibre damage(12). In general there are mainly two processes which are well known, the first is sulphite pulping and the second is alkaline pulping.

1.2.3.1 <u>**SULPHITE PROCESS**</u>

The process of treating fibrous plant materials with a solution of sulphurous acid in water with or without the addition of sulphites or other salts of equivalent properties, and then heated in a closed vessel under pressure to a sufficient temperature. The added chemicals and the heat is to degrade the intercellular incrusting or cementing constituents of vegetable substances so as to leave that undissolved product in a fibrous form, suitable for the manufacture of paper, paper pulp, cellulose, or for the other purposes, according to the nature of the material employed(2).

The pH of the resultant cooking liquor will vary according to the excess SO_2 present, and a variety of processes have resulted. To specify the type being used, a nomenclature based on the ion concentration has been adopted generally over 50% (HSO_3^-). The cooking liquor is called X bisulphite, where X is the cation used. The nomenclature and process definitions are given in Table 1.1(2).

1.2.3.2 <u>**ALKALINE PROCESS**</u>

The two principal alkaline processes used for the pulping of wood are the soda and the sulphate processes. In both processes, sodium hydroxide is present as the major cooking chemical, and in the sulphate process, sodium sulphide is also present. The alkaline solution of caustic soda and sodium sulphide, termed white liquor, to remove the lignin binding the

Table 1.1 : Nomenclature of sulphite pulping methods according to pH range(2).

Item	*Nomenclature*	*predominant chemical agent in cooking liquor*	*Approximate initial pH at 25 °C*
1	Acid sulphite	H_2SO_3+$XHSO_3$	1-2
2	Bisulphite	$XHSO_3$	2-6
3	Neutral sulphite	XSO_3+XCO_3 (XOH or none)	6-9
4	Alkaline sulphite	XSO_3+XOH (or Na_2S)	≥10

cellulose fibres together in the wood(13). The advantages of the sulphate process are : [1] maximum flexibility with regard to species (any species can be used, even cull wood), [2] cooking times are short, [3] the pulp can be bleached to high brightness levels (although at greater cost than with sulphite pulps), [4] no pitch problems, [5] high pulp strength, [6] valuable products are produced in the form of tall oil and turpentine, and [7] the recovery of spent liquor is relatively easy(12).

Some of the disadvantages of the sulphate process are : [1] air pollution, [2] dark colour of the unbleached pulp, [3] high cost of bleaching, when white pulp is required(13).

1.2.3.2.1 **REACTIONS IN ALKALINE PULPING**

The rate of attack of the wood in alkaline pulping has been shown by several observers to follow an approximate first order reaction. Alkali is consumed : [1] in reaction with lignin, [2] in dissolution of carbohydrates, [3] in reaction with various organic acids, both those present in the original wood and those produced by hydrolysis, [4] in reaction with resinous matter in the wood, and, [5] a small part in adsorption by the fibres. Tannins present in the original wood tend to buffer the alkali in the cooking liquor and gradually release it as delignification proceeds(14).

Brauns and Grimes(15) found that of the 16% alkali applied in a normal soda cook, about 1.5% was consumed by neutralization of organic acids, 3 to 4% was acting in dissolving lignin, and most of the remaining 10.5% to 11.5% was used for dissolution alkali soluble carbohydrates.

Others(16) have reported that about 12% from the total 16% alkali was consumed by hemicellulose, but only 3% in actual dissolving hemicelluloses, whereas the remaining 9% was utilized in neutralizing acids produced from hemicellulose during cooking. These neutralized saccharinic acids show up in the black liquor. The hexosans appear to be more readily attacked and destroyed than the pentosans(17) .

In the case of hardwoods and grasses, the reaction of alkali with carbohydrates proceeds at a greater rate in the initial stages than the reaction with lignin(18). On the other hand, in the case of softwoods, there is little pentosan removed prior to delignification(19). Alkaline cooking liquors would be expected to have less degrading effect on cellulose than acid (sulphite) cooking liquor. However, cellulose is susceptible to strong alkaline solutions at any temperature and is susceptible to weak alkaline solutions at temperatures higher than 100 °C.

Coppick(20) has shown that in alkaline pulping some depolymerization of the carbohydrates took place continuously and uniformly during delignification. Increasing the temperature of cooking to very high levels accelerates the removal of carbohydrates relative to that of lignin. At 160 °C, the lignin and other incrustants are dissolved about twelve times as rapidly as the cellulose(21,22),but at higher temperatures, the ratio decreases, and eventually at very high temperatures (more than 160 °C) the rate of removal of cellulose becomes about equal to that of the removal of lignin and other incrustants. The exact mechanism by which alkali reacts with the lignin in alkaline pulping is not well understood. It is reasonably certain that sodium phenolate groups are formed from the hydroxyl groups in the lignin molecule. It is also likely that additional hydroxyl groups are liberated in the lignin molecule during cooking, and that those are also transformed to phenolates. The reactions in the sulphate process are partly similar to those in the soda process but additional reactions with sodium sulphide have also to be considered. Its first step is hydrolyzis, according to the following equation :

$$Na_2S + H_2O \rightleftharpoons NaOH + NaSH$$

The produced sodium hydrosulphide acts as a buffer and tends to reduce the degrading effects of sodium hydroxide on the cellulose. The most important effect of the hydrosulphide, however, is its reaction with the lignin in producing thiolignin. The most widely accepted explanation for the role of sulphur in sulphate digestion is that of Hägglund's(23).

He supposed that sulphur combined the reactive groups in lignin molecules, thereby preventing their self condensation. This would explain why sulphate lignins are more soluble than soda lignins, namely because they have a lower average molecular mass(24). The reactive groups with which the sulphur combines could be p-hydroxybenzyl alcohol or alkyl ether groups(24). This reaction of sulphur makes the lignin more readily soluble in alkali and thus reduces the temperature and time required for pulping(25).

Aurell and Hartler(26) conducted pulping experiments on pine to target kappa number by simultaneously increasing the effective alkali charge to the digester and by decreasing the time at elevated temperature (170 °C). An increase in the charge of alkali in kraft pulping of pine resulted in a lower pulp yield at a given kappa number and shorter cooking time. The drop in the pulp yield was the result of a decrease in the yield of arabinoglucuronoxylan and galactoglucomannan in the pulp. Also, there was a change in the ratio of galactoglucomannan to arabinoglucuronoxylan as the amount of effective alkali increased in a study involving slash pine.

Matthews(27) demonstrated high losses in the mass of galactoglucomannan polymers at low temperatures, whereas their retention occurred at high temperatures. The opposite behavior was observed for the arabinoglucuronoxylan polymer, with retention at low temperature but high losses at high temperature. Similar results were observed for lignin. He concluded that, a more significant portion of the total loss in hemicellulose occurs in the lower temperature regimes, or in the earlier stages of cooking. This uneven loss was confirmed by Kondo and Sarkanen(28), who estimated that as much as 7% of the mass of wood was directly dissolved in the form of hemicelluloses during the initial stage of the pulping process. This compares favorably with the temperature data of Matthews(27). Kondo and Sarkanen also suggested that once the initial dissolution of hemicelluloses has occurred, subsequent losses would occur via peeling reactions, as more hemicelluloses become available to chemical attack. This hypothesis was reached indirectly in an earlier study by Dillen and Noreus(29). In their work on series of short-duration cookings, these authors suggested that losses of hemicelluloses would be quite high in the earlier stages of treatment. Presumably, this early loss involves the directly dissolved hemicelluloses.

Dillen and Noreus also suggest that the molecular mass of the components lost in the early stages would be high as well. Again this would be consistent with direct dissolution as opposed to fragment losses from peeling reactions. Not only should the quantity of dissolved material diminish with the progress of scouring, but the molecular mass of that material should diminish as well. This development was also observed by Dillen and Noreus.

According to Sandstrom, Lindberg, and Teder(30) the concepts of pulping selectivity and efficiency are represented by pulping viscosity. They present a mathematical model for continuous digesters that describes different ways of delignifying pulps while optimizing pulp viscosity. Their specific objective was, in fact, extended delignification without loss in strength. The authors hypothesize selective delignification without carbohydrate degradation.

Several specific guidelines are established in their work. They recommend that the alkali concentration be leveled out over the duration of scouring, as opposed to an initial high concentration that gradually diminishes thoughout the treatment.

One can hypothesize that this step would minimize direct dissolution of carbohydrates. They also recommended that the concentration of HS^- ions be high. Presumably, this would result in diminished carbohydrate peeling reactions. They recommended that the ionic strength be maintained at a low level.

Presumably, this would best accomplished by maintaining low levels of lignin and sodium ions. This helps to minimize lignin condesation and solubility respectively, particularly at the end of pulping.

Finally, they recommend low initial and final pulping temperatures. This is consistent with earlier studies by Kondo and Sarkanen(28) showing higher carbohydrate losses with higher initial temperatures. It is also supported indirectly by Matthews(27) work, that high loss in xylan is due to high temperatures in addition to the high losses in mannan observed in the low-temperatures stages of cooking. Sandstrom et al.(30) also recommend low temperature at the end of cooking in order to minimize carbohydrate degradation.

1.3 **Bleaching**

The objective in bleaching is the production of a white pulp of stable colour obtained at reasonable cost and a minimum deleterions effect on the physical and chemical properties of the pulp. Two principal reactions take place in bleaching : [1] solubilization and removal of the colouring matter, and [2] changing of the colouring matter to a colourless form which is as stable as possible to colour and heat.

Lignin is the main offender as far as colour is concerned. Cellulose and the hemicelluloses are inherently white. The principal bleaching and purifying agents used are chlorine, chlorine dioxide, and hypochlorite. Other bleaching agents used in smaller quantities are peroxide and chlorite.

In a sense, the chlorination and caustic extraction stages in multistage bleaching are purification rather than bleaching operations, since the lignin is removed as alkali-soluble chlorlignins and the pulp is made no whiter. During these stages the loss of carbohydrate is very small (less than 1%), while the lignin removal is about 9.5% in chlorination and 4% in caustic extraction(31). On the other hand, in bleaching with peroxide the lignin is mostly decolorized without removal. In the case of hypochlorite and chlorine dioxide, the impurities are both removed and decolorized.

The loss in yield may vary from 1% or less in peroxide bleaching of mechanical pulp to 10 to 20% in multistage bleaching of semichemical pulps. Normally, the loss varies between 3 to 10% of the original oven dry wood for the bleaching of regular chemical wood pulps. The cost of removing lignin is less in the cooking process than in the bleaching process, and for this reason, it is generally more economical, when making brightness pulps, to cook to an "easy bleaching" pulp than to attempt the bleaching of a "raw" or undercooked pulp. In one sense, bleaching may be considered to be a continuation of the cooking process, since both are concerned with purification.

Exessive bleaching may cause chemical degradation of cellulose, and consequently bleaching conditions must be chosen to hold degradation to a minimum. Sulfite pulps bleach more readily than sulfate pulps probably because the residual lignin in sulfite pulps has been rendered partially soluble by the action of sulfite cooking liquor. Fines have an undesirable effect on bleaching. Removal of about 4% fines from spruce sulfite pulp was found by Keller and coworkers(32) to reduce chlorine consumption in two-stage bleaching by 20% and to shorten the time required in the second stage by 20 to 50%.

In general, chemical wood pulps are bleached with chlorine compounds, either direct chlorine plus hypochlorite, hypochlorite alone, or chlorine dioxide. Semichemical pulps may be bleached with chlorine compounds or with peroxide. Groundwood pulps are generally bleached with peroxide, but hardwood and groundwood pulps can be bleached with hypochlorite.

Table 1.2 summarizes the advantages and disadvantages of the principal commercial bleaching chemicals, the oxidants : chlorine, oxygen, hypochlorite, chlorine dioxide, hydrogen peroxide, and ozone; the only reductant used, hydrosulfite; and

Table 1.2: Chemicals used in bleaching.

Oxidants	**Symbol**	Form	Function	Advantages	Disadvantages
Chlorine	C	Gas	Oxidize and chlorinate lignin	Effective, economical delignification and good particle bleaching	Can cause loss of pulp strength if used improperly
Oxygen	O	Gas used with NaOH solution	Oxidize and solubilize lignin	Low chemical cost. Provides chloride-free effluent for recovery	Used in large amounts requires expensive equipment. Can cause loss of pulp strength
Hypochlorite	H	$Ca(OCl)_2$ or NaOCl solution ~40 g/L	Oxidize, brighten and solubilize lignin	Easy to make and use. Good particle bleaching	Can cause loss of pulp strength if used improperly. Expensive
Chlorine Dioxide	D	7-10 g/L ClO_2 solution in water	1) Oxidize, brighten and solubilize lignin 2) (In small amounts with Cl_2) Protect against degradation of pulp	Achieves high brightness without pulp degradation. Good particle bleaching	Expensive. Must be made on-site
Hydrogen Peroxide	P	2-5% solution	Oxidize and brighten lignin in chemical and high yield pulps	Easy to use. Low capital cost	Expensive, poor particle bleaching
Ozone	Z	Gas	Oxidize, brighten and solubilize lignin	Effective. Provides chloride-free effluent for recovery	Expensive. Degrades pulp. Poor particle bleaching
Reductant					
Hydrosulfite		Solution of $Na_2S_2O_4$ or made on-site from $NaBH_4$ solution plus SO_2	Reduce and brighten lignin in high yield pulps	Easy to use. Low capital cost	Decomposes readily. Limited brightness gain
Alkali					
Sodium Hydroxide	E	5-10% NaOH solution	Hydrolyze chlorolignin & solubilize lignin	Effective and economical	Darkens pulp.

the only alkali used, sodium hydroxide.

Because of their greater economy, chlorine and oxygen are used in early stages of bleaching for lignin removal, but can not be used for more extensive treatment because their poor selectivity results in cellulose degradation. Chlorine is used in virtually all bleach plants treating chemical pulp. Chlorine is invariably followed by extraction to hydrolyze and dissolve chlorolignin. Oxygen is widely used in the first extraction stage, called the E_O stage. Chlorine dioxide, hypochlorite, and peroxide can be used in the later stages of bleaching because of their greater selectivity. Because of their higher cost, they should be used under the most efficient possible conditions. Chemicals are also selected because of environmental impact. For instance, increased concern about chlorinated organic compounds has led to elimination of many hypochlorite stages, which produce significant quantities of chloroform, and to increasing substitution of chlorine dioxide for chlorine.

1.3.1 **Bleaching process conditions**

The process conditions in each bleaching stages are a vital factor in achieving optimal performance from chemicals and equipment. The amount of chemical applied in each stage plays an important role in optimization. As more chemical is applied in a given stage, it becomes less and less efficient. Maximum brightness and minimum cost will be achieved when the appropriate rate of application is used in each stage. This choice must be tempered by recognition of the damage done by less selective chemicals. Further, it is desirable to use as little as possible of more expensive chemicals, for instance hypochlorite, peroxide, and chlorine dioxide.

Temperature and oxidant concentration control the rate of delignification and bleaching reactions. An increase in either or both will increase the rate of reaction and thus the amount of chemical consumed in a given time. Oxidant concentration is frequently measured at the end of the stage and reported as residual. High residual oxidant is expensive in terms of chemical losses and corrosion. Higher temperature costs more in energy to heat the pulp. Retention time also determines the extent of reaction, so long as there is a residual throughout the reaction time. The maximum time available is fixed by the volume of the retention towers available.

The consistency has relatively little effect on the efficiency or rate of bleaching in the normal range of consistency fluctuations. Three percent consistency is used in conventional chlorination to allow immediately complete dissolution of the chlorine gas. The consistency in the later stages is determined by the rotary drum washer of the preceding stage. Washer discharge consistency will normally be about 12% but it may fluctuate from as low as 8 to as high as 18%.

pH has a vital effect on all bleaching processes. Efficiency, selectivity, and cleanliness are affected to varying degress by pH. Usually the pH at the end of the stage is used as a target.

A few studies have been performed on delignification of lignocellulosic materials with alkaline hydrogen peroxide.

Gould(33) found that approximately half the lignin present in agricultural residues, such as wheat straw, could be solubilized when the residue was treated at 25 °C with an alkaline solution of hydrogen peroxide. The delignification was most effective at pH 11.5 .

McDonough et al(34) studied the delignification of southern pine kraft pulp with alkaline hydrogen peroxide. They also found that approximately half the lignin present in the pulp could be removed. Acidic hydrogen peroxide is a much stronger oxidizing agent than alkaline hydrogen peroxide. Under acidic conditions, the lignin macromolecule is extensively degraded and dissolved by hydrogen peroxide(35,36). It seemed likely, therefore, that acidic solutions of hydrogen peroxide should more readily delignify wood than alkaline solutions.

Kraft and soda, as well as neutral sulphite pulping procedures were applied to hemp. Peroxide bleaching produced greatest response when the neutral sulphite and kraft methods were used.

Hypochlorous acid pretreatment (3% available chlorine) prior to peroxide bleaches increased the over-all bleaching efficiency without major yield loss (1.5%). Peroxide's value appears to lie in its ability to bleach at high yield.

Felton(37) investigated hemp and flax as agricultural residues during alkaline sulphite pulping. He produced good-quality cigarette papers from the high freeness pulps.

Mita(38) pulped hemp with $NaOH-H_2O_2$ system applying EDTA and anthraquinone additives.

Hernadi and Rusznak(39) pulped hemp stems of various chopped sizes with sulphate, alkaline anthraquinone and alkaline peroxide methods.

Marpillero(40) pulped whole hemp stems with acidic sulphite process.

1.4 **DISSOLVING PULP WITH SPECIAL RESPECT TO CELLULOSE NITRATE**

Highly purified wood pulp is composed of 95-99% cellulose and is known by such terms as "chemical cellulose" and "dissolving pulp". Until the beginning of World War I, the only raw material available for nitration was cellulose obtained from cotton in the form of bleached linters (as flakes or crape).

This was due to the high degree of purity (alpha cellulose content more than 98%), which allowed a high yield and products with good clarity and little yellowing.

Especially in times when linters were scarce, it was possible to produce gunpowder from wood cellulose, even unbleached, other cellulose fibres (annual plants), and even from wood if attention was given to the adequate disintegration of the raw materials. The development of highly purified chemical-grade wood pulp by refinement with hot and cold alkali having alpha-cellulose values of 92-95% allows this type of raw materials which currently are used only for the production of special and highly viscous CN types. The highly refined prehydrolyzed sulfate pulps with alpha cellulose values of above 96% are especially well-suited for nitration. The viscosity range of CN products can be adjusted in advance by choosing an initial cellulose with an adequate DP. A low ash content, and above all a low calcium content of the cellulose are important in preventing calcium sulfate precipitation during industrial nitration.

A comparative study on the nitrating behavior of linters and wood pulps(41) demonstrated that the morphological factors of the fibres (fibre length and distribution, cross-section, and thickness of the secondary wall, and fine structure including packing density, degree of crystallinity, and lateral arrangement of the fibrils), the chemical changes in the cellulose and in its macromolecular characteristics (DP and polydispersity) as well as the type, quantity, and topographic distribution of the accompanying hemicellulose and lignin were responsible for the nitrating capability of cellulose. These factors determine also the swelling properties and thereby the uniformity of nitration, as well as the compressibility and the relaxation capacity of the fibres, which in turn influence the water retention capacity of the fibre mass.

A viscose pulp which is extremely reactive toward xanthation was obtained from wheat straw by soda-AQ pulping(42). The straw was subjected to prehydrolysis soda and prehydrolysis soda-AQ pulping (using 0.05% AQ). This was followed by multistage CEH bleaching. Reactivity was determined by adding insufficient xanthation; this differentiates between pulps with small differences in their reactivity. In the absence of AQ, an additional bleaching step with sodium chlorite had to be applied after the CEH treatments in order to increase whiteness. However, the presence of 0.05% AQ resulted in a high degree of whiteness without the chlorite step. AQ increased the yield, improved whiteness, and produced an extremely reactive pulp. This pulp was much more reactive than a commercial softwood viscose pulp.

Following prehydrolysis with 1% sulfuric acid solution, dissolving pulps were obtained from wheat straw by alkaline (1.7% NaOH) pulping with various H_2O_2 concentrations, ranging from 0.5-5%(43). The pulps were bleached by the CEH sequence, followed by sodium chlorite treatment. Increasing H_2O_2 concentration increased the pulp yield, degree of delignification, and degree of whiteness and decreased the bleachability. The alpha-cellulose content increased with 0.5% H_2O_2, but decreased with H_2O_2 concentration of 1-5%. The H_2O_2 concentration also resulted in the best filterability for the obtained viscose. The additional chlorite step after the CEH bleaching sequence increased the alpha-cellulose content and the degree of whiteness and reduced the pentosans content. Addition of 0.1% magnesium carbonate to the H_2O_2 pulping decreased the degree of delignification, the degree of whiteness, and the alpha-cellulose content, and increased the bleach requirement.

Dissolving pulps were prepared from jute (*Corchorus olitorius*) stems by alkaline cooking with nitrobenzene (to aid delignification and increase yield) at 125-165 °C for 2.5-4.5 hour(44). After removal of excess nitrobenzene by steam distillation, the pulp was bleached in a 5-stage process : chlorination, alkaline extraction, chlorine dioxide treatment, a second alkaline extraction, and a final chlorine dioxide treatment. Chemical analysis of the pulp revealed that it was comparable to dissolving wood pulps.

Nitration-grade kraft pulps from jute wastes (*caddies, cuttings, and sticks*) were obtained in 44.5% yield (based on o.d. wastes) with alpha-cellulose contents of 96.5% (*caddies or cuttings*) and 92.6% (*sticks*), pentosan content of 2.6 and 4.2%, and ash contents of 0.13 and 0.11%, respectively(45).

The pulps were nitrated with aqueous nitric/sulfuric acid mixtures at 15-20 °C to obtain heat-resistant CN containing 6.5-17.7% N, suitable for preparation of lacquers, explosives and celluloid plastics. The yield of CN and its content passed through a maximum with increasing water ratio in the acid mixture.

1.5 **NITRATION MECHANISM**

In the mechanism of nitration, the formation of a cellulose oxonium ion is being followed by the nucleophilic substitution by an acid residue and the splitting off of water.

Nitration is in equilibrium with the reverse hydrolytic reaction, which can be inhibited largely by binding the resulting water molecules.

$$R_{cell}(OH)_3 + mHNO_3 \overset{H_2SO_4, H_2O}{\rightleftharpoons} R_{cell}(OH)_{3-m}(ONO_2)_m + mH_2O$$

It is believed that nitonium ion NO_2^+ is the nitrating species(46). This ion is produced according to the following reactions:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

Much of the functional hydroxyl groups on the anhydroglucose units are involved in forming intramolecular and intermolecular hydrogen bonds and, therefore, they are not freely accessible for the reaction partners. The following two reaction types are under discussion:

a An intercrystalline and intermicrofibrillar reaction, which initially depends on the penetration of the reaction partner into the so-called amorphous regions between the highly organized cellulose microfibrils and crystallites and proceeds during the course of nitration from the surface to the innermost regions of the crystallites and microfibrils. The rate of the reaction is determined by diffusion.

b An intracrystalline or permutoid reaction, in which the reagent penetrates all regions including the crystallites so that practically all cellulose molecules react almost simultaneously. The reaction speed is specified by adjustment of the esterification equilibrium(47).

Arguments for both mechanisms are based on X-ray analysis. The dominance of any of the two reaction types or else their simultaneous occurence depend mainly on the composition of the the acid mixture and on the temperature.

1.6 EXPERIMENTAL DESIGN AND NON-LINEAR REGRESSION

Before the study of any process in the laboratory scale, it is necessary to determine the parameters which have a considerable effect on the system behavior, or the factors that influence the system responses.

So one must carry out several number of experiments to cover the effect of each parameter as well as the interactions between these parameters if they are not independent. The systematic method which satisfies the above function with minimum number of experiments is called experimental design.

The general form of a quadratic (second order) polynomial is illustrated by the equation for two X-variables:

$$Y = b_o + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 + e \quad ..(1.1)$$

Where : e is experimental error.

The surface contains linear terms in X_1, X_2 forms; squared terms in X_1^2, X_2^2 forms; and the cross-product term X_1X_2. In order to estimate the regression coefficients in this model, each variable X_i must take at least three different levels. This suggests the use of factorial designs of the 3^k series (k is number of independent variables).

If the three levels of any X are coded as -1,0,+1, the second order surface is easy to fit to the results of a 3^k factorial. The main disadvantage of 3^k series, however, is that with more than three X-variables the experiments become large. Furthermore the coefficients b_{11}, b_{22} of the squared terms are estimated with low precision(48).

Box and Wilson(49) developed new designs specifically for fitting second order response surfaces. Their earliest designs, called composite designs, are contracted by adding further treatment combinations to these obtained from 2^k factorial.

If the coded levels of each X-variable are -1 and +1 in the 2^k factorial, the new designs are as follows:-

Central composite designs test the (2k+1) additional factor combinations:

$(0,0,...,0);(-\alpha,0,..,0);(\alpha,0,..,0);$
$(0,-\alpha,..,0);(0,\alpha,...,0);$
$(0,0,...,\alpha);(0,0,..,\alpha)$

The total number of treatment combinations is (2^k+2k+1). For 2,3 and 4 X-variables, the experiment requires 9,15, and 25 units respectively, as compared with 9, 27, and 81 in the 3^k series.

The value of α can be chosen to minimize the bias that is resulted if the true form response surface is not quadratic, and give the design property of being rotatable.

The general formula for the actual values of X_1 and X_2 may be written as in table 1.3 . The factor α is the radius of the circle on which the points lie.

1.6.1 **Central composite rotatable design**

This method is most likely to be useful in practice(49). Figure 1.4 shows the design in two X-variable, obtained from table 1.3 by putting n2 = 8, n1 = 5, $\alpha = \sqrt{2}$ the design may be subdivided into three parts :

1. The four points (-1,-1), (1,-1), (-1,1) and (1,1) constitute a 2^2 factorial.
2. The four points $(-\sqrt{2},0),(\sqrt{2},0),(0,-\sqrt{2})$ and $(0,\sqrt{2})$ are the extra points included to form a central composite design with $\alpha=\sqrt{2}$. The figure formed by these points is called a star.
3. Five points are added at the center to give roughly equal precision for the function within a circle of radius 1.

The value of α must be $2^{(k/4)}$ in order to make the design rotatable. Table 1.4 shows the design for k = 3,4,5, and 6.

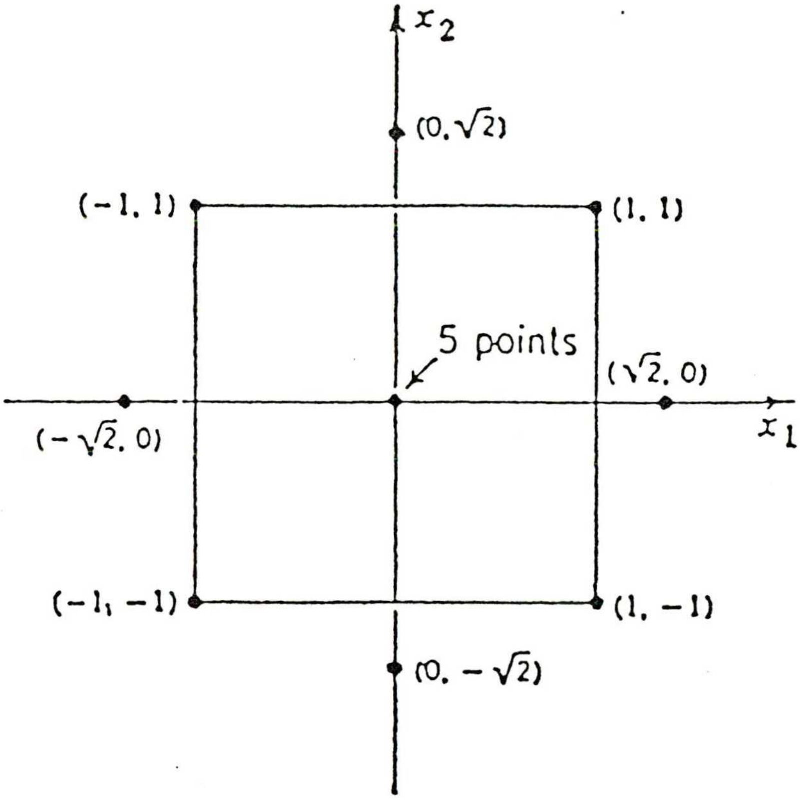


Figure 1.4 : Central composite rotatable design in two variables.

$$
\begin{array}{cc l}
x_1 & x_2 & \\
\alpha\cos\theta & \alpha\sin\theta & \\
\alpha\cos 2\theta & \alpha\sin 2\theta & \\
\cdot & \cdot & \left.\right\} n_2 \text{ points on the circumference} \\
\cdot & \cdot & \quad \theta = 2\pi/n_2 \\
\cdot & \cdot & \\
\alpha\cos n_2\theta & \alpha\sin n_2\theta & \\
0 & 0 & \\
0 & 0 & \\
\cdot & \cdot & \\
\cdot & \cdot & \left.\right\} n_1 \text{ points at the center} \\
\cdot & \cdot & \\
0 & 0 &
\end{array}
$$

Table 1.3 : Rotatable second order designs in two variables.

No. of x-variables k	Number of points in 2^k factorial	Star	Center	Total N	Value of α
3	8	6	6	20	1.682
4	16	8	7	31	2.000
5	16	10	6	32	2.000
6	32	12	9	53	2.378

Table 1.4 : Components of central composite rotatable design.

1.6.2 Application of experimental design in pulping processes

Central composite rotatable designs have been widely used in indutrial experimentation work especially in the pulping studies(50). In the late 1980, Mcdonough and Drunen(51) used mathematical expressions to describe the responses of pulping system of loblolly pine, these expressions were performed by standard least squares method from experimental results arranged using central composite rotatable design. The responses were screened yield, kappa number (KN), and viscosity as functions of input parameters (independent variables), time, effective alkali, anthraquinone (AQ) charge, and sulfidity, optimization analysis was done using the constrained direct search algorithm of Luus and Jaakola(52) to minimize the kappa number (KN) at various levels of viscosity, subjected to constraints on the cooking time and temperature.

Ruiz(53) studied the behavior of oak wood in laboratory tests. Regressions were obtained from a series of experimental kraft cooks by use of statistical analysis based on multiple correlations designed to predict principal pulp characteristics: kappa number (KN), viscosity, yield, and rejects against pulping temperature, time at maximum temperature, percentage active alkali based on dry wood, sulfidity, and concentration.

Blain(54) used the rotatable design of four variables in his study on the influence of sulfidity on the bleachability and strength properties of alkaline-AQ softwood pulps. In this study five levels for each variable were taken.

Al-Mudaffer(55) studied the possibilities of pulping reed and typha together as mixed raw materials, to show the effect of mixing different percentages of typha on pulp characteristics : screened yield, and kappa number, also to show the influence of typha on physical and mechanical properties of produced paper sheets. Experimental planning followed the second order central composite rotatable design of four independent variables : maximum pulping temperature, time at maximum temperature, active alkali charge percent on dry chips, and typha ratio in reed-typha mixture.

Second order polynomial regression of pulp screened yield and kappa number gave a quadratic functions which adequatly described the system behaviour.

Abdul Karim(56) studied the soda-anthraquinone pulping process of reed. The pulping experiments were planed to form a second-order central composite rotatable design of four process conditions (time, temperature, active alkali charge, and AQ charge). Second-order polynomial regression analysis of the objective function (screened pulp yield) and the equality constraints (the kappa number and rejects percent, based on moisture-free raw material) gave three equations, which adequately described the behaviour of the process throughout the region studied. Abdul Karim found the addition of AQ as a catalyst improves pulp yield by 12% for the soda process and nearly 3% for the kraft process.

Abdul Karim et al(57) carried out systematic research work, using statistical methods of experimental planning, in order to achieve optimum conditions of dissolving pulp production, gained from eucalyptus wood.

Abdul Karim et al(58) studied the optimum conditions of the dissolving pulp production, gained from wheat straw, using statistical methods of experimental design. He found the dissolving pulp from wheat straw could be made suitable for the production of cellulose derivatives.

Abdul Karim et al(59) found the reed dissolving pulp used for rayon and cellulose derivatives production can be approached. Attempts were performed in the preparation of several experimental design to achieve data related to kraft method approach in the pulping process of reed. A model was arranged in such away that the variables of the kraft method used to form a second central composite rotatable design.

1.7 OPTIMIZATION

Optimization is the process of seeking the best solution for a system or activity. If we consider the system responses to be related to the independent variables by a mathematical model of the form :

$$y_j = g_j(X_i,\ i= 1,\dots, n),\ j = 1,\dots, m \qquad \dots(1.2)$$

Then optimization entails a manipulation of the X_i's to achieve optimum values of the Y_j's. When known mathematical forms, exist for equation (1.2), the well-known procedures can be employed to obtain a solution to the problem.

There are several schemes by which optimization techniques can be classified. The first scheme of optimization is by the number of independent variables. Single-variable methods are used with a function of a single variable $g(X)$, and multivariable methods are used for optimizing a function of several variables $g(X_1, \dots, X_n)$.

A second scheme for classifying methods of optimization depends on whether the method employs derivatives. There are derivative methods and numerical methods. Derivative methods seek to determine those values of $X_1, \dots, X_n$ for which the first derivative vanishes ; that is for a single variable, the value of X for which :

$$y` = \frac{d\ g(X)}{dX} = g`(X) = 0 \qquad \dots(1.3)$$

A third scheme to classify optimization methods is to distinguish between unconstrained and constrained problems. In constrained problems, the solution must satisfy special conditions. Equation (1.2) gives the unconstrained case; that is, we would seek to optimize a function $g(X_1, \dots, X_n)$.

The general form of the constrained problem is as follows :

$$\text{optimize} \quad y_o = g_o(X_1, \dots, X_n) \qquad \dots(1.4)$$

$$\text{subject to } a_i \leq X_i \leq b_i \quad i = 1, \ldots, n \qquad \ldots(1.5)$$

Equation (1.5) limits the range of values that the ith independent variable can assume, that is, X_i can range between lower bound a_i and upper bound b_i. These bounds might be due to specifications of products, to limitations in the equipment's capability, or costs in a competitive market place(60).

1.7.1 **Random search method**

It is a random investigation of the solution space for the optimum. This method of almost minimal assumptions : no foreknowledge of the likely position of the optimum is assumed, so that its position is equally likely throughout the experimental region. In unconstrained problems it is not even necessary that the objective function be continuous.

The general optimization problem for random search algorithms is given by :

$$\begin{aligned} &\text{maximize } y_o(X) \\ &\text{subject to} \\ &a \leq X \leq b \end{aligned}$$

Where the limits on the X define the experimental region. A simple random search generates search points $X^{(i)}$ according to(61):

$$X^{(i)} = a + r_i\,(b-a) \qquad \ldots(1.6)$$

Where the r_i are uniform random numbers in the interval (0,1). Each observation $y_o[X^{(i)}]$ is compared with the current maximum. If it is greater than the current maximum, the latest point becomes the newest estimate of the optimum location. The search can be terminated at a set number of evaluations passes without improving the current estimate of the optimum. Figure 1.5 shows a logic diagram for random technique.

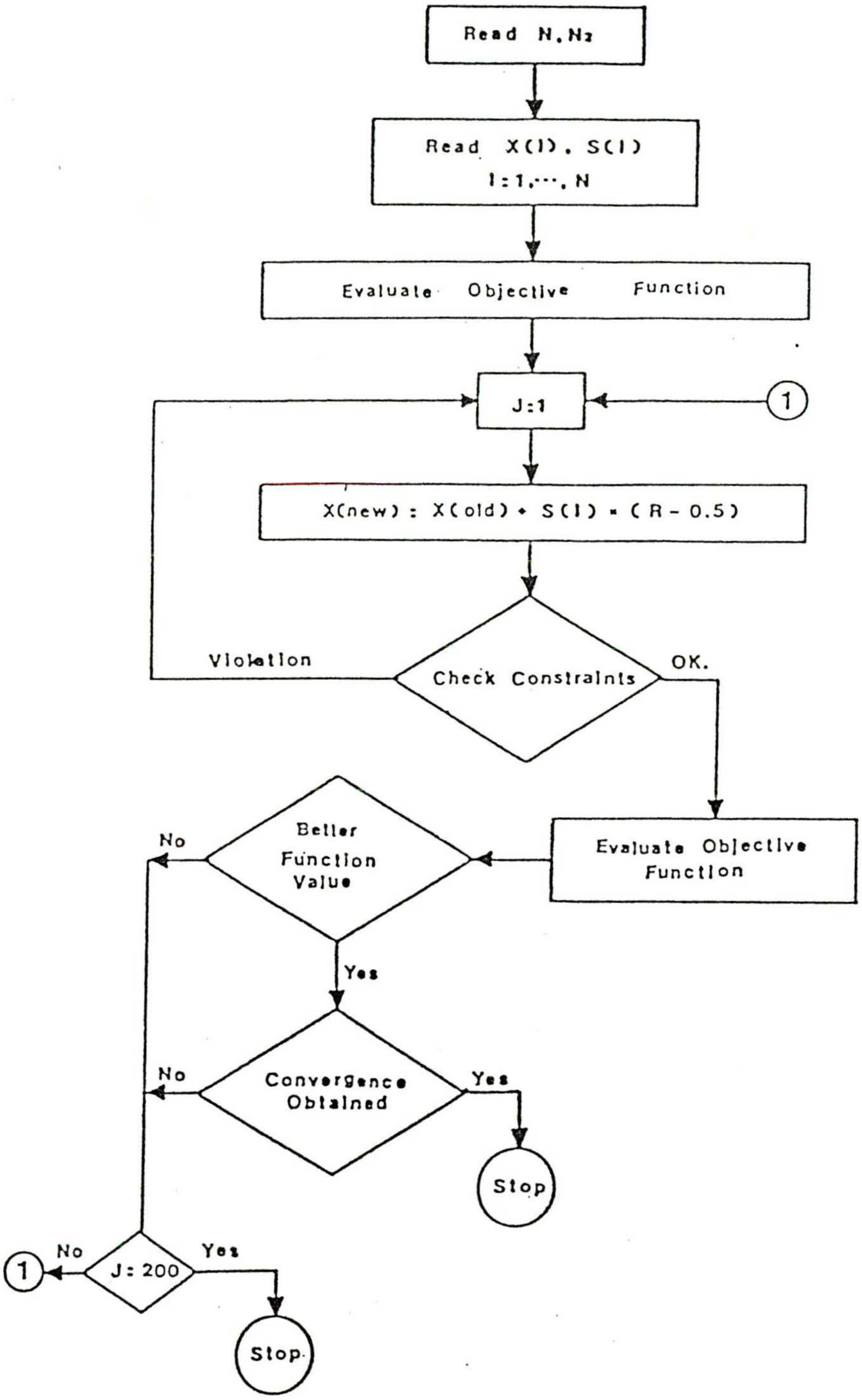


Figure 1.5 : A logic diagram for random technique.

CHAPTER TWO
INTRODUCTION

2.1 INTRODUCTION

The cellulose nitrate is an important material in the industry of many modern products. Paints, artifical leather, photographic film, smokeless powder, explosives, and many other applications are all related to each other by virtue of production from cellulose that has been nitrated to higher or lower degree of nitration.

The raw materials used in manufacturing of cellulose nitrate are cellulose, nitric acid, and sulfuric acid. When fibres are steeped in a bath consisting essentially of nitric acid, sulfuric acid, and water, esterification, oxidation, and hydrolysis may take place to a greater or lesser extent, according to the composition of the bath, the temperature, the ratio of liquid to cellulose, the intensity of agitation, and the physical condition of the cellulose.

Several cellulose sources were involved in the making of cellulose nitrate along the past sixty years. The most important cellulose sources are cotton linter, softwood, and hardwood dissolving pulps. The cellulosic raw material should ordinarily be as nearly free as possible from impurities and from hydrolyzed or oxidized cellulose. Consequently, in preparing pulps for conversion into high-grade nitrates relatively free from coloring matter, the attainment of whiteness with a minimum oxidation of the cellulose is highly desirable.

Wood pulp may be nitrated in at least three different forms:

a. As tissue or relatively thin paper.
b. In a shredded or fluffed linter-like condition.
c As chipped dryer sheets, that is as clippings of the relatively thick sheets produced on the usual dryers with which all modern pulp mills are equipped.

The manufacturing of cellulose derivatives from dissolving pulps is the major consummer to the wood and non-wood pulps in the world. This industry grew up fastly during the recent years.

2.2 Aim of present work

This study was carried out to achieve optimum conditions of the dissolved pulp production process. Furthermore to achieve optimum conditions for the nitration reaction of the dissolved pulps.

Different plants have been used for the preparation of the dissolved pulp. This study was subdivided into two researches:

1. Preparation of dissolving pulps from the reed, eucalyptus, wheat straw, and hemp.
2. Prepration of the cellulose nitrate from them.

In the first and second research works, the production of dissolving pulp, and cellulose nitrate was carried out through an optimization investigation study. Approximate chemical analysis of the studied raw materials have been done, showing the difference between their main constituents.

Attempts were performed in the preparation of several experimental work to achieve data related to kraft method approach in the pulping process of the raw materials, and the production of the cellulose nitrate.

Empirical models were arranged in such a way that the variables of the kraft method and nitration reaction used to form a second order central composite rotatable design.

Results were obtained from this models indicated that optimum pulp properties could be achieved. A comparison was done between experimental and calculated data, it was found to be within the standard error. Therefore the reed, eucalyptus, wheat straw, and hemp dissolving pulps could be produced in acceptable quality for cellulose nitrate industry.

CHAPTER THREE

MATERIALS & METHODS

3. MATERIALS AND METHODS

3.1 Characteristics of the studied materials

Before carrying out the pulping experiments, approximate chemical analysis of the studied reed, eucalyptus, wheat straw, and hemp was done to determine the compositions, according to Tappi standard methods. The obtained data are demonstreted in Table 3.1 .

A small portion of chips was ground in Wiley mill to a fine particle size to permit complete reaction of the wood with reagents used in the analysis. The fraction that passed a 0.4 mm. (40 mesh) screen was used in the following analysis(63):

3.1.1 Moisture content(63)

The following procedure applies to paper, paperboard, and nonwood fibres, except those containing significant quantities of materials other than water that are volatile at 105 ± 2 °C or less. Moisture is significant for economic reasons and for its effect on such properties as printability, shrinkage, dimensional stability, physical strength, and paper runnability.

3.1.2 Alcohol-Benzene solubility(64)

This method describes a procedure for determining the amount of solvent-soluble, non-volatile material in wood and pulp. Extraction with 1/3 ethanol and 2/3 benzene gives reproducible extraction and includes some additional compounds.

3.1.3 Lignin content(65)

This method describes a procedure which can be applied to the determination of acid-insoluble lignin in wood and in all grades of unbleached pulps. In semi-bleached pulp the lignin content should not be less than about 1% to provide a sufficient amount of lignin, about 20 mg, for an accurate weighing. This method is not applicable to bleached pulps containing only small amounts of lignin.

3.1.4 Alpha-cellulose content(66)

This method for determination of alpha-, beta- and gamma-cellulose can be applied to bleached or delignified pulps only. Unbleached and semi-bleached pulps must be delignified before testing.

3.1.5 **Pentosan content**(67)

This method for determination of pentosan content can be applied to both wood and to unbleached or bleached pulps.

3.1.6 **Holocellulose content**(68)

This method is used to determine the whole cellulose composition of wood and wood pulp.

3.1.7 **Ash content**(69)

These are inorganic residues after combustion at a temperature of 575±25 °C. It is an approximate measure of the mineral salts and other inorganic matter in wood.

The following characteristics of the experimentally produced dissolving pulp were determined:

- Permanganate number of the unbleached pulp(70).
- Alpha-cellulose content of the bleached pulp(66).
- Degree of polymerization of the bleached pulp(71).
- Kappa number of the unbleached pulp(72).

Table 3.1 : Characeristics of the studied materials.

Characeristics	*reed*	*eucalyptus*	*wheat straw*	*hemp*
Moisture cont. (%)	10.5	6.5	13.3	12.7
Ethyl alcohol:Benzene solubility.	1.40	6.95	5.76	2.80
Lignin cont. (%)	19.0	28.1	20.7	17.5
Alpha-cell. cont.(%)	40.9	37.2	46.4	54.5
Pentosan cont. (%)	24.5	25.2	21.4	25.1
Holocellulose cont. (%)	73.0	75.3	78.3	79.6
Ash cont. (%)	5.50	1.35	6.51	3.41

3.2 **Pulping trials**

Three parameters, among others, are influencing sensitively the delignification process. These are, the temperature, the time at cooking temperature, and the concentration of active alkali (as Na_2O), while the ratio of the liquor to the pulp was kept constant and was adjusted to 5:1 .

For optimization the above parameters, the central composite rotatable design method was employed for designing the programme of experiments$^{(48)}$.

For the purpose of designing the experimental programme, the range of the variables had to be specified first, thus:

a. For reed:

$$X_1 = \frac{T-155}{5} \qquad \ldots\ldots.(3.1)$$

$$X_2 = \frac{t-120}{30} \qquad \ldots\ldots.(3.2)$$

$$X_3 = \frac{AA\%-12}{2} \qquad \ldots\ldots.(3.3)$$

b. For eucalyptus:

$$X_1 = \frac{T-165}{5} \qquad \ldots\ldots.(3.4)$$

$$X_2 = \frac{t-255}{20} \qquad \ldots\ldots.(3.5)$$

$$X_3 = \frac{AA\%-18}{2} \qquad \ldots\ldots.(3.6)$$

c. For wheat straw, and hemp:

$$X_1 = \frac{T-170}{5} \qquad \ldots\ldots.(3.7)$$

$$X_2 = \frac{t-3}{0.5} \qquad ....(3.8)$$

$$X_3 = \frac{AA\%-14}{2} \qquad ....(3.9)$$

Where : T= maximum pulping temperature, °C.

t= time of pulping at maximum temperature, in minute for reed and eucalyptus, and in hour for wheat straw and hemp.

AA%= active alkali (as Na_2O) percent related to the mass of moisture free material.

The values of variables are coded as shown on Tables 3.2, 3.3, and 3.4 respectively. The number of different levels for each of the variables was always five (regardless of the number of variables). A preliminary step was the setting up to each coded levels, the corresponding X_j real process variables (where j= 1,2, and 3). The calculations were based upon equations (3.1) , (3.2), (3.3), (3.4), (3.5), (3.6), (3.7), (3.8), and (3.9) respectively.

According to experimental design of variables, there were twenty experiments carried out in the sequence shown in Tables 3.5, 3.6, and 3.7 respectively.

The results of experiments were translated into a mathematical formation. The form of this relationship was given by:

$$Y = b_o + b_i X_i + b_{ii} X_i^2 + b_{ij} X_i X_j \qquad ....(3.10)$$

For alpha-cellulose, bleached and unbleached pulp yields, degree of polymerization, and kappa number as function of process variables under investigation X_j. The b values are constant, computed by standard method of least squares.

Table 3.2 : The coded and experimental values of process variables for reed pulping process.

Coded level	*Operating temperature (°C)*	*Time at operating temperature (min)*	*AA% as Na_2O*
-1.682	145	60	8
-1.0	150	90	10
0.0	155	120	12
+1.0	160	150	14
+1.682	165	180	16

Table 3.3 : The coded and experimental values of process variables for eucalyptus pulping process.

Coded level	*Operating temperature (°C)*	*Time at operating temperature (min)*	*AA% as Na_2O*
-1.682	155	215	14
-1.0	160	235	16
0.0	165	255	18
+1.0	170	275	20
+1.682	175	295	22

Table 3.4 : The coded and experimental values of process variables for wheat straw and hemp pulping processes.

Coded level	*Operating temperature (°C)*	*Time at operating temperature (hr)*	*AA% as Na_2O*
-1.682	160	2.0	10
-1.0	165	2.5	12
0.0	170	3.0	14
+1.0	175	3.5	16
+1.682	180	4.0	18

Table 3.5 : Sequence of experiments according to central composite design for reed pulping process.

Experiment No.	*Coded variables* X_1	X_2	X_3	*Real variables* *Temp. (°C)*	*Time (min)*	*AA (%)*
1	-1	-1	-1	150	90	10
2	+1	-1	-1	160	90	10
3	-1	+1	-1	150	150	10
4	+1	+1	-1	160	150	10
5	-1	-1	+1	150	90	14
6	+1	-1	+1	160	90	14
7	-1	+1	+1	150	150	14
8	+1	+1	+1	160	150	14
9	-1.682	0	0	145	120	12
10	+1.682	0	0	165	120	12
11	0	-1.682	0	155	60	12
12	0	+1.682	0	155	180	12
13	0	0	-1.682	155	120	8
14	0	0	+1.682	155	120	16
15	0	0	0	155	120	12
16	0	0	0	155	120	12
17	0	0	0	155	120	12
18	0	0	0	155	120	12
19	0	0	0	155	120	12
20	0	0	0	155	120	12

Table 3.6 : Sequence of experiments according to central composite design for eucalyptus pulping process.

Experiment	*Coded variables*			*Real variables*		
No.	X_1	X_2	X_3	*Temp. (°C)*	*Time (min)*	*AA (%)*
1	-1	-1	-1	160	235	16
2	+1	-1	-1	170	235	16
3	-1	+1	-1	160	275	16
4	+1	+1	-1	170	275	16
5	-1	-1	+1	160	235	20
6	+1	-1	+1	160	235	20
7	-1	+1	+1	170	275	20
8	+1	+1	+1	170	275	20
9	-1.682	0	0	155	255	18
10	+1.682	0	0	175	255	18
11	0	-1.682	0	165	215	18
12	0	+1.682	0	165	295	18
13	0	0	-1.682	165	255	14
14	0	0	+1.682	165	255	22
15	0	0	0	165	255	18
16	0	0	0	165	255	18
17	0	0	0	165	255	18
18	0	0	0	165	255	18
19	0	0	0	165	255	18
20	0	0	0	165	255	18

Table 3.7 : Sequence of experiments according to central composite design for wheat straw and hemp pulping processes.

Experiment No.	*Coded variables*			*Real variables*		
	X_1	X_2	X_3	*Temp. (°C)*	*Time (hr)*	*AA (%)*
1	-1	-1	-1	165	2.5	12
2	+1	-1	-1	175	2.5	12
3	-1	+1	-1	165	3.5	12
4	+1	+1	-1	175	3.5	12
5	-1	-1	+1	165	2.5	16
6	+1	-1	+1	175	2.5	16
7	-1	+1	+1	165	3.5	16
8	+1	+1	+1	175	3.5	16
9	-1.682	0	0	160	3.0	14
10	+1.682	0	0	180	3.0	14
11	0	-1.682	0	170	2.0	14
12	0	+1.682	0	170	4.0	14
13	0	0	-1.682	170	3.0	10
14	0	0	+1.682	170	3.0	18
15	0	0	0	170	3.0	14
16	0	0	0	170	3.0	14
17	0	0	0	170	3.0	14
18	0	0	0	170	3.0	14
19	0	0	0	170	3.0	14
20	0	0	0	170	3.0	14

3.3 **Prehydrolysis process**

In order to prepare high α-cellulose pulp, the chips were subjected to a prehydrolyzation process with slightly acidic water under the following conditions:

a. For reed, wheat straw, and hemp chips:

Chips : liquor ratio.	1:5
H_2SO_4 in the cooking liquor,(%).	0.1
Temperature of cooking,°C.	160
Time of cooking, minute.	60

b. For eucalyptus chips:

Chips : liquor ratio.	1:5
H_2SO_4 in the cooking liquor,(%).	0.2
Temperature of cooking,°C.	100
Time of cooking, minute.	160

The chips were filtered, washed with hot water.

3.4 **Pulping process**

The sequence of steps to manufacture pulp were as follows:

a. Preparation of raw materials: chips were hand cut to 1-2 cm length.

b. The chips were pulped in electrically heated, stainless steel, rotatable digester.

The established charge was made of 100 g moisture free chips, the chemicals were mixed to reach the calculated charge of active alkali with 25% sulfidity. Chemicals were added to chips in an aqueos solutions. Liquor to straw ratio was adjusted to 5 cm^3 liquor: 1 g chips.

As chips and chemicals had been in the digester the lid was closed. The electrical heater and motor were switched on. The thermometer readings were recorded every ten minutes until they reached the set value. The time of heating up was about one hour.

c. Afterwards, when the digester pressure had been reduced to atmospheric level, the autoclave was left to cool. Subsequently the pulp was collected on a muslin cloth, and washed with tap water.

d. Disintegration of pulp was done by a three bladed propeller mixer for three minutes with pulp consistency of 1.5%.

e. Subsequently the pulp was screened on the vibrating flat plat screen of 0.2 mm slot size.

The screened yield was determined by weighing the air dried pulp and measuring its moisture content. The rejects were dried in oven and weighed.

3.5 **Bleaching process**

All work was done on laboratory scale samples for cellulose bleaching. 30 g oven dried disintegrated unbleached pulp was suspended in a bleaching solution. Bleaching experiments were carried out in the sequence shown in Tables 3.8, 3.9, and 3.10 respectively.

After each stage of bleaching, the pulp was washed thoroughly by hot water. In the final stage of bleaching the pulp was washed by distilled water.

a. Bleaching of the reed pulp.

Table 3.8 : Bleaching sequence for the reed pulp.

Stage serial No.	*Bleaching agent, and other chemicals*	*Concentration of the bleaching agent, or the Chemicals*	*Other bleaching parameters*
First	chlorine (as solution)	3 g/L	pulp conc.=3% temp.=20 °C time=60 min.
Second	alkali extraction (by NaOH)	4 g/100 g pulp	pulp conc.=5% temp.=70 °C time=60 min.
Third	NaOCl	2 g Cl/L	pulp conc.=5% temp.=25 °C time=60 min.
Fourth	ClO_2	2 g $NaClO_2$ 4 ml CH_3COOH	pulp conc.=8% temp.=70 °C time=120 min.
Fifth	alkali extraction (by NaOH)	6 g/100 g pulp	pulp conc.=5% temp.=70 °C time=60 min.
Sixth	acidification (by H_2SO_4)	1% conc.	pulp conc.=5% temp.=25 °C time=20 min.

b. Bleaching of the eucalyptus pulp.

Table 3.9 : Bleaching sequence for the eucalyptus pulp.

Stage serial No.	*Bleaching agent, and other chemicals*	*Concentraion of the bleaching agent, or the chemicals*	*Other bleaching parameters*
First	chlorine (as solution)	3 g/100 g pulp	pulp conc.=3% temp.=20 °C time=60 min.
Second	alkali extraction (by NaOH)	2 g/100 g pulp	pulp conc.=5% temp.=70 °C time=60 min.
Third	NaOCl	1 g Cl/100 g pulp	pulp conc.=5% temp.=20 °C time=60 min.
Fourth	ClO_2	1 g Cl/100 g pulp	pulp conc.=8% temp.=70 °C time=180 min.

c. Bleaching of the wheat straw and hemp pulps.

Table 3.10 : Bleaching sequence for the wheat straw and hemp pulps.

Stage serial No.	*Bleaching agent, and other chemicals*	*Concentration of the bleaching agent, or the chemicals*	*Other bleaching parameters*
First	hydrogen peroxide (as solution) Prestogen® (as catalyst)	5 g H_2O_2/100 g pulp 0.2 g/100 g pulp	pulp conc.=4% temp.=80 °C time=60 min. PH=10-11
Second	same as in the previous stage.		
Third	alkali extraction (by NaOH)	3.5 g/100 g pulp	pulp conc.=4% temp.=25 °C time=60 min.
Fourth	acidification (by 98% H_2SO_4)	10 g/100 g pulp	pulp conc.=4% temp.=60 °C time=60 min.

3.6 NITRATION PROCESSES

3.6.1 Characteristics of the studied dissolving pulps

The main characteristics of the experimentally produced reed, eucalyptus, wheat straw, and hemp dissolving pulps were determined in comparison with those of bleached cotton linters according to Tappi standard methods, and are demonstrated in Table 3.11 .

3.6.2 Nitration trials

Nitration of cellulose is most significantly influenced by two parameters, the temperature and the duration of reaction, while the composition of the acid mixture as well as its ratio to the pulp were kept constant.

For optimization the named two parameters, the central composite rotatable design method was employed, resulting in the programme of the experiments(48).

In designing the experimental programme, the range of the variables had to be specified first, thus:

$$X_1 = \frac{T-30}{5} \quad .....(3.11)$$

$$X_2 = \frac{t-40}{10} \quad .....(3.12)$$

Where: T= temperature of nitration in °C, (20-40) °C.
t= time of nitration in minutes, (20-60) min.

The values of variables are coded as shown on Table 3.12. A preliminary step was the setting up to each coded level X_j, (where j=1,2) the corresponding real process variables. The calculations were based upon equations (3.11), and (3.12).

According to experimental design of variables, ten experiments were carried out in the sequence shown in Table 3.13 .

Table 3.11 : Characteristics of the studied dissolving pulps in comparison with those of bleached cotton linters (standard cellulose required for nitration).

Characteristics	*Reed pulp*	*Eucalyptus pulp*	*Wheat straw pulp*	*Hemp pulp*	*Cotton linters*
Appearance	white, no mechanical impurities				
Moisture cont.(63)	4.89	3.92	5.75	4.78	≤8.00
Ash cont.(69)	0.21	0.23	0.27	0.29	≤0.30
Calcium carbonate, hypochlorite and sulphate content.	in trace amounts only				
Alpha-cellulose cont. (%).(66)	89.97	88.43	90.62	92.67	≥97.50
Dimethyl ether extract (%).(73)	0.24	0.22	0.25	0.21	≤0.25
Copper No.(74)	0.23	0.30	0.37	0.27	≤0.50
Viscosity.(75)					
(1% dissolved in CUOXAM, mPa.s)	47.0	24.1	39.6	42.7	≥10.9
(0.5% dissolved in CUOXAM, mPa.s)	11.07	6.15	9.67	10.61	≥4.40
Alkali solubility, (%)(76)	8.97	7.15	7.88	8.65	≤5.00

Table 3.12 : The coded and experimental values of process variables.

Coded level	*Operating temperature (°C)*	*Time at operating temperature (min)*
-1.414	20	20
-1.0	25	30
0.0	30	40
+1.0	35	50
+1.414	40	60

Table 3.13 : Coded and real points of experimental design produced by central composite rotatable design for nitration of studied dissolving pulps.

Experiment serial No.	*Coded variables*		*Real variables*	
	X_1	X_2	*temp. (°C)*	*time (min)*
1	-1	-1	25	30
2	+1	-1	35	30
3	-1	+1	25	50
4	+1	+1	35	50
5	-1.414	0	20	40
6	0	-1.414	30	20
7	+1.414	0	40	40
8	0	+1.414	30	60
9	0	0	30	40
10	0	0	30	40

3.6.3 **Nitration methods and procedures**

All work was done on laboratory scale samples designed for cellulose nitration. 5.0 g oven dried disintegrated pulp sample was suspended in 200 g mixed acid solution (HNO_3: H_2SO_4:

H_2O) gradually within five minutes under continuous stirring.

The temperature of the reaction ought to be kept constant according to the programme in Table 3.13 .

Dissolving pulps were nitrated under conditions established by a series of combination of two variables (temperature and time of nitration), using the method described in a previous work(77). At the end of reaction, the mixture was filtered and washed (through a sintered glass funnel). The produced cellulose nitrate was boiled with water four times and with 3% concentration of sodium bicarbonate solution at 70-80 °C for six hours, until high stability was achieved(78).

After drying, the produced cellulose nitrate was subjected to chemical analysis for the following characteristics:

a. Nitrogen content(78).
b. Ethanol-dimethyl ether solubility(79).
c. Viscosity(78).

Two types of cellulose nitrate can be distinguished, CN_1, of high nitrogen content (12.8-13.8%), and CN_2 of lower one (10.9-12.9%). Proportions of the components (HNO_3: H_2SO_4: H_2O) in the nitrating acid mixture are disclosed in Table 3.14 .

Table 3.14: Relative proportion of acids and water (HNO_3: H_2SO_4: H_2O) in the mixed acid solution used for the production of CN of high and low nitrogen content respectively.

Type of substrate	*Nitrogen content*	*HNO_3 %*	*H_2SO_4 %*	*H_2O %*
Reed, wheat straw,	high	24.61	65.16	10.23
and hemp pulps	low	22.66	60.88	16.46
Eucalyptus pulp	high	24.43	65.41	10.19
	low	22.90	60.07	17.03

CHAPTER FOUR

OXYGEN BLEACHING & TOTALLY CHLORINE-FREE BLEACHING OF KRAFT WHEAT STRAW PULP

4.1 OXYGEN BLEACHING

4.1.1 Aim of the present work

The objective of the present work was to determine optimum conditions for oxygen bleaching of the kraft wheat straw cellulose using statistical methods of experimental planning.

Good fits were obtained between calculated and experimental values for bleached pulp yields and some polynomial models were obtained. Using optimum processing conditions oxygen bleaching could be made suitable for the production of bleached wheat straw cellulose.

4.1.2 Introduction

Oxygen bleaching has become a commercial process for the removal of lignin from kraft pulp. The main incentive for using oxygen bleaching is that lignin, which can otherwise form different types of polluting substances in bleaching reactions, particularly chlorination, is retained to a greater extent within the mill.

Conventional oxygen bleaching is carried out at medium consistency in the presence of sodium hydroxide. The bleaching is initiated at pH above 13 and finished at pH about 10. To avoid severe carbohydrate degradation the bleaching is interrupted after about 50% of the lignin has been removed(80).

In order to fully optimize and control the oxygen bleaching stage, information on oxygen bleaching kinetics is required. A mathematical kinetic model combined with the stoichiometry of the process (amount of bleaching chemicals required to reach a given kappa number) can be used to describe and control industrial bleaching stages(81).

Two competing reactions occur simultaneously during oxygen bleaching : a delignification reaction and an undesirable carbohydrate degradation. The kinetic study of oxygen bleaching must thus include kinetics of both delignification and carbohydrate degradation.

The importance of the kinetics of oxygen bleaching was first observed fairly recently in connection with studies on process control of oxygen delignification(82,83,84). In the development of the process control models, the bleaching experiments are usually carried out at simulated industrial conditions(82,83). The pulp concentration has been 30% and 1.5% (82,83). The alkali concentration has decreased to a different extent during these bleaching experiments. This has led to some contradictory conclusion about the kinetics of delignification since it has been difficult to separate the effects of the different bleaching variables.

Järrehult and Samuelson(85) have studied the oxygen bleaching at extremely low pulp consistency (0.2%), so that the change in the hydroxide concentration has been negligible. However, in this work, not only the effect of sodium hydroxide concentration during the bleaching was studied. No general kinetic equations were given.

No studies on the kinetics of carbohydrate degradation during oxygen bleaching have so far been reported.

The aim of this investigation has been to obtain the optimum bleaching conditions that describe both the deligninfication and carbohydrate degradation during oxygen bleaching.

The optimization of oxygen bleaching were studied by model bleaching experiments performed under constant bleaching conditions on each run. Different levels of the variables were investigated in separate experiments. The variables were : reaction time (minute), alkali concentration (g NaOH/100 g cellulose), remained alkali (mg Na_2O/g cellulose).

4.1.3 **Chemistry of oxygen bleaching**

For many processes molecular oxygen is a uniquely suitable oxidizing agent. In the normal form of oxygen, i.e., the electronically stable form, two of the electrons are unpaired. It has a strong tendency to react with organic substances, and radical chain reactions are initiated. The oxidation oroceeds via several intermediates, e.g., peroxides, organic radicals, and the hydroxyl radical. Unlike oxygen, some of these intermediates are nonspecific oxidative agents, and in bleaching it is necessary to control their formation if severe degradation of the cellulose is to be avoided.

4.1.3.1 **Reaction with lignin**

The primary reaction of oxygen with lignin under alkaline conditions has been suggested(86,87) to proceed via resonance stabilized phenoxy radical (Fig.4.1). The nature of further oxidation steps of the phenoxy radical is not clear. Results(88) indicate close similarities between the degradation of lignin during peroxide bleaching and oxygen bleaching.

A substantial part of the degradation of lignin may thus proceed via oxidation of phenolic units followed by degradation to aliphatic acids, as has been demonstrated for the degradation of lignin by hydrogen peroxide(89) (Fig. 4.2).

Oxidative cleavage of the C_3-side chain of lignin monomers seems to constitute another important part of lignin degradation. An analogy may be drawn with the oxidation of lignosulfonate to vanillin.

4.1.3.2 **Reaction with Polysaccharides**

Degradation of cellulose and other wood polysaccharides may be reflected in decreased pulp yield and viscosity. Peeling reactions are generally the most important source of yield loss in alkaline processes. During oxygen bleaching of hydrocellulose, however, it was found(90) that peeling reactions were of little significance. A higher yield was obtained compared with alkaline treatment in the absence of oxygen under otherwise identical conditions.

Treatment with oxygen/alkali yielded small amounts of metasaccharinic acid end groups, but mainly aldonic acid end groups; the latter renders the polysaccharide stable toward attack by alkali. The main end groups formed(90,91) were arabinonic, mannonic, and erithronic acids, whereas only small amounts of gluconic acid could be detected (Fig. 4.3). The main products were the same as those found in other oxidative alkaline processes such as cellulose aging and polysulfide cooking. The same reaction pattern was also found during alkaine treatment of glucosone(92), which indicated that the formation of aldonic acid end units followed the oxidation of glucose units to glucosone units.

Reactions leading to decreased viscosity may sometimes be considerable during oxygen bleaching(91). Similar reactions occur during aging of alkali cellulose and have also similarities with degradative reactions which occur under various bleaching conditions(93). The mechanism shown in Fig. 4.4 was originally suggested for the oxidative degradation of cellulose by hydrogen peroxide in alkaline solution(94) and has been strongly supported by experiments using model compounds(93). The cellulose is oxidized at carbon 2 or 3 giving rise to an enediol equilibrium and a rapid ß-alkoxy-elimination initiated at carbon 4, with consequent cleavage of the glucosidic linkages. The new glucose end units formed in equilibrium with fructose and mannose units are then further oxidized to aldonic acid end units as described above.

4.1.3.3 **Magnesium Compounds as Inhibitors**

Undesirable degradation of polysaccharides during oxygen bleaching is diminished by the presence of magnesium carbonate(95). Despite considerable investigation, the mechanism of this effect has not been fully elucidated. It has been shown that carbonyl groups formed during oxygen bleaching act as initiators for peroxide formation, and that peroxide concentration increases when Mg^{2+} ions are present(96) . Stabilization of peroxides is thought to be achieved by formation of a magnesium-peroxide complex.

The discovery that magnesium complexes in solution inhibit polysaccharide degradation was a major contribution to oxygen bleaching(97). The use of other magnesium salts for this purpose has disadvantages. When a water-soluble salt, e.g., magnesium sulfate, is added to the pulp alkali mixture, magnesium precipitates as virtually inactive $Mg(OH)_2$ with a resultant decrease in alkali concentration. If $MgCO_3$ is used, a relatively high concentration is required to provide sufficient protection. However, if suitable magnesium complexes are added to the pulp alkali mixture, they will not precipitate during the operation. Thus, recirculation of the waste liquor allows recovery of most of the active constituents. Furthermore, the high efficiency of the magnesium complexes permits the use of very low additions (0.03-0.05%) as magnesium ions based on pulp (Fig.4.5). The addition needed is frequently less than magnesium content of the wood itself.

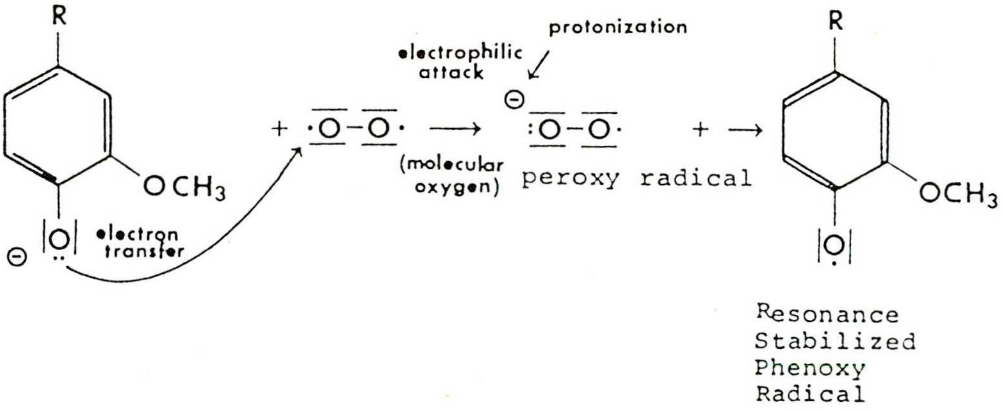


Figure 4.1 Initial attack of oxygen on phenolic nuclei.

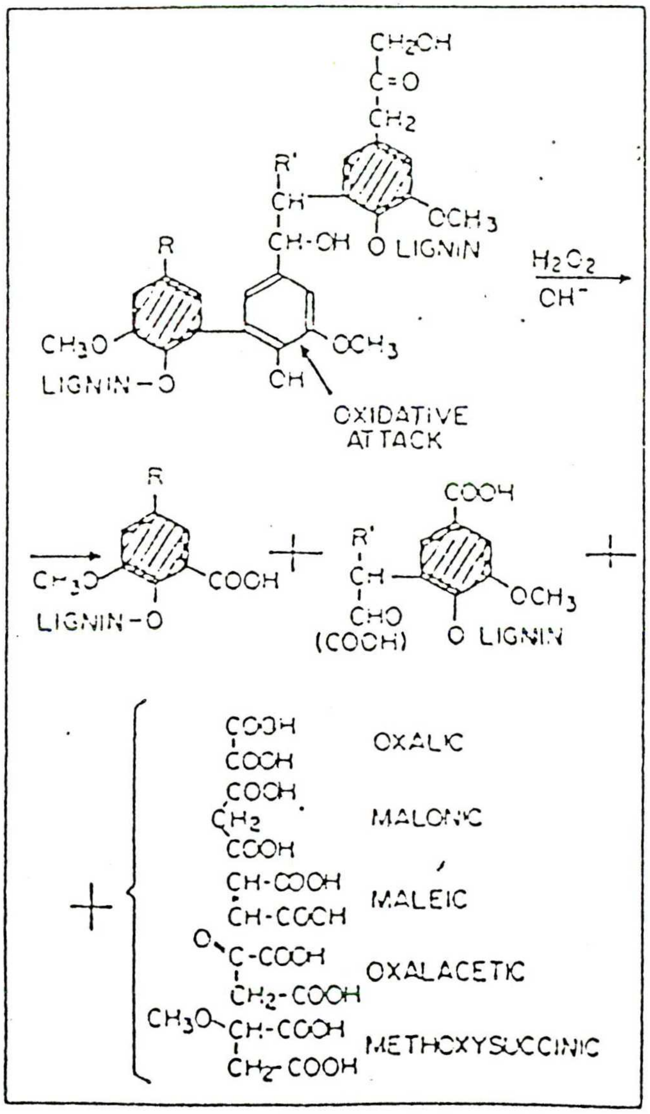


Figure 4.2 Reaction of hydrogen peroxide with lignin.

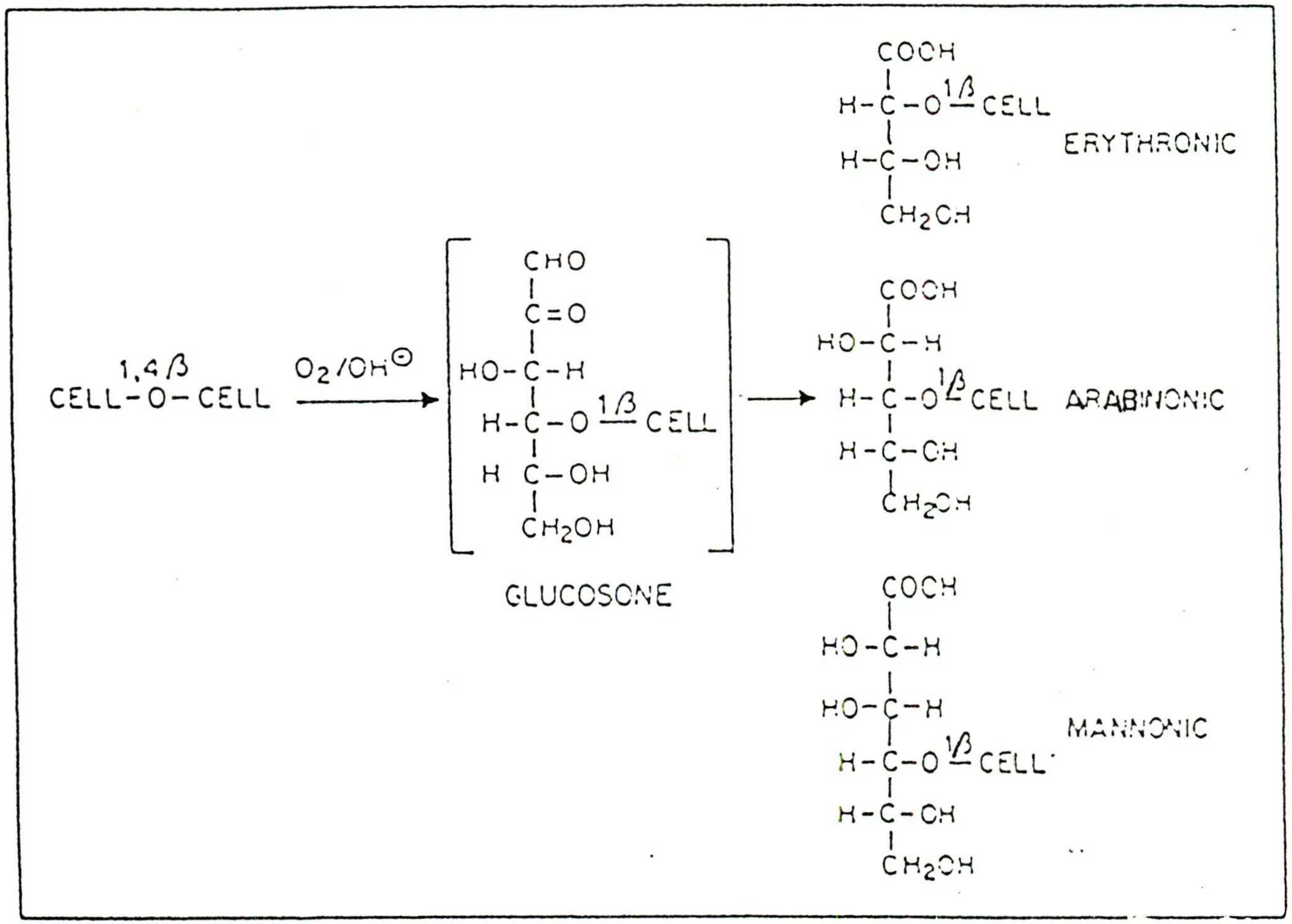


Figure 4.3 Degradation of cellulose by oxygen-alkali.

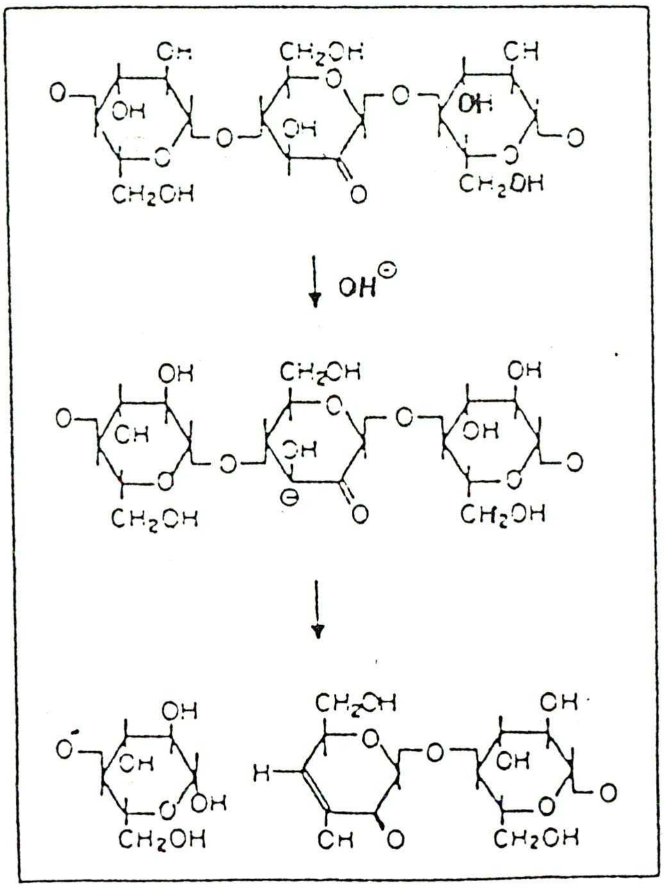


Figure 4.4 Alkaline degradation of oxidized cellulose.

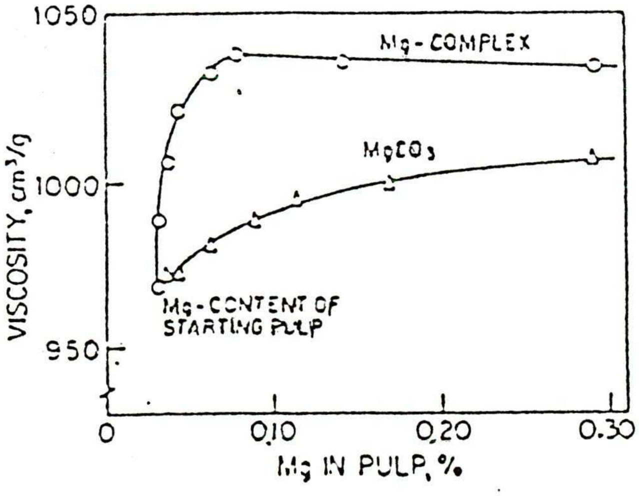


Figure 4.5 Protective influence of magnesium during oxygen bleaching:comparison at Kappa No. 17 .

4.1.4 MATERIALS AND METHODS

4.1.4.1 Characteristics of the studied wheat straw pulp

Before carrying out the bleaching experiments, approximate analysis of the studied pulp was performed according to Tappi standard methods(98-103). The obtained data are shown in Table 4.1.

Table 4.1: Characteristics of the wheat straw pulp.

Characteristics	Results
Kappa number(98)	17.4
Brightness,%(99)	29.0
Slowness,SR°(100)	31.0
Tear index,mNm^2/g(101)	5.5
Tensile index,Nm/g(102)	73·5
Burst index,Kpa.m^2/g(103)	5.5

4.1.4.2 Bleaching Process

The sequence of steps to bleach pulp were as follows:

a. The pulp was bleached in electrically heated, stainless steel, rotatable digester.

The established charge was made of 50 g moisture free pulp, the chemicals were mixed to reach the calculated charge of active alkali. Chemicals were added to chips in an aqueous solutions. Pulp to liquor ratio was adjusted to 12% consistency. Magnesium sulfate charge was added directly to the pulp (0.5%).

After that pulp and chemicals were put in the digester, and then the lid was closed. After setting the required maximum temperature (95 °C), the electrical heater and motor were switched on. Afterwards the digester pressure was set to the according O_2 pressure (see Tables 4.4-4.5) .

b. Afterwards the digester pressure was reduced to atmospheric pressure, the autoclave was left to cool. The pulp was then collected on a musline cloth, and washed for two hours with tap water.

4.1.5 EXPERIMENTAL DESIGN AND NON-LINEAR REGRESSION

Three parameters, among others, were investigated. These are, the remained alkali concentration (as Na_2O), the concentration of active alkali (as NaOH), and the duration of bleaching, while the ratio of the pulp to the liquor, temperature of bleaching, and pressure of oxygen were kept constant.

For optimization the above parameters, the central composite rotatable design method was employed for designing the programme of experiments$^{(104)}$.

For the purpose of designing the experimental programme, the range of the variables had to be specified first, thus:

$$X_1 = \frac{RA-12.5}{6.25} \quad \ldots\ldots\ldots \quad (4.1)$$

$$X_2 = \frac{AA\%-1.3}{0.65} \quad \ldots\ldots\ldots \quad (4.2)$$

$$X_3 = \frac{t-67.5}{11} \quad \ldots\ldots\ldots \quad (4.3)$$

Where: RA : remained alkali (as mg Na_2O/g cellulose).

AA% : active alkali (as NaOH) percent related to the mass of moisture free material.

The values of variables are coded as shown on Table 4.2, the number of different levels for each of the variables was always five (regardless of the number of variables).A preliminary step was the setting up to each coded levels, the corresponding X_j real process variables (where j=1,2, and 3). The calculations were based upon equations (4.1), (4.2), and

(4.3).

As a result of this experimental design of variables, fifteen experiments were carried out in the sequence shown in Table 4.3 . The results of these experiments were used to develop a mathematical model for bleached pulp yield, kappa number, slowness, brightness, tear index, tensile index, and burst index as functions of process variables (X_j) under investigation. The form of this relationship is given by :

$$Y = b_o + b_i X_i + b_{ii} X_i^2 + b_{ij} X_i X_j \qquad ....(4.4)$$

The b values are constants, computed by least squares standard method.

Table 4.2 The coded and experimental values of process variables.

Coded level	Remained alkali (mg Na_2O/g cell.)	Active alkali (%)	Time (min)
-1.682	0.0	0.00	45
-1.0	6.2	0.65	56
0.0	12.5	1.30	67
+1.0	18.7	1.95	78
+1.682	25.0	2.60	90

4.1.6 **RESULTS AND DISCUSSIONS**

4.1.6.1 **Regression analysis**

Tables 4.4 and 4.5 summarize results of oxygen bleaching of wheat straw pulp at oxygen pressure of 0.6 Mpa. and 0.4 Mpa. respectively. Bleached yield, kappa number, brightness, slowness, tear index, tensile index, and burst index are shown as a function of process parameters.

The computer assisted second-order polynomial analysis of the objective function (bleached pulp yield), as well as of the other functions (kappa number, brightness,....etc) led to the equations as shown in Tabels 4.6 and 4.7 respectively.

The F-values of these equations all exceed the tabulated F-value of 2.2 determined for 10 degrees of freedom and 95% confidence limits(105). The estimated standard deviation values were found to be less than 1, therefore equations in Tabels 4.6 and 4.7 describe the process behaviour through the region studied.

Table 4.3 Sequence of experiments according to central composite rotatable design.

Exp. No.	Coded variables X_1	X_2	X_3	Real variables RA	AA%	t
1	-1	-1	-1	6.25	0.65	56
2	+1	-1	-1	18.75	0.65	56
3	-1	+1	-1	6.25	1.95	56
4	+1	+1	-1	18.75	1.95	56
5	-1	-1	+1	6.25	0.65	78
6	+1	-1	+1	18.75	0.65	78
7	+1	+1	+1	18.75	1.95	78
8	-1.682	0	0	0.00	1.30	67
9	+1.682	0	0	25.00	1.30	67
10	0	-1.682	0	12.50	0.00	67
11	0	+1.682	0	12.50	2.60	67
12	0	0	-1.682	12.50	1.30	45
13	0	0	+1.682	12.50	1.30	90
14	0	0	0	12.50	1.30	67
15	0	0	0	12.50	1.30	67

4.1.6.2 **Process optimization**

Based upon the described regression analysis, the optimization problem could be formulated as follows :

> The bleached yield (objective function) i.e. $Y = f(X_1,X_2,X_3)$ should be maximized, subjected to the other functions (kappa number, brightness,...etc) constraints.

These optimization problems have been investigated by Rosenbrock's method$^{(106)}$ in order to locate the optimum process controlling parameters. Computer programmes were set up to

Table 4.4 Coded and real variables and the corresponding fibre characteristics for the oxygen bleaching of wheat straw cellulose at 0.6 Mpa pressure

Exp.No.	Coded Variables			Real Variables			Results						
	X_1	X_2	X_3	RA (mg Na_2O/ gm cell.)	AA (%)	t (min)	Yield (%)	Kappa. No.	Slowness SR	Tear index mNm^2/gm	Burst index $Kpa.m^2/gm$	Tensile index Nm/gm	Brightness (%)
1	-1.228	-1	-1	4.15	0.65	56	94.75	8.73	24	5.38	4.59	69.77	35
2	-0.560	-1	-1	9	0.65	56	90.82	8.23	26	4.92	5.21	80.95	36
3	-1.228	+1	-1	4.15	1.95	56	90.74	7.02	23	5.74	4.66	70.49	39
4	-0.560	+1	-1	9	1.95	56	92.73	8.52	25	6.29	5.31	80.84	38
5	-1.228	-1	+1	4.15	0.65	78	93.89	10.9	23	5.55	4.82	72.66	35
6	-0.560	-1	+1	9	0.65	78	89.63	7.55	25	4.70	5.25	77.32	37
7	-0.560	+1	+1	9	1.95	78	87.38	7.00	25	5.51	5.68	73.53	40
8	0.312	-1.682	0	14.45	0	67	87.25	7.54	24	5.14	4.82	65.92	40
9	0.312	+1.682	0	14.45	2.60	67	85.42	6.37	24	5.42	4.96	66.01	39
10	0.312	0	-1.682	14.45	1.30	45	87.02	11.9	24	6.56	4.82	67.92	39
11	0.312	0	+1.682	14.45	1.30	90	82.12	7.30	26	5.49	4.59	60.94	33
12	0.312	0	0	14.45	1.30	67	83.12	6.39	24	6.16	4.70	74.80	44
13	0.312	0	0	14.45	1.30	67	82.51	6.89	24	5.93	4.67	72.91	43

Table 4.5 Coded and real variables and the corresponding fibre characteristics for the oxygen bleaching of wheat straw cellulose at 0.4 Mpa pressure

Exp.No.	Coded Variables			Real Variables			Results						
	X_1	X_2	X_3	RA (mg Na_2O/ gm cell.)	AA (%)	t (min)	Yield (%)	Kappa. No.	Slowness SR	Tear index mNm^2/gm	Burst index $Kpa.m^2/gm$	Tensile index Nm/gm	brightness (%)
1	-1.228	-1	-1	4.15	0.65	56	94.07	8.73	25	5.38	4.52	56.88	35
2	-0.560	-1	-1	9	0.65	56	92.45	7.82	27	4.94	5.23	73.97	35
3	-1.228	+1	-1	4.15	1.95	56	89.74	7.42	24	6.58	4.65	64.34	37
4	-0.560	+1	-1	9	1.95	56	93.44	7.72	26	4.30	5.31	80.84	38
5	-1.228	-1	+1	4.15	0.65	78	95.04	8.92	24	6.35	4.74	65.97	35
6	-0.560	-1	+1	9	0.65	78	92.56	8.23	27	7.48	5.22	87.58	35
7	-0.560	+1	+1	9	1.95	78	90.78	7.90	23	5.71	4.67	74.61	42
8	0.542	-1.682	0	15.89	0	67	84.25	10.7	23	6.09	4.72	69.57	33
9	0.542	+1.682	0	15.89	2.60	67	83.42	7.44	24	6.67	5.09	71.73	39
10	0.542	0	-1.682	15.89	1.30	45	89.32	8.06	24	5.78	4.61	67.35	36
11	0.542	0	+1.682	15.89	1.30	90	81.22	8.63	25	6.87	4.92	67.65	36
12	0.542	0	0	15.89	1.30	67	82.32	8.39	23	6.26	4.83	67.22	36
13	0.542	0	0	15.89	1.30	67	82.62	7.89	24	6.43	4.77	69.81	37

Table 4.6 Results of regression analysis at 0.6 Mpa. pressure of oxygen.

$Y = 85.180-6.866X_1-0.579X_2-1.456X_3+0.951X_1X_2-0.388X_1X_3-0.682X_2X_3-2.291X_1^2+1.212X_2^2+0.620X_3^2$ ...(for bleached yield).

$K = 6.479+0.210X_1-0.316X_2-1.018X_3+0.328X_1X_2-1.460X_1X_3-0.161X_2X_3+0.974X_1^2+0.111X_2^2+1.046X_3^2$ ...(for kappa number).

$Br= 42.658+2.271X_1+0.283X_2-0.991X_3-2.025X_1X_2-1.840X_1X_3+0.557X_2X_3+1.367X_1^2-1.413X_2^2-2.650X_3^2$ ...(for brightness).

$Fr= 24.810-1.723X_1-0.089X_2+0.320X_3-0.289X_1X_2+0.705X_1X_3+0.151X_2X_3-2.802X_1^2-0.0000006X_2^2+0.453X_3^2$ ...(for slownees).

$Tn= 80.41-15.969X_1-0.330X_2-2.147X_3+1.135X_1X_2-0.764X_1X_3-1.499X_2X_3-16.186X_1^2-2.788X_2^2-3.331X_3^2$ ...(for tensile index).

$Bu= 5.063-0.919X_1-0.070X_2-0.007X_3-0.071X_1X_2-0.191X_1X_3+0.096X_2X_3-0.942X_1^2+0.072X_2^2+0.007X_3^2$ ...(for burst index).

$Tr= 5.789+0.625X_1+0.205X_2-0.274X_3-0.126X_1X_2-0.259X_1X_3-0.056X_2X_3+0.616X_1^2-0.270X_2^2-0.007X_3^2$ ...(for tear index).

Table 4.7 Results of regression analysis at 0.4 Mpa. pressure of oxygen.

$Y = 87.824-7.664X_1-0.496X_2-1.506X_3+0.839X_1X_2-1.706X_1X_3-0.267X_2X_3-4.085X_1^2+0.482X_2^2+0.989X_3^2$ ...(for bleached yield).

$K = 7.606-0.579X_1-0.666X_2+0.190X_3-0.389X_1X_2-0.083X_1X_3+0.098X_2X_3+0.748X_1^2+0.328X_2^2+0.072X_3^2$ ...(for kappa number).

$Br= 37.403-1.242X_1+2.055X_2+0.460X_3-0.389X_1X_2-0.804X_1X_3+1.196X_2X_3-0.784X_1^2-0.176X_2^2-0.176X_3^2$ ...(for brightness).

$Fr= 25.439-1.780X_1-0.364X_2-0.238X_3+1.084X_1X_2+1.017X_1X_3-0.886X_2X_3-3.318X_1^2-0.000002X_2^2+0.354X_3^2$ ...(for slownees).

$Tn= 79.988-9.760X_1-0.118X_2+0.522X_3+0.982X_1X_2-0.205X_1X_3-4.741X_2X_3-21.046X_1^2+0.754X_2^2-0.358X_3^2$ ...(for tensile index).

$Bu= 5.157-0.269X_1+0.006X_2-0.009X_3+0.181X_1X_2+0.154X_1X_3-0.212X_2X_3-0.720X_1^2+0.037X_2^2-0.012X_3^2$ ...(for burst index).

$Tr= 5.729+0.688X_1-0.009X_2+0.465X_3+0.059X_1X_2-0.006X_1X_3-0.308X_2X_3+0.823X_1^2+0.012X_2^2-0.007X_3^2$ ...(for tear index).

Table 4.8 Calculated and experimental optimum oxygen bleaching conditions and product characteristics at 0.6 and 0.4 Mpa pressure of oxygen.

Results	Coded Variables			Real Variables			Results						
	X_1	X_2	X_3	RA (mg Na_2O/ g cell.)	AA (%)	t (min)	Yield (%)	Kappa. No.	Slowness SR°	Tear index mNm^2/g	Burst index Kpa.m^2/g	Tensile index Nm/g	Brightness (%)
1-optimum NO.1 (0.6 MPa oxygen pressure)													
Calc.	-1.498	-1.682	1.682	1.682	0	90	99.33	15.40	21	5.15	4.46	56.69	26
2-optimum NO.2 (0.4 MPa oxygen pressure)													
Calc.	-0.932	-1.682	1.682	6.675	0	90	99.63	9.534	28	11.05	5.46	88.25	31
Appl. optimum NO.2													
cal.	-1.149	-1.682	1.682	4.88	0	90	99.24	10.96	27	7.50	5.67	82.2	33
exp.	-1.149	-1.682	1.682	4.88	0	90	96.01	11.27	27	6.88	5.27	79.5	33

generate the solutions of the above optimization problems using regression equations. The results presented in Tables 4.8 define the optimum pulping conditions. According to these results, bleaching at optimum NO.2 (see Table 4.8) represents the best and optimum conditions for oxygen bleaching of wheat straw pulp. These calculated data were later confirmed experimentally (see Table 4.8).

Satisfactory agreement is indicated between calculated and experimental optimal values.

4.1.6.3 **Effect of process variables on the characeristics of bleached pulp**

Effects of remained alkali charge, active alkali charge, and duration of bleaching on oxygen bleached pulp yield and kappa number under different oxygen partail pressure are shown for kraft wheat straw oxygen delignification in figures 4.6-4.11.

4.1.6.3.1 **Bleached pulp yeild vs. process variables**

The bleached pulp yield of kraft wheat straw pulp continously decreased under 0.6 and 0.4 MPa oxygen partial pressure as the remained alkali charge, active alkali charge, and duration of delignification increased. The carbohydrate degradation and rate of delignification during oxygen bleaching increased with increasing the process variables.

The bleached pulp yield decreased by (30%) and (40%) under 0.6 and 0.4 MPa oxygen partail pressure, respectively over the range of remained alkali charge from 0 through 25 mg Na_2O/g cellulose and at the same conditions of active alkali charge (0%) and duration of delignification (90 minute) (figure 4.6).

Also it decreased by (11%) and (4.5%) under 0.6, 0.4 MPa and 1.68, 6.67 mg Na_2O/g cellulose, respectively and for the same duration of delignification (90 minute) over the range of active alkali charge from 0 through 1.95%. Mininmum bleached pulp yield was achieved and leveled off after pulping with 1.95%

active alkali charge (figure 4.7).

A small (1%) and (2.5%) losses in bleached pulp yield was caused in kraft wheat straw pulp by an (11%) increase in duration of delignification under 0.6, 0.4 MPa and 1.68, 6.68 mg Na_2O/g cellulose, respectively. Minimum bleached pulp yield was achieved and leveled off after pulping for 56 minutes (figure 4.8).

4.1.6.3.2 **Kappa number vs. process variables**

The same trend of behaivour for the kappa number was with the processing variables. The kappa number decreased by (60%) and (30%) under 0.6 and 0.4 MPa oxygen partail pressure, respectively over the range of remained alkali charge from 0 through 25 mg Na_2O/g cellulose and at the same conditions of active alkali charge (0%) and duration of delignification (90 minute) (figure 4.9).

The delignification rate during the rapid initial phase as well as in the slow final phase of oxygen bleaching increases with increased alkali concentration (figure 4.10). Kappa number decreased by (26%) under 0.6, 0.4 MPa and 1.68, 6.68 mg Na_2O/g cellulose, respectively and for the same duration of delignification (90 minute) over the range of active alkali charge from 0 to 2.6%.

The decrease in kappa number with reaction time during oxygen bleaching for two kraft pulps, of kappa numbers 15.6 and 12.5, is shown in figure 4.11. The kappa number decreased with reaction time in the same way, irrespective of the initial kappa number. The oxygen partial pressure and remained alkali charge were different, while the alkali concentration and the temprature were kept constant during these experements. This means that if the reaction had been of first order with respect to lignin content in the pulp, as has sometimes been assumed, a straight line would have been obtained. A (40%) and (30%) reduction in the degree of delignification was achieved over the range of oxygen reaction time under 0.6 and 0.4 MPa.

4.1.6.3.3 **Bleached pulp yield vs. kappa number**

We can see from figure 4.12 that when the oxygen bleaching is prolonged to kappa numbers below 10 the yield curve starts to drop faster (higher yield loss per kappa number unit), which means that the process is getting more and more unselective. This is showing that from yield and selectivity point of view, the oxygen bleaching stage should be performed with about 40-45% degree of delignification (example from kappa 17 to kappa 10). At these levels the specific yield values are 94-96% at kappa number 10. When oxygen bleaching is prolonged to lower kappa numbers (below 7), the specific yield values are too low. An optimal kappa number level is around 10, which corresponds to our results.

4.2 **TOTAL CHLORINE-FREE BLEACHING OF WHEAT STRAW KRAFT PULPS**

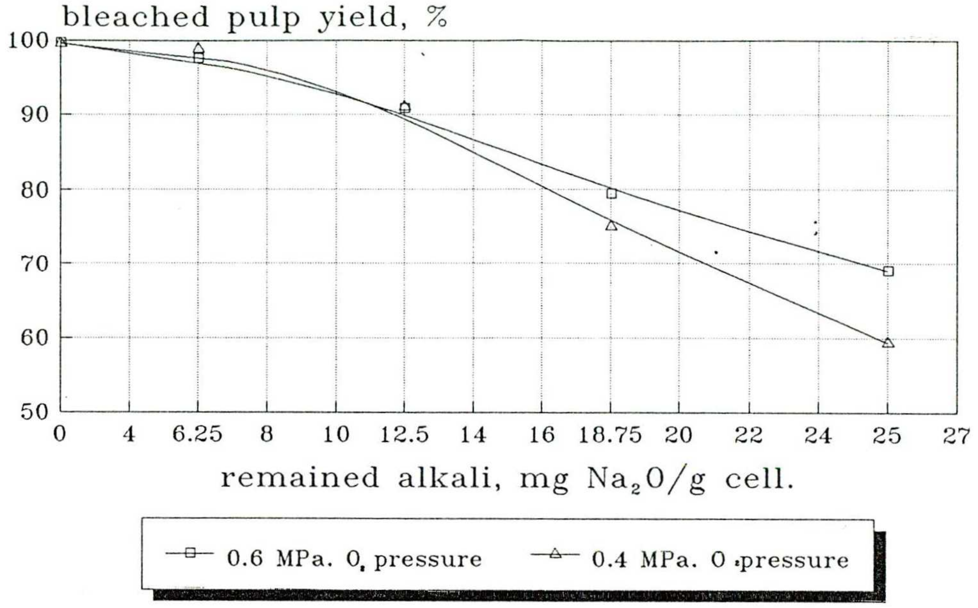
The aim of this work was to prepare bleached wheat straw kraft pulps of 80% brightness with good pulp strength properties and viscosity above 730 dm^3/kg without the use of chlorine bleaching compounds. Oxygen delignification, (EOP), and hydrogen peroxide bleaching stages were used, producing only 0.004 kg/odt of AOX.

Several alternatives have been studied to partially or totally eliminate chlorine compounds from bleached plants. Efforts have concentrated mainly on the removal of molecular chlorine since formation of chlorinated organics (AOX, EOX) has been proven to be linearly proportional to chlorine consumption, which in turn is proportional to the incoming kappa number of the brownstock(107).

Although it has recently been reported(108) that AOX and EOX cannot be directly related to bioaccumulation and lethal or sublethal effects in exposed aquatic organisms, it is generally agreed that many of the chlorinated organic compounds resulting from first-stage chlorination and subsequent alkaline extraction are bioacumulating(109) and mutagenic(110).

Furthermore, it has been shown that the formation of the major part of the controversial polychlorinated dibenzodioxins (PCDOS) and dibenzofurans (PCDFS) occurs in the C-stage of the

Figure 4.6:The effect of remained alkali upon bleached pulp yield.



AA%=0, t=90 min

Figure 4.7:The effect of active alkali upon bleached pulp yield.

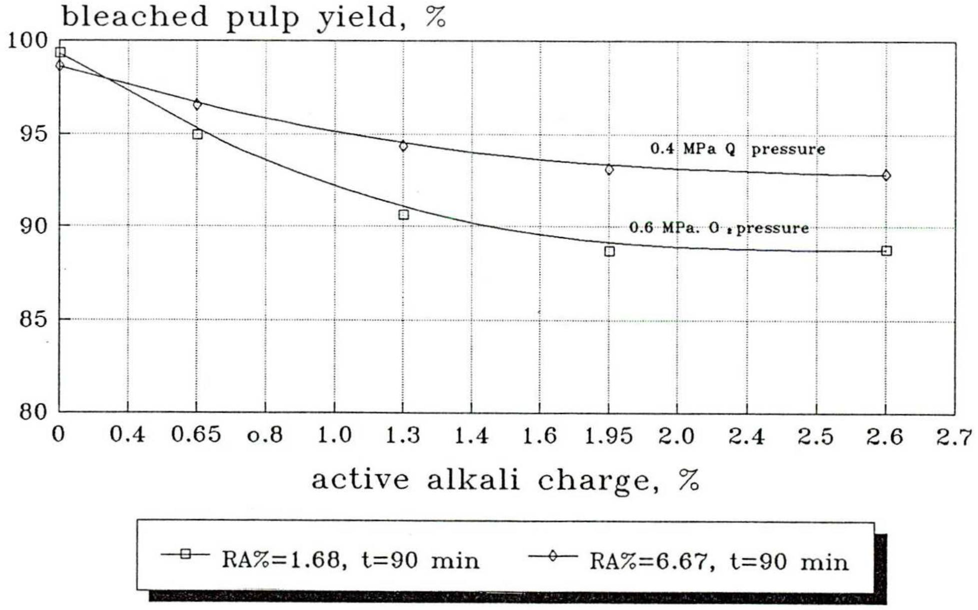


Figure 4.8: The effect of time of bleaching upon bleached pulp yield.

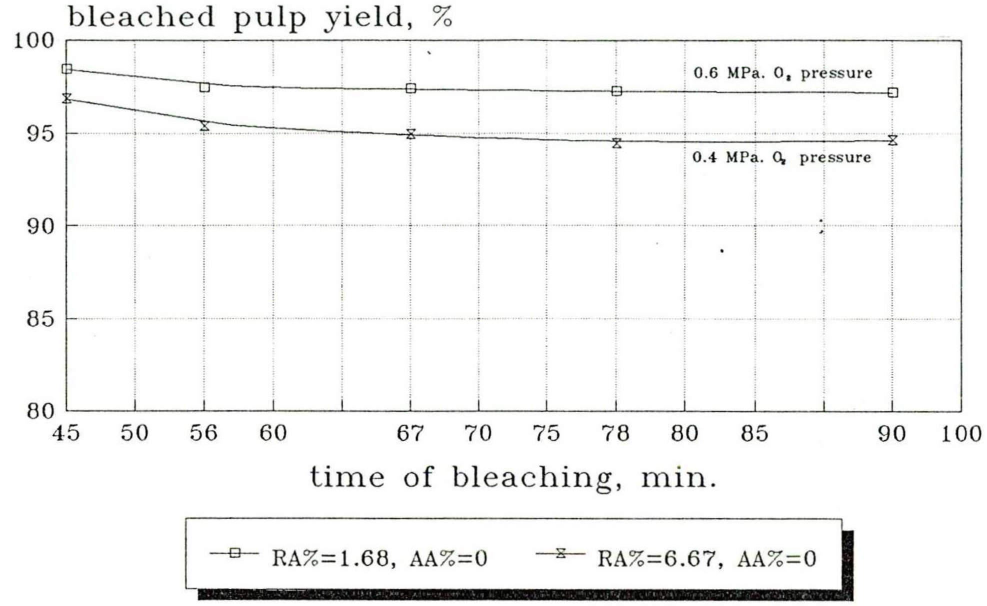
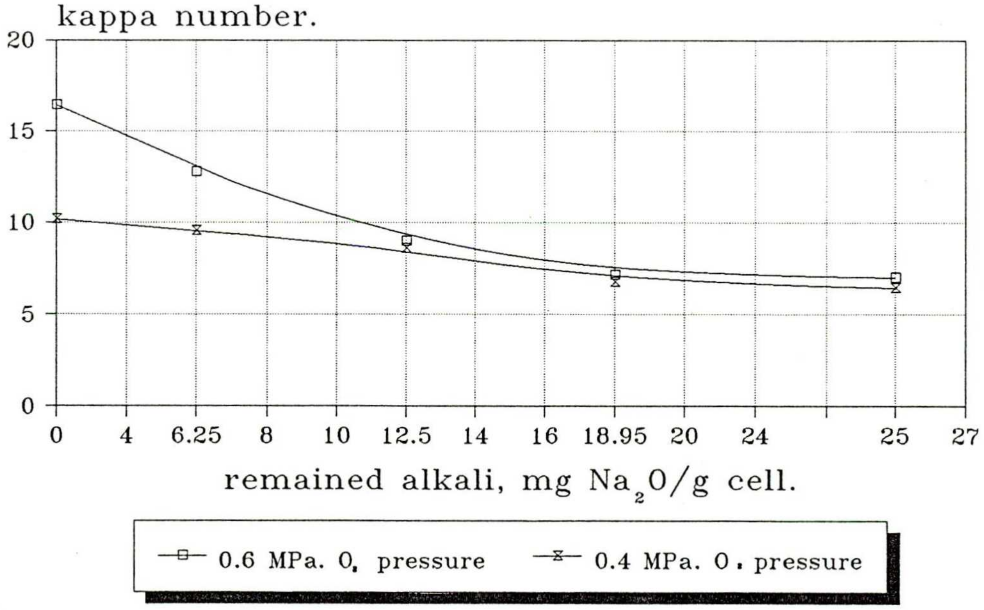


Figure 4.9:The effect of remained alkali upon Kappa No.



AA%=0, t=90 min.

Figure 4.10: The effect of active alkali upon Kappa No.

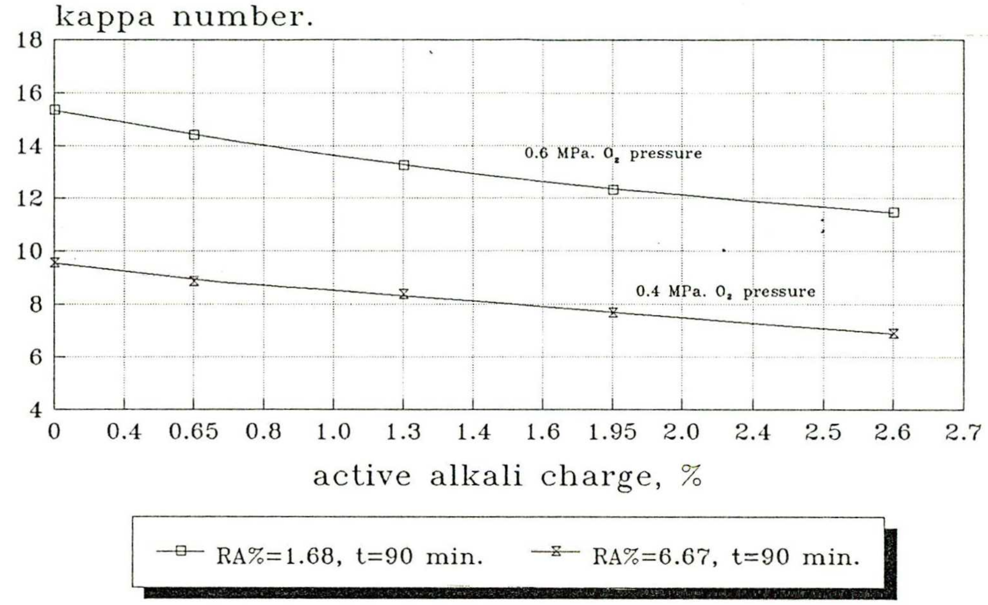


Figure 4.11: The effect of time of bleaching upon kappa number.

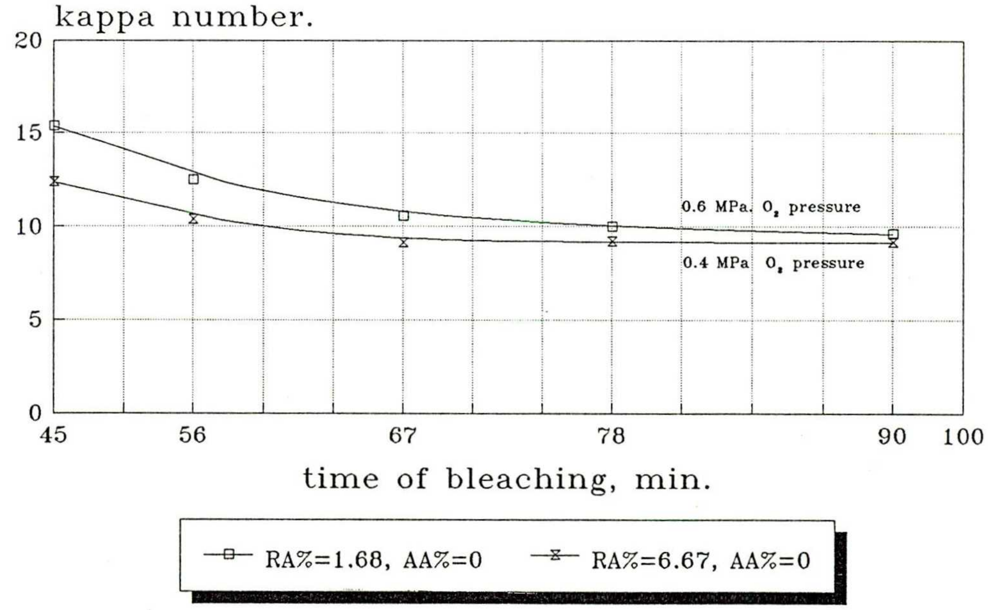
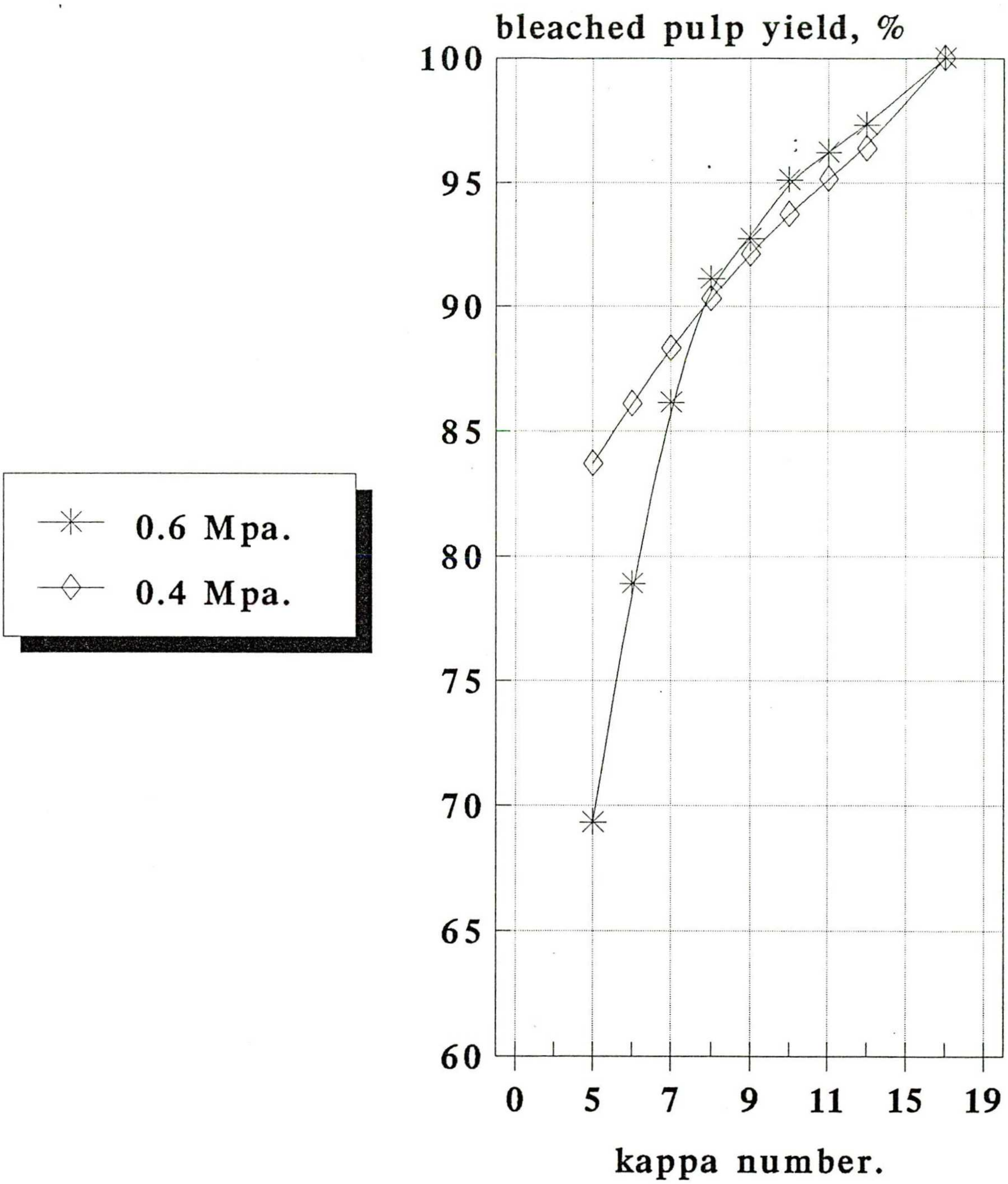


Figure 4.12:effect of kappa number upon bleached pulp yield.



bleaching sequence(107,111) and that the chlorine charge used in this stage is the most significant factor affecting PCDD and PCDF levels in the effluent(112,113). Despite the fact that recently reported(114) biological dechlorination treatment achieves over 90% AOX removal from pulp mill wastewaters, most industry effort has concentrated on reducing the formation of AOX by modifying the bleaching process.

The most commonly used method proposed to decrease or eliminate chlorine compounds from bleaching sequences are based either on lowering kappa number as much as possible before bleaching and/or on the use of less conventional nonchlorine bleaching chemicals. Such alternatives, as recently reviewed(115,116) include conventional medium or high consistency oxygen delignification, combined extended and oxygen delignification, acid or alkaline oxygen delignification reinforced with hydrogen peroxide, conventional and "hot" alkaline extraction reinforced with oxygen or oxygen and hydrogen peroxide, peroxide bleaching, ozone bleaching, ozone/peroxide bleaching and oxygen/ozone/peroxide bleaching. In addition, two stage oxygen delignification with(117) and without(118,119) lignin activation between stages, acid peroxide delignification in the absence(120), or presence(121,122) of catalysts, alkaline peroxide delignification(123) and delignification with peroxyacids(124,125) have also been proposed.

The possibility of further increasing the degree of deligninfication and improving the selectivity of the oxygen delignification of kraft pulps was studied by reinforcing with alkaline extraction. The oxidation of reducing end groups in carbohydrates to aldonic acid groups reduces the extent of peeling reactions, which in turn leads to a better pulp yield.

The objective of this study was to bleach wheat straw kraft pulp to 80% without chlorine compounds through combinations and improvement of some of the aforementioned alternatives. The alternatives studied include:

- Oxygen delignification at 90 °C.
- Hot alkaline extraction reinforced with oxygen and hydrogen peroxide.

- Final bleaching with hydrogen peroxide.

4.2.1 MATERIAL AND METHODS

4.2.1.1 Characteristics of the studied wheat straw pulp

Before carrying out the bleaching experiments, approximate analysis of the studied pulp was done to determine the characteristics according to TAPPI standard methods. The obtained data are demonstrated in Table 4.9.

Table 4.9: Characteristics of the wheat straw pulp.

Characteristics	Results
Kappa number(98)	12.30
Brightness, %(99)	35.00
Slowness, SR°(100)	32.00
Tear index, mNm^2/g(101)	4.46
Tensile index, Nm/g(102)	65.33
Intrinsic viscosity, dm^3/kg(126)	950

4.2.1.2 Bleaching process

The established charge was made of 300 g moisture free pulp. The chemicals were mixed to reach the calculated charges according to Table 4.10 . Bleaching were carried out in a 2-L stainless-steel rotating autoclave.

Chemicals were added to pulp in a aqueos solutions. A multistage process O(EOP)P was used for the bleaching of pulp. Details are included in Table 4.10.

After each stage of bleaching, the pulp was washed throughly by hot water.

4.2.2 Cost estimation

Cost of bleached wheat straw pulp was carried out according to the Dunaújvàros mill cost estimation basis. Details are included in Table 4.11. Cost of production of one ton totally bleached wheat straw kraft pulp, 80% brightness according to CEH sequance bleaching is 26924 HUF.

Table 4.10: O(EOP)P bleaching sequence.

Conditions of bleaching	Unbleached pulp	Oxygen bleaching	EOP	peroxide
Time, min		90	120	180
Consistency,%		12	12	12
Peroxide,%		-	1	2
Temperature, °C		90	150	90
O_2, MPa		0.4	0.4	-
NaOH,%		1.5	2	0.5
pH		11	11	11
MgO,%		0.5	0.5	-
EDTA,%		-	0.2	0.2
Charasteristics				
Yield,%	-	97.2	94	96
Kappa No.	12.8	9.79	4.54	-
Viscosity,dm^3/kg	817	955	870	732
Alpha-cell. cont., %	-	-	-	92
Ash cont., %	-	-	-	0.23
Brightness,%	35	40	56	80
Tensile index, Nm/g	65.33	56.1	49.3	37.4
Tear index, mNm^2/g	4.46	6.63	7.01	7.88
Double fold, No.	29	250	125	57
Fibre AOX, mg Cl/kg	6.67	4.35	4.01	3.96
Waste water AOX mg Cl/l	-	0.12	0.25	0.12

Table 4.11:Totally Chlorine-free O(EOP)P bleaching cost estimation per ton of a bleached pulp.

Material	Quantity	Cost (HUF/unit)	Cost (HUF)
NaOH,kg	220	33.30	7319
H_2O_2,kg	60	77.85	4671
EDTA,kg	4	206	824
O_2,kg	32	10	320
CaO,kg	200	4.8	960
Na_2SO_4,kg	70	21.8	966
SO_2,kg	0.4	71.9	29
Heat,(Gj)	200	340	6800
Energy,Mw	750	5.8	4350
Water,m^3	180	10	1800
Wheat straw,ton	2.857	2887	8250

total 36289 HUF

Figure 4.13: Change of kappa number with sequence of bleaching

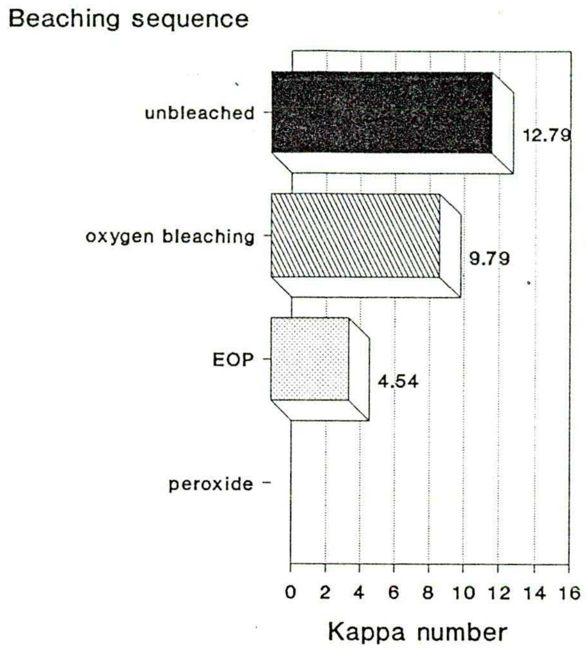


Figure 4.14: Change of bleached yield with sequence of bleaching

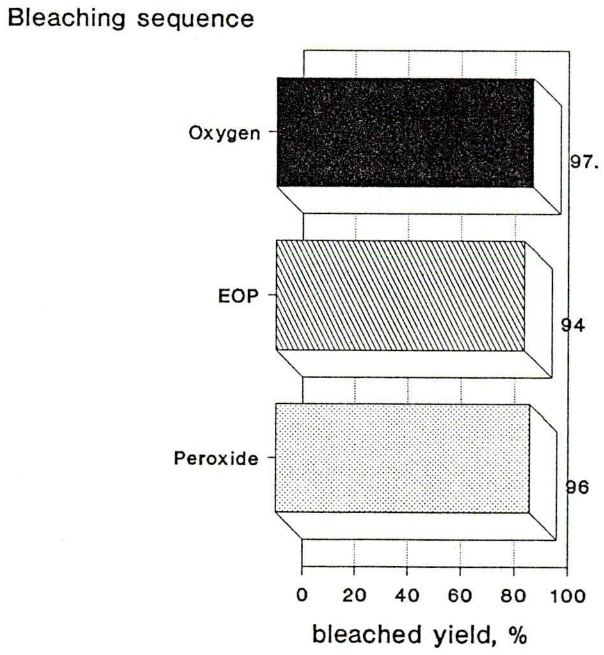


Figure 4.15: Change of brightness with sequence of bleaching

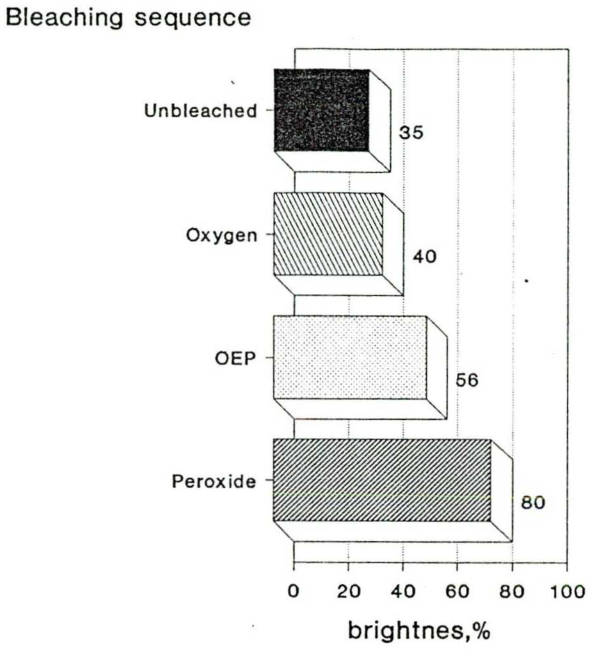


Figure 4.16:Change of AOX with sequence of bleaching

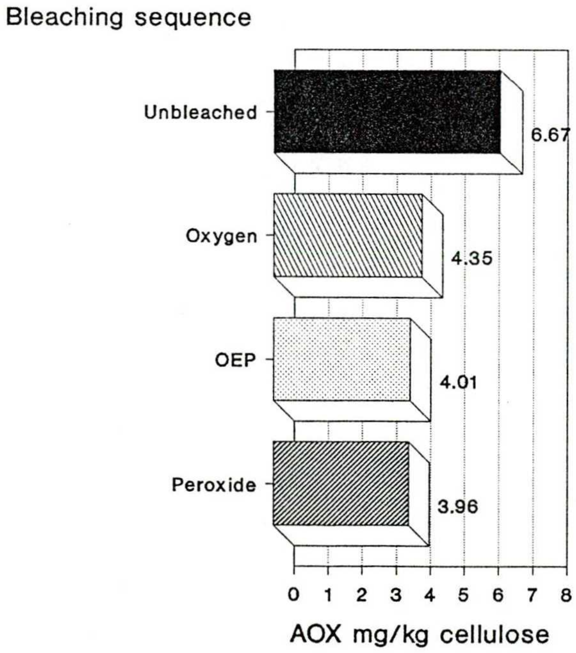


Figure 4.17: Change of viscosity with sequence of bleaching

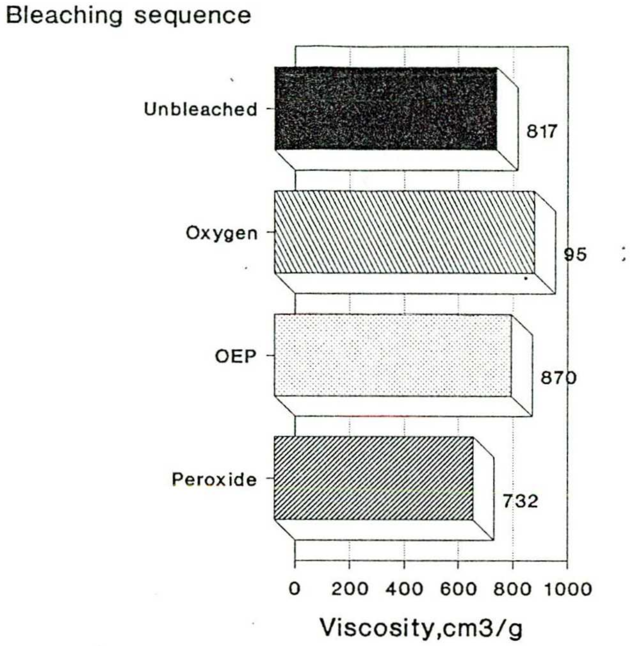


Figure 4.18: Change of tensile index with sequence of bleaching

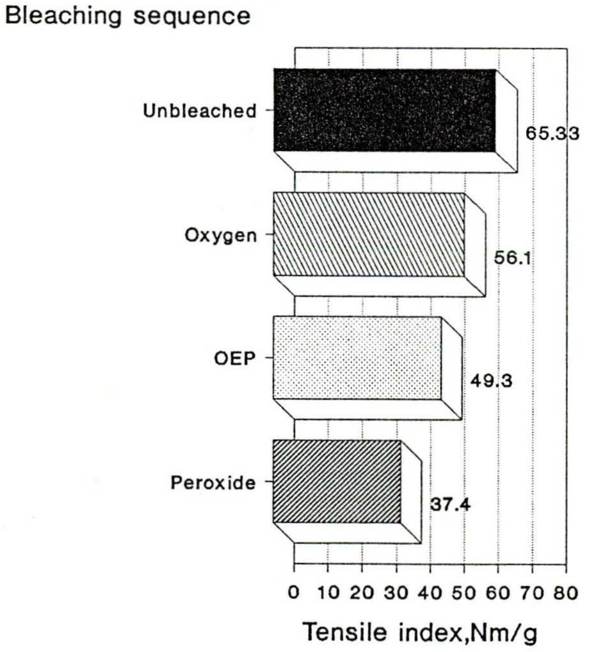


Figure 4.19: Change of tear index with sequence of bleaching

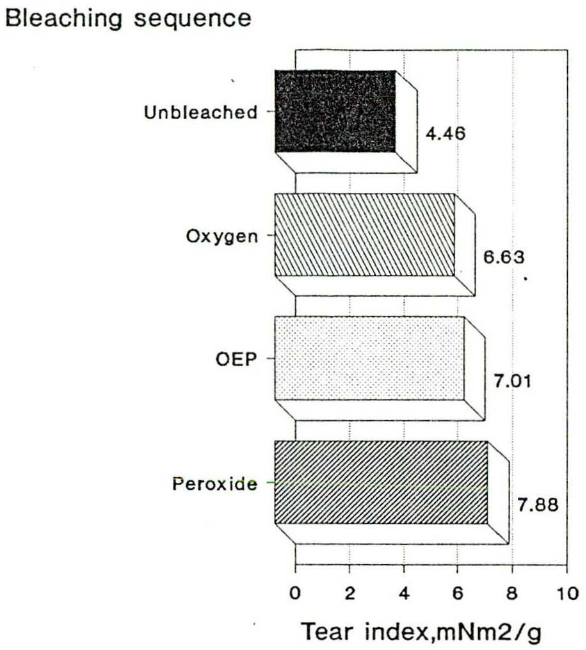


Figure 4.20: Change of double fold with sequence of bleaching

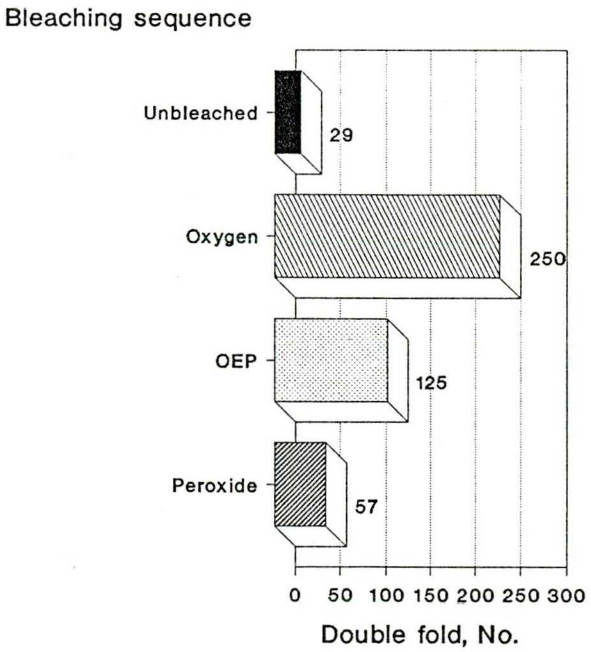


Figure 4.21: Change of AOX of waste water with sequence of bleaching

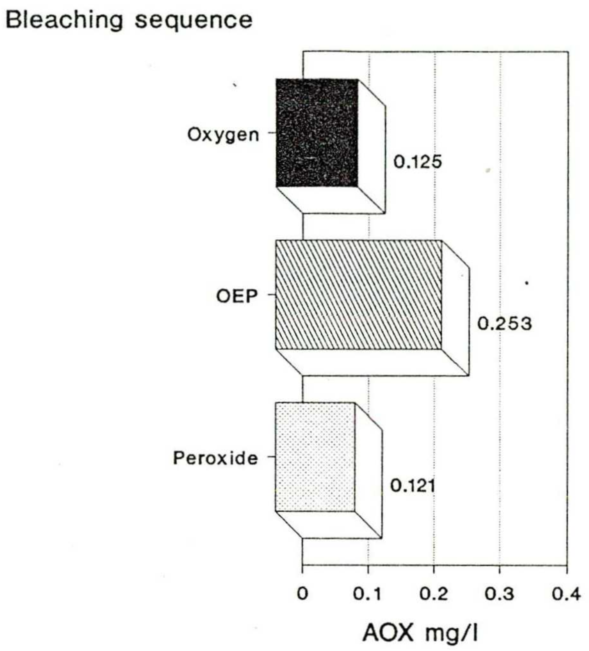
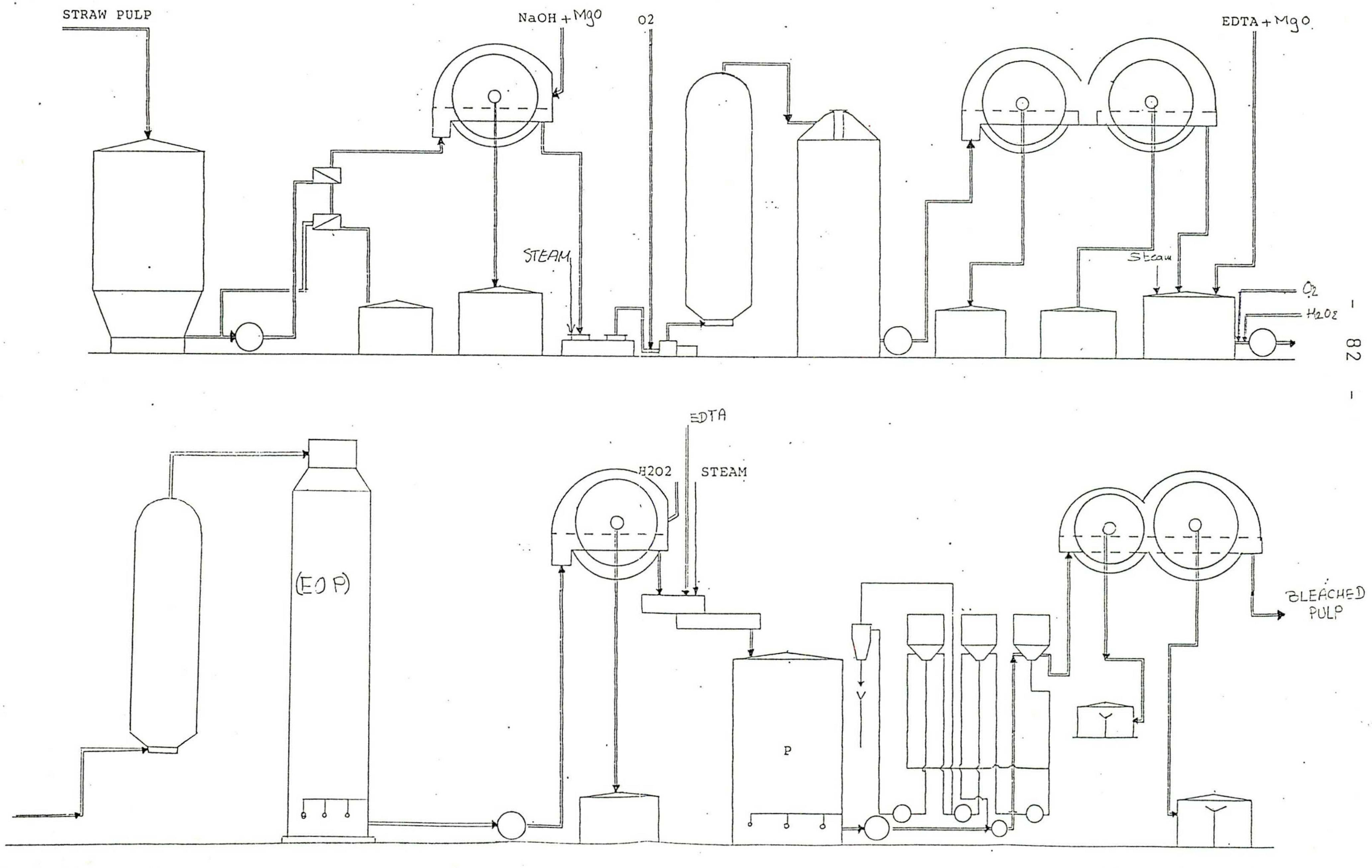


Figure 4.22:O(EOP)P bleaching sequence flow sheet digram.



4.2.3 **Results and discussion**

As was shown, prebleaching wheat straw kraft pulps with oxygen delignification rendered the residual lignins very susceptible leading to a substantial decrease in the kappa number. Kappa number as low as 9-10 was obtained for wheat straw kraft pulp after oxygen delignification (Figure 4.13).

The possibility of further increasing the degree of delignification and improving the selectivity was studied by reinforcing with alkaline and/or peroxide at the oxygen stage (Table 4.10). The oxidation of reducing end groups in carbohydrates to aldonic acid groups reduces the extent of peeling reactions, which in turn leads to better pulp yield (Figure 4.14). The oxidition reactions might be accelerated by adding alcohols at the oxidative stage.

The brightness of the unbleached wheat straw kraft pulp increased from 35% to 80% in a three-stage O(EOP)P bleaching sequence. The brightness increases in the EOP and peroxide stages were 56% and 80% respectively. This high increase is due to high rate of delignification in both stages (Figure 4.15).

The effluent characteristics of selected bleaching sequence are presented in Table 4.10. As can be seen, the short sequence produced 3.96 mg/kg AOX (see Figure 4.16).

The estimated characteristics values (Table 4.10) are in good agreement with measured values for those sequences using chlorine bleaching (CEH) (see Figures 4.17-4.21).

Finally, cost of production of bleached pulp with O(EOP)P sequence will be more expensive than that of CEH sequence about 35% . Figure 4.22 shows the process flow digram. Clearly can be seen that is possible to modify the CEH sequence bleaching to O(EOP)P sequence bleaching with a keeping the same lines.

CHAPTER FIVE

RESULTS & DISCUSSION

5.1 POLYNOMIAL REGRESSION ANALYSIS

5.1.1 Pulping processes polynomial regression analysis

As already mentioned in chapter three, the kraft pulping process, which was considered in this work, was studied throughout the regression analysis of the objective function (bleached and unbleached pulp yields) and the equality constraints (alpha-cellulose content, degree of polymerization, and kappa number). The results are presented in Tables 5.1, 5.2, 5.3, and 5.4 which show the characteristics of the studied pulp as a function of the process conditions. The results of the seconed order regression analysis of the objective function (bleached and unbleached pulp yields) and the equality constraints (alpha-cellulose content, degree of polymerization, and kappa number) gave equations 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 5.10, and 5.11 respectively as shown in Table 5.5 .

The F-values of these equations, (in Table 5.5) are greater than a tabulated F-value of 2.2 at 10 degree of freedom (the difference between the number of experiments and the number of coefficients) and within 95% confidence limits(81). Therefore these equations adequately described the behavior of the process throughout the region studied.

5.1.2 Nitration reactions polynomial regression analysis

Tables 5.6 and 5.7 summarize results of nitration reactions. Nitrogen content, viscosity, and ethanol-dimethyl ether solubility are shown in function of process controlling parameters (temperature, and duration of reaction).

The results of a computer assisted second-order polynomial analysis of the objective function (nitrogen content) have been the following equations(56):

$$N\% = 12.965 + 0.052X_1 + 0.126X_2 - 0.079X_1X_2 - 0.018X_1^2 - 0.093X_2^2 \quad ..(5.12)$$

for reed, and

$$N\% = 12.995 - 0.0193X_1 + 0.126X_2 + 0.031X_1^2 - 0.008X_2^2 \quad ..(5.13)$$

for eucalyptus.

Table 5.1 . Coded and real variables and the corresponding fibre characteristics for kraft pulping of reed

Exp. No.	Coded variables			Real variables			Unbleached	Kappa	Bleached	Alpha-	Degree of
	X_1	X_2	X_3	T,(°C)	t,(min)	A.A,(%)	yield,(%)	No.	yield,(%)	cellulose,(%)	polymerization
1	-1	-1	-1	150	90	10	53.41	47.81	49.63	90.11	2562
2	+1	-1	-1	160	90	10	49.21	51.75	43.21	93.92	1500
3	-1	+1	-1	150	150	10	49.71	44.92	43.79	89.32	2432
4	+1	+1	-1	160	150	10	52.10	55.82	45.25	92.35	1505
5	-1	-1	+1	150	90	14	48.72	31.62	47.82	89.52	1853
6	+1	-1	+1	160	90	14	47.94	37.24	46.25	91.71	1809
7	-1	+1	+1	150	150	14	47.12	35.80	46.51	93.81	2100
8	+1	+1	+1	160	150	14	48.91	32.23	46.71	90.92	1776
9	-1.682	0	0	146	120	12	52.62	47.81	46.31	94.41	2800
10	+1.682	0	0	163	120	12	54.21	41.72	49.01	94.01	2012
11	0	-1.682	0	155	60	12	46.81	45.78	45.81	93.12	1321
12	0	+1.682	0	155	180	12	45.31	43.86	45.01	94.36	1445
13	0	0	-1.682	155	120	8	41.71	48.75	34.90	91.58	2117
14	0	0	+1.682	155	120	15	44.61	30.59	41.71	90.12	1700
15	0	0	0	155	120	12	42.01	38.73	41.61	92.51	2842
16	0	0	0	155	120	12	47.41	38.74	46.31	91.45	2700
17	0	0	0	155	120	12	45.19	38.94	43.47	94.89	2900
18	0	0	0	155	120	12	46.41	38.26	44.01	95.83	2890
19	0	0	0	155	120	12	45.87	37.99	43.97	93.95	2901
20	0	0	0	155	120	12	45.97	38.09	44.35	92.99	2876

Table 5.2: Coded and real variables and the corresponding fibre characteristics for kraft pulping of wheat straw

Exp. No.	Coded variables			Real variables			Unbleached Yield %	Permanganate No. before bleaching	Bleached Yield %	Alpha Cellulose %	Degree of polymerization	Ash %
	X_1	X_2	X_3	T, °C	t, hr	A.A %						
1	-1	-1	-1	165	2.5	12	53.61	11.91	32.12	94.34	1699	2.70
2	+1	-1	-1	175	2.5	12	56.49	14.82	30.23	90.67	1617	1.60
3	-1	+1	-1	165	3.5	12	54.57	18.53	30.52	93.67	1971	2.74
4	-1	-1	-1	165	2.5	16	46.27	9.07	28.41	94.99	1948	2.68
5	+1	+1	-1	175	3.5	12	45.15	11.42	29.80	90.02	1667	0.99
6	+1	-1	+1	175	2.5	16	49.71	7.20	33.81	92.77	1194	1.95
7	-1	+1	+1	165	3.5	16	59.81	7.01	29.34	89.89	1648	2.49
8	1	1	1	175	3.5	16	41.45	10,32	30.43	90.22	1850	1.03
9	-1,682	0	0	160	3	14	41.94	8,83	29.60	88.37	1549	1.56
10	+1.682	0	0	180	3	14	32,86	14.42	28.32	87.27	1100	3.78
11	0	-1.682	0	170	2	14	34.92	9.31	27.02	86.78	2023	2.14
12	0	+1.682	0	170	4	14	34,51	11.40	28.85	87.68	1579	0.63
13	0	0	-1.682	170	3	10	40.14	11.21	36.37	90.68	2014	2.03
14	0	0	+1.682	170	3	18	36.06	8.62	32.34	88.89	1251	1.26
15	0	0	0	170	3	14	40.76	7.51	32.61	93.36	2010	0.06
16	0	0	0	170	3	14	40.15	9.12	32.28	89.28	1800	2.89
17	0	0	0	170	3	14	39.78	7.41	32.56	88.39	1980	0.77
18	0	0	0	170	3	14	39.08	9.22	33.67	94.68	1959	1.02
19	0	0	0	170	3	14	39.48	9.90	32.84	88.39	2093	2.38
20	0	0	0	170	3	14	39.92	10.12	33.26	93.58	2038	3,95

Table 5.3: Coded and real variables and the corresponding fibre characteristics for kraft pulping of hemp

Exp. No.	Coded variables			Real variables			Unbleached yield %	Permanganate No. before bleaching	Bleached yield %	Alpha-cellulose %	Degree of polymerization	Ash %
	X_1	X_2	X_3	T, C°	t, hr	A.A%						
1	-1	-1	-1	165	2.5	12	51.63	17.11	42.28	89.00	565	0.67
2	+1	-1	-1	175	2.5	12	42.86	20.00	39.13	91.00	560	0.59
3	-1	+1	-1	165	3.5	12	50.45	17.01	40.63	86.51	493	0.51
4	-1	-1	+1	165	2.5	16	46.67	12.30	37.56	87.61	554	0.71
5	+1	+1	-1	175	3.5	12	53.30	12.60	38.25	90.21	585	0.89
6	+1	-1	+1	175	2.5	16	44.70	10.10	38.66	91.77	585	0.21
7	-1	+1	+1	165	3.5	16	46.57	8.600	40.00	86.71	495	0.71
8	1	1	1	175	3.5	16	46.86	7.810	37.44	92.00	563	0.78
9	-1.682	0	0	160	3	14	50.26	13.00	42.90	90.01	567	0.35
10	+1.682	0	0	180	3	14	51.83	11.31	38.33	91.20	570	0.31
11	0	-1.682	0	170	2	14	50.51	13.27	40.36	89.90	538	0.90
12	0	+1.682	0	170	4	14	56.00	14.41	37.01	86.31	516	0.63
13	0	0	-1.682	170	3	10	51.00	17.01	40.00	86.38	530	0.37
14	0	0	+1.682	170	3	18	45.50	13.20	39.59	92.10	590	0.12
15	0	0	0	170	3	14	51.30	14.81	43.50	90.11	560	0.62
16	0	0	0	170	3	14	48.60	14.00	43.99	91.10	550	0.68
17	0	0	0	170	3	14	51.60	11.80	42.41	92.60	560	0.77
18	0	0	0	170	3	14	50.70	14.42	39.30	90.01	563	0.12
19	0	0	0	170	3	14	51.11	15.81	40.60	89.21	540	0.32
20	0	0	0	170	3	14	46.43	13.81	40.91	89.70	555	0.55

Table 5.4 . Coded and real variables and the corresponding fibre characteristics for kraft pulping of eucalyptus.

Exp.	Coded variables			Real variables			Unbleached	Kappa	Reject
	X_1	X_2	X_3	T,(°C)	t,(min)	A.A,(%)	yield,(%)	No.	(%)
1	-1	-1	-1	160	235	16	32.12	54.01	4.91
2	+1	-1	-1	170	234	16	30.21	59.91	4.42
3	-1	+1	-1	160	275	16	30.51	34.94	1.12
4	+1	+1	-1	170	275	16	29.81	37.45	1.05
5	-1	-1	+1	160	235	20	28.42	29.52	0.25
6	+1	-1	+1	170	235	20	33.81	29.02	0.12
7	-1	+1	+1	160	275	20	29.31	21.61	0.12
8	+1	+1	+1	170	275	20	30.47	24.62	0.30
9	-1.682	0	0	156	255	18	29.61	41.02	0.37
10	+1.682	0	0	170	255	18	28.32	28.51	0.27
11	0	-1.682	0	165	215	18	27.01	30.51	2.07
12	0	+1.682	0	165	295	18	28.81	35.01	0.31
13	0	0	-1.682	165	255	14	36.31	45.01	1.15
14	0	0	+1.682	165	255	22	32.01	17.01	0.05
15	0	0	0	165	255	18	32.61	22.61	0.11
16	0	0	0	165	255	18	32.21	22.03	0.13
17	0	0	0	165	255	18	32.98	23.01	0.13
18	0	0	0	165	255	18	33.01	22.98	0.15
19	0	0	0	165	255	18	32.97	21.90	0.09
20	0	0	0	165	255	18	31.88	22.97	0.07

Tables 5.5: Second-order polynomial regression results for the bleached and unbleached pulp yields, alpha-cellulose content, degree of polymerization and kappa number of the studied materials .

---

a. **For reed**:

$$Y_b=43.63-0.18X_1-0.43X_2+1.23X_3+1.20X_1X_2+0.45X_1X_3+0.36X_2X_3+1.95X_1^2+1.07X_2^2-1.43X_3^2 \quad \ldots\ldots\ldots(5.1)$$

$$AC=93.01-0.41X_1+0.24X_2-0.16X_3-0.73X_1X_2-0.94X_1X_3+0.77X_2X_3+0.12X_1^2-0.04X_2^2-1.06X_3^2 \quad \ldots\ldots\ldots(5.2)$$

$$Dp= 2807.69 - 269.61X_1 + 21.78X_2- 85.11X_3- 18.12X_1X_2+ 202.62X_1X_3+42.37X_2X_3-122.42X_1^2-484.02X_2^2-298.27X_3^2 \quad \ldots(5.3)$$

b. **For wheat straw**:

$$Y_b=32.62+0.11X_1-0.08X_2-0.55X_3-0.37X_1X_2+1.15X_1X_3-0.09X_2X_3-1.23X_1^2-1.61X_2^2+0.61X_3^2 \quad \ldots\ldots\ldots(5.4)$$

$$AC=90.35-1.02X_1-0.81X_2-0.53X_3+0.03X_1X_2+0.39X_1X_3-1.34X_2X_3-0.23X_1^2-0.45X_2^2+0.43X_3^2 \quad \ldots\ldots\ldots(5.5)$$

$$Dp=1946.44- 207.16X_1-88.20X_2-20.25X_3-50.36X_1X_2-162.8X_1X_3-138X_2X_3-221.21X_1^2-52.78X_2^2-112.34X_3^2 \quad \ldots\ldots\ldots(5.6)$$

c. **For hemp**:

$$Y_b=41.80-1.07X_1-0.51X_2-0.53X_3-0.35X_1X_2+0.50X_1X_3+0.47X_2X_3-0.48X_1^2-1.17X_2^2-0.77X_3^2 \quad \ldots\ldots\ldots(5.7)$$

$$AC=89.81+1.26X_1-0.74X_2+0.79X_3+0.33X_1X_2+0.45X_1X_3+0.34X_2X_3+0.30X_1^2-0.58X_2^2-0.21X_3^2 \quad \ldots\ldots\ldots(5.8)$$

$$Dp=554.64+ 15.56X_1- 11.71X_2+ 7.17X_3+ 17.37X_1X_2+1.87X_1X_3-3.62X_2X_3+3.08X_1^2-9.64X_2^2+2.02X_3^2 \quad \ldots\ldots\ldots(5.9)$$

d. **For eucalyptus** (unbleached pulp yield and kappa number):

$$Y_u=30.69-0.34X_1-0.9X_2-0.24X_3-0.001X_1X_2-0.29X_1X_3-0.42X_2X_3-0.65X_1^2-0.55X_2^2+0.72X_3^2 \quad \ldots\ldots\ldots(5.10)$$

$$K_p=33.11-2.10X_1-2.91X_2-7.33X_3-0.64X_1X_2+1.33X_1X_3+0.13X_2X_3+0.14X_1^2+1.13X_2^2+2.75X_3^2 \quad \ldots\ldots\ldots(5.11)$$

Where: Y_b, and Y_u= are the bleached and unbleached pulp yields, % based on moisture free raw material.

AC= is the alpha-cellulose content, % based on moisture-free raw material.

Dp= is average degree of polymerization of produced bleached pulp.

K_p= is the kappa number.

X_j, j=1-3, are the coded variables of the process conditions.

Table 5.6: Coded and real points of experimental design produced by central composite rotatable design for the nitration of reed dissolving pulps.

Experiment (series No.)	Coded variables		Real variables		N% of CN	Viscosity of CN mPa.s	Rea % of CN
	X_1	X_2	Temp.°C	Time,min			
1	-1	-1	25	30	12.62	1408.02	13.23
2	+1	-1	35	30	12.87	694.54	15.16
3	-1	+1	25	50	12.98	1384.30	17.81
4	+1	+1	35	50	12.91	534.60	15.57
5	0	-1.414	30	20	12.57	1087.02	15.29
6	-1.414	0	20	40	12.85	2054.64	11.25
7	0	+1.414	30	60	13.02	998.70	12.38
8	+1.414	0	40	40	13.00	258.87	17.81
9	0	0	30	40	12.90	316.25	14.71
10	0	0	30	40	13.03	1496.41	10.46

Note: Viscosity: that of a 1% solution of CN in acetone solvent.

N%: nitrogen content of CN.

Rea% : solubility of CN in ethyl alcohol-dimethyl ether (1:2 by volume) mixture.

Table 5.7: Coded and real points of experimental design produced by central composite rotatable design for the nitration of eucalyptus dissolving pulps.

Experiment (series No.)	Coded variables		Real variables		N% of CN	Viscosity of CN mPa.s	Rea % of CN
	X_1	X_2	Temp °C	Time, min			
1	-1	-1	25	30	13.02	258.87	15.39
2	+1	-1	35	30	12.90	144.58	14.77
3	-1	+1	25	50	13.11	252.56	10.18
4	+1	+1	35	50	12.99	252.99	11.88
5	0	-1.414	30	20	12.98	599.83	12.77
6	-1.414	0	20	40	13.04	309.38	11.25
7	0	+1.414	30	60	13.00	224.95	11.18
8	+1.414	0	40	40	13.10	116.80	15.09
9	0	0	30	40	13.02	233.61	10.84
10	0	0	30	40	12.97	189.47	10.94

Note: Viscosity: that of a 1% solution of CN in acetone solvent.

N%: nitrogen content of CN.

Rea% : solubility of CN in ethyl alcohol-dimethyl ether (1:2 by volume) mixture.

The F-values of these equations are 5.695 and 2.211 respectively, and both are exceeding the tabulated F-value of 2.2 determined at 4 degrees of freedom and within 95% confidence limits(81).

The estimated standard deviation values were found to be 0.06 and 0.068 respectively, therefore equations 5.11 and 5.12 adequately describe the process behaviour through the region studied.

5.2 PROCESS OPTIMIZATION RESULTS

5.2.1 Pulping processes optimization results

As already explained in chapter three, the optimization problem is to maximize the objective function (bleached and unbleached pulp yields) at certain levels of the equality constraints (alpha-cellulose content, average degree of polymerization, and kappa number).

Based upon the described regression analysis, the optimization problem could be formulated as follows:
The bleached pulp yield (for reed, wheat straw, and hemp), and the unbleached pulp yield (for eucalyptus) as objective function i.e.

Y_b, and $Y_u = f_1(X_1,X_2,X_3)$ should be maximized as depicted by equations (5.1), (5.4), (5.7), and (5.10) subjected to the degree of polymerization, alpha-cellulose content, and kappa number constraints, i.e. to:

$Dp = f_2(X_1,X_2,X_3)$ as depicted by equations (5.3), (5.6), and (5.9), and to,

$AC = f_3(X_1,X_2,X_3)$ as depicted by equations (5.2), (5.5), and (5.8).

$K_p = f_4(X_1,X_2,X_3)$ as depicted by equation (5.11).

These equality constraints have been investigated by random search method(61) in order to locate the optimum process controlling parameters. Random search method utilize pseudo random numbers generation over a region .

Table 5.8: Calculated and experimental optimum conditions and product characteristics.

Results	Process conditions			Characteristics		
	X_1 temp,°C	X_2 time,hr	X_3 AA%	bleached pulp yield,%	alpha-cell.,%	DP
1.Reed						
Calculated	-1.682	-1.682	-0.04	56.59	91.81	1021
	(145)	(1)	(12)			
Experimental	-1.682	-1.682	-0.04	55.21	92.42	1073
	(145)	(1)	(12)			
2.Wheat straw						
Calculated	0.0	0.0	-1.682	35.24	92.45	1662
	(170)	(3)	(10)			
Experimental	0.0	0.0	-1.682	36.32	90.62	2014
	(170)	(3)	(10)			
3.Hemp						
Calculated	-1.103	0.0	-0.381	42.51	88.69	540
	(164)	(3)	(13.24)			
Experimental	-1.103	0.0	-0.381	40.99	92.67	595
	(164)	(3)	(13.24)			
4.Eucalyptus				unbleached pulp yield,%	alpha-cell.,%	DP
Calculated	-0.263	-0.821	1.682	33.43	-	-
	(167)	(3.9)	(22)			
Experimental	-0.263	-0.821	1.682	34.01	92.42	850
	(167)	(3.9)	(22)			

Where : temp.= maximum pulping temperature, °C.

time = time of treatment at maximum temperature, hour.

AA% = active alkali (as Na_2O) percent related to moisture free material.

DP = average degree of polymerization of produced bleached pulp.

Table 5.9: Process optimization results calculated from experimental data of the nitration of eucalyptus, reed , wheat straw, and hemp dissolving pulps.

Types of pulp	Process controlling parameters		N% of CN	Viscosity of CN mPa.s	Rea% of CN	Nitrating mixture		
	X_1 (T,°C)	X_2 (t,min)				H_2SO_4 %	HNO_3 %	H_2O %
1. Eucalyptus (Calculated)	-1.414 (20)	1.414 (60)	13.11					
Eucalyptus for high N-content			13.10	290.44	9.25	65.41	24.43	10.19
Eucalyptus for low N-content			11.88	51.04	97.40	60.07	22.90	17.03
2. Reed (Calculated)	1.414 (40)	0.0 (40)	13.00					
Reed for high N-content			13.00	258.87	17.81	65.16	24.61	10.23
Reed for low N-content			11.71	126.52	97.10	60.88	22.66	16.46
3. Wheat straw (Calculated)	1.414 (40)	0.0 (40)	13.00					
Wheat straw for high N-content			12.97	275.78	18.05	65.23	24.73	10.04
Wheat straw for low N-content			11.78	132.95	98.02	60.78	21.87	17.35
4. Hemp (Calculated)	1.414 (40)	0.0 (40)	13.00					
Hemp for high N-content			13.02	254.65	17.45	65.23	24.73	10.04
Hemp for low N-content			11.97	119.96	97.85	60.78	21.87	10.04

Note: Viscosity: that of a 1% solution of CN in acetone solvent.
N %: nitrogen content of CN.
Rea: solubility of CN in ethyl alcohol-dimethyl ether (1:2 by volume) mixture.

Table 5.8 shows the final results of the optimization, obtained by above method. The optimum conditions generated were later confirmed experimentaly, the results clearly indicated the agreement between calculated and experimental optimum values.

5.2.2 **Optimization results of nitration reactions**

As already mentioned, based upon the described regression analysis, the optimization problem was carried out on reed and eucalyptys dissolving pulps and formulated as follows:
The nitrogen content (objective function) i.e. ;

N% $= f_5(X_1,X_2)$ should be maximized as depicted by equations (5.12) and (5.13).

Computer programmes were set up to generate the solutions of the above optimizatiom problem using regression equations (5.12) and (5.13) and random searching method$^{(61)}$.

The results presented in Table 5.9 define the optimum conditions applied with the acid mixture described in Table 3.14 .

The optimum conditions generated by reed were later confirmed experimentally by wheat straw and hemp. The results shown in Table 5.9 indicate the agreement between calculated and experimental optimal values.

5.3 **EFFECT OF PROCESS VARIABLES ON CHARACTRISTICS OF PRODUCED PULPS AND CELLULOSE NITRATES**

Effects of temperature, time of treatment and concentration of active alkali, respectively on bleached pulp yield, and alpha-cellulose content , respectively, are shown for reed, wheat straw, and for hemp on Figures 5.1-5.24 .

Increasing temperature decreased the bleached pulp yield of reed from 145 through 165 °C, and of wheat straw from 160 through 170 °C, rather rapid drop occurred however at higher temperatures. The numerically higher bleached pulp yield of hemp started to decrease, without any initial increase, also at temperature, higher than 170 °C.

The relative loss in bleached pulp yield between pulping at 145 and 165 °C was 17.5% for a reed (Figure 5.1), same trend occurred in the pulping of wheat straw and hemp. The relative loss in bleached pulp yield between pulping at 160 and 180 °C was 16.7% for wheat straw and 9.5% for hemp (Figures 5.2-5.3). The drop in bleached pulp yield is due to the, with the increasing pulping temperature steadily higher rate of cellulose degradation. This phenomenon is bringing about partial dissolution of hemicellulose and smaller molecular cellulose fractions in the pulping alkali solution, simultaneously with the removal of solubilized lignin.

Long time of treatment decreased the bleached pulp yield for a reed. While different trend occurred in a case of wheat straw and of hemp. Increasing time of treatment increased the bleached pulp yield. Maximum peak occurred at a treatment for 1 hour for a reed, and 3 hours for both a wheat straw and for a hemp. Longer pulping caused well detectable loss in yield. 14.61% decrease occurred in yield of reed pulping (Figure 5.4). 20% increase in yield is detectable for wheat straw between the starting point and the maximum peak, and 11% loss occurred between the peak and the endpoint of the curve (Figure 5.5). 5% increase and 7% drop in bleached pulp yield of hemp occurred in the corresponding time of treatment ranges of pulping (Figure 5.6). These phenomena are due to the faster delignification and to the slower cellulose degradation.

Increasing active alkai charge increased the bleached pulp yield of reed from 8% through 16%, rather rapid drop occurred however at higher changes. Initially rapid drop in bleached pulp yield of wheat straw stopped arriving at a limiting value with the increasing concentration of active alkali in the pulping liquor. In the case of hemp, however the initially constant yield dropped continuously in the studied range of active alkali charge. The gain in yield for reed was 7.61% (Figure 5.7). The loss in yield for wheat straw and hemp, between the starting and final value was 11% (Figures 5.8-5.9). The higher was the concentration of the sodium hydroxide solution, the faster was the degradation of cellulose and the solubilization of its fractions.

Alpha-cellulose content of reed was increased with a temperature increasing (Figure 5.10). The initially higher (95%) alpha-cellulose content of wheat straw pulp continuously decreased to 89% with the increase in pulping temperature (Figure 5.11). The initially lower (91%) alpha-cellulose content of hemp pulp did not change, however in the studied range of pulping temperature (Figure 5.12). The higher DP of wheat straw cellulose (1600-2000) was much more sensitive to alkaline degradation, than the much lower, the limiting value approaching one of hemp cellulose. Consequently more detectable amount of alkali soluble low molecular fractions were generated by the higher temperature from wheat straw cellulose, than from hemp cellulose.

The initially high (92%) alpha-cellulose content of reed pulp contiuously increased to 97% with the increase in time of tretment (Figure 5.13). Completely same tendency could be detected for changes in alpha-cellulose content under the action of steadily increasing time of pulping. In the case of wheat straw at 170 °C the rate of delignification was exceeding that of the alkaline cellulose degradation in the full range of the studied time of treatment. Consequently 5% increase was observed in alpha-cellulose content in that range (Figure 5.14). Opposite was the case with hemp. The rate of its delignification was relatively low at 170 °C, therefore the 4.5% drop in alpha-cellulose content might be due to the detectable detrimental effect of alkali on cellulose under the action of pulping lasting longer than for 3 hours (Figure 5.15).

3% loss in alpha-cellulose content was caused in wheat straw by 80% increase in active alkali charge (Figure 5.17), and practically no change occurred in that of a reed and of a hemp under similar conditions (Figures 5.16-5.18).

The DP of the wheat straw pulp cellulose increased in the range of pulping temperature from 160 °C through 170 °C by 73%. At higher temperatures (from 170 °C through 180 °C) DP decreased continuously, but still remained by 21% higher than the values obtained at 160 °C (DP=950) (Figure 5.19). No change in the DP of hemp pulp cellulose (DP=580) occurred, however, in the full range (160-180 °C) of pulping temperature (Figure 5.20).

The DP of wheat straw pulp cellulose increased by 40% in the range of duration of pulping from two through four hours. Maximal DP was, however remained already in pulping for three hours (Figure 5.21).

The DP of hemp pulp cellulose decreased with the increasing duration of pulping (2.0-4.0 hours) by 14%. No significant drop in DP occurred, however between two and three hours long pulping (Figure 5.22).

The DP of wheat straw pulp cellulose increased in the range of active alkali charge from 10 through 14% by 18%. It dropped, however with higher alkali concentrations by 3% of the DP corresponding with a pulping active alkali charge of 10% (Figure 5.23).

No dependence of the DP of hemp pulp cellulose could be observed on the active alkali concentration of the pulping liquor (Figure 5.24)).

The unbleached yield of eucalyptus pulp decreased by 9% in the range of temperature from 155 °C through 175 °C. Maximal unbleached pulp yield was, however remained already in pulping temperature of 167 °C (Figure 5.25).

The unbleached pulp yield of eucalyptus decreased also with the increasing duration of pulping from 3.5 hours through 4.2 hours by 17.64%. Longer pulping cause well detectable loss in yield (Figure 5.26).

No significant change in unbleached pulp yield of eucalyptus (30%-32%) occurred, however, in the full range (14%-22%) of pulping active alkali charge (Figure 5.27).

Kappa number of eucalyptus pulp cellulose increased with a temperature increasing. 6.45% increase occurred in kappa number due to the condensation of lignin at a higher temperatures (Figure 5.28). While completely different tendency could be detected for changes in kappa number under the action of steadily increasing in duration of pulping and of active alkali charge.

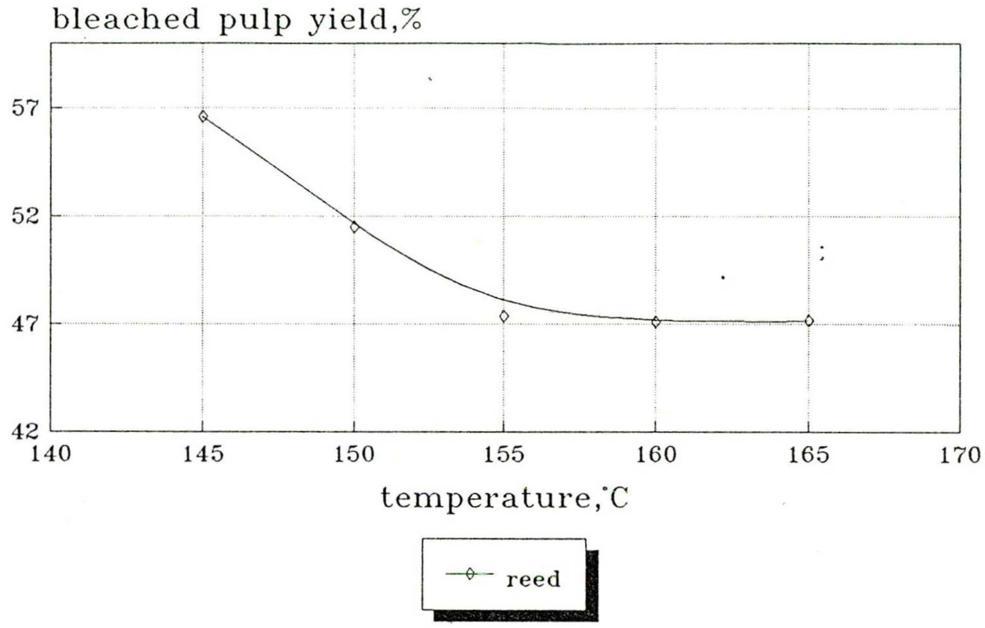
The initially high kappa number continuously decreased with the increase in duration of pulping and active alkali charge. This was due to the high rate of delignification through these ranges of duration of pulping and of active alkali charge. After 4.5 hours and 20% of active alkali charge no change in kappa number was occurred (Figure 5.29-5.30).

Effects of temperature and duration of nitration on nitrogen content of the produced cellulose nitrates are demonstrated for eucalyptus and reed dissolving pulps on Figures 5.31-5.32 .

Increasing temperature increased the nitrogen content of reed cellulose nitrate from 20 through 40 °C (Figure 5.31). The initially higher (13.25%) nitrogen content of eucalyptus cellulose nitrate continuously decreased to 13.18% with the increase in nitration temperature (Figure 5.31). The gain in nitration of reed dissolving pulps was 1.16% , while the loss in eucalyptus dissolving pulps nitration was 2.41%. This loss was due to the decomposition of cellulose nitrate at a higher temperature.

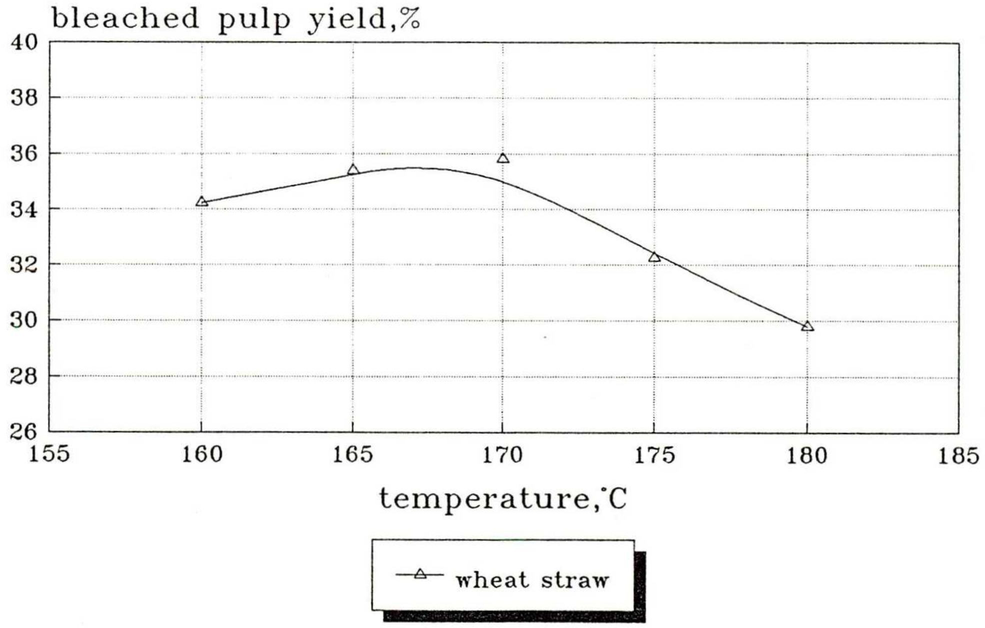
Long duration of nitration increased the nitrogen content of cellulose nitrates for both dissolving pulps of reed and eucalyptus (Figure 5.32). Maximum peak for reed dissolving pulps nitration occurred at a treatment for 40 minutes. Longer nitration caused well detectable loss in nitration. 2.79% increase in nitrogen content is detectable for eucalyptus cellulose nitrate between the starting and end points of nitration. 1.64% increase and 0.3% drop of reed cellulose nitrate in the corresponding duration of treatment ranges of nitration (Figure 5.32).

Figure 5.1: The effect of temperature upon bleached pulp yield.



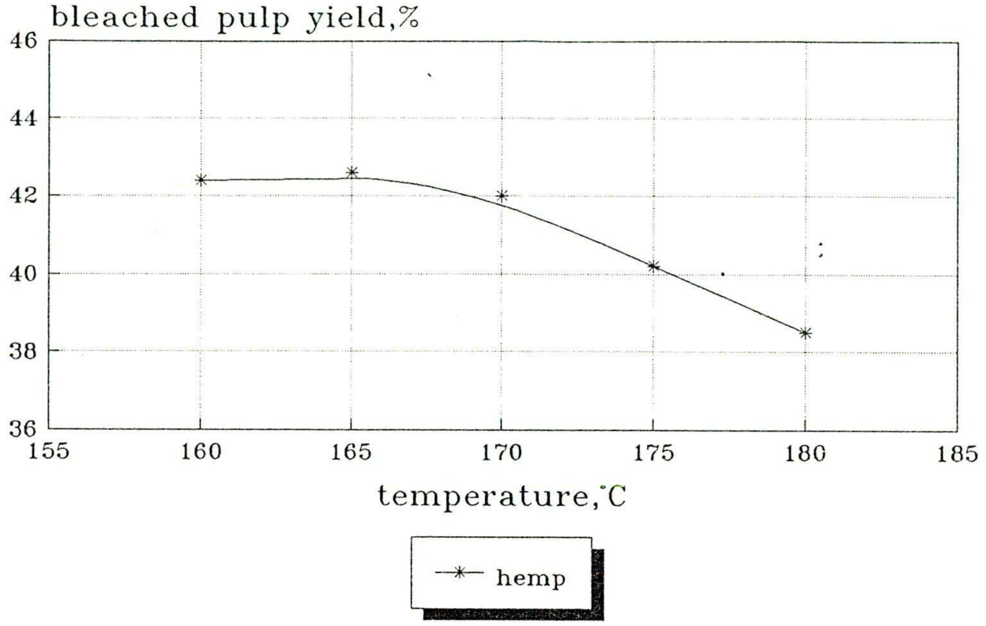
time=1 hour, and active alkali=12%

Figure 5.2: The effect of temperature upon bleached pulp yield.



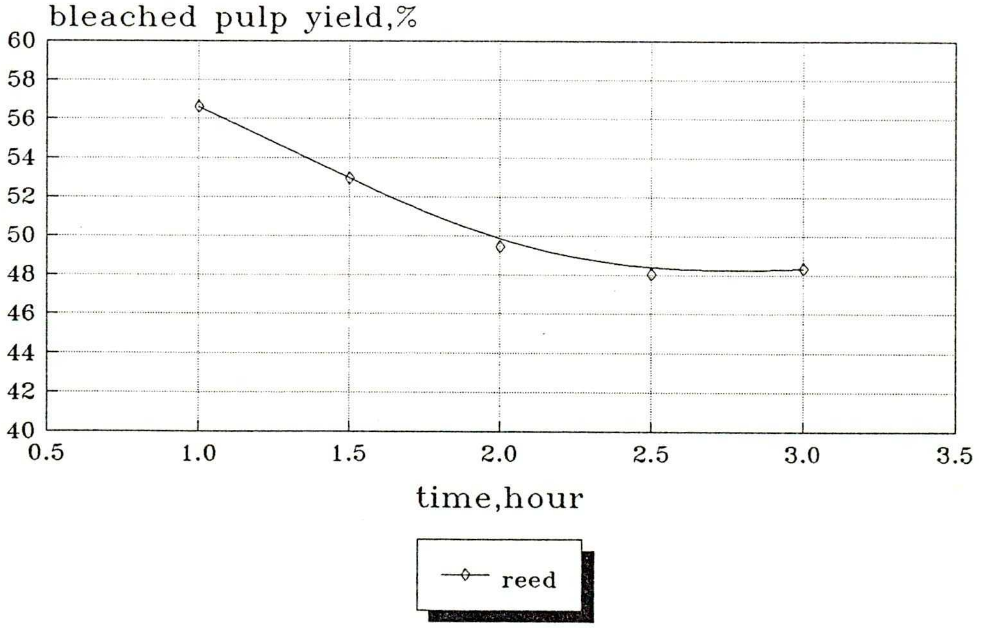
time =3 hour, and active alkali=10%

Figure 5.3: The effect of temperature upon bleached pulp yield.



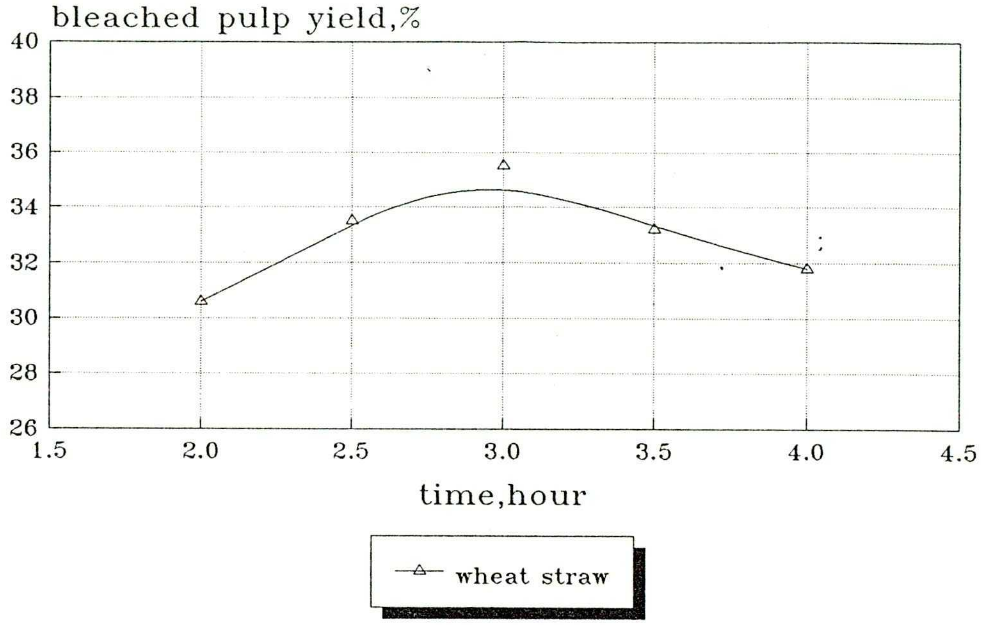
time=3 hour, and active alkali=13.24%

Figure 5.4: The effect of time upon bleached pulp yield.



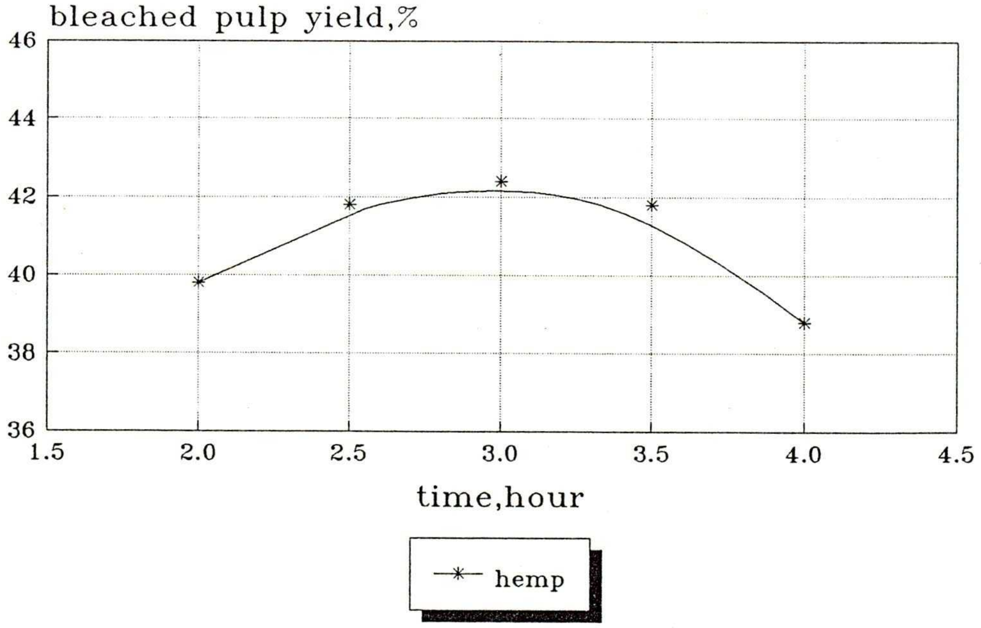
temp.=145 °C, and active alkali=12%

Figure 5.5: The effect of time upon bleached pulp yield.



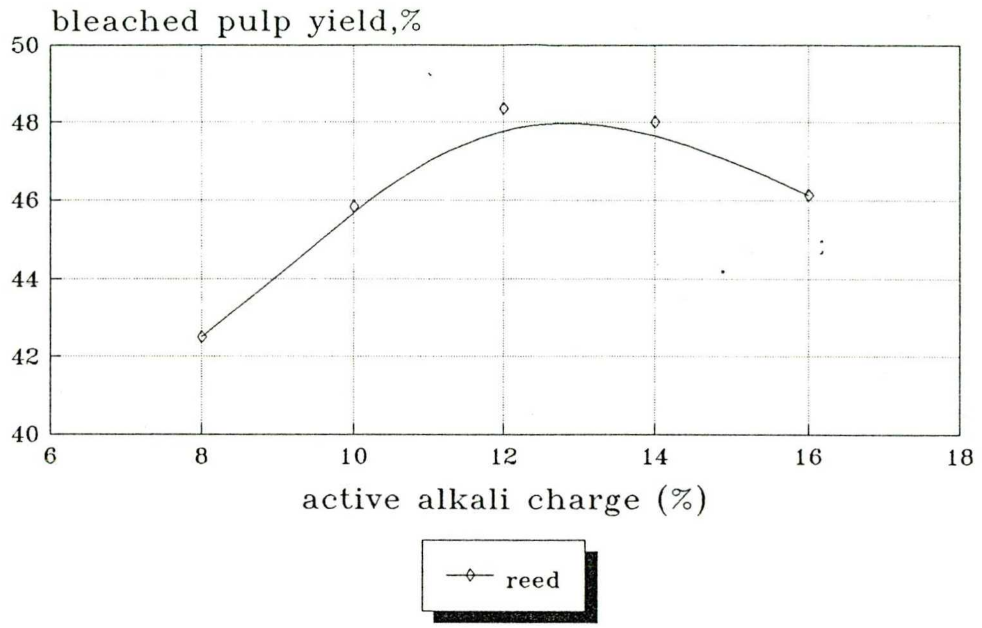
temp.=170 °C, and active alkali=10%

Figure 5.6: The effect of time upon bleached pulp yield.



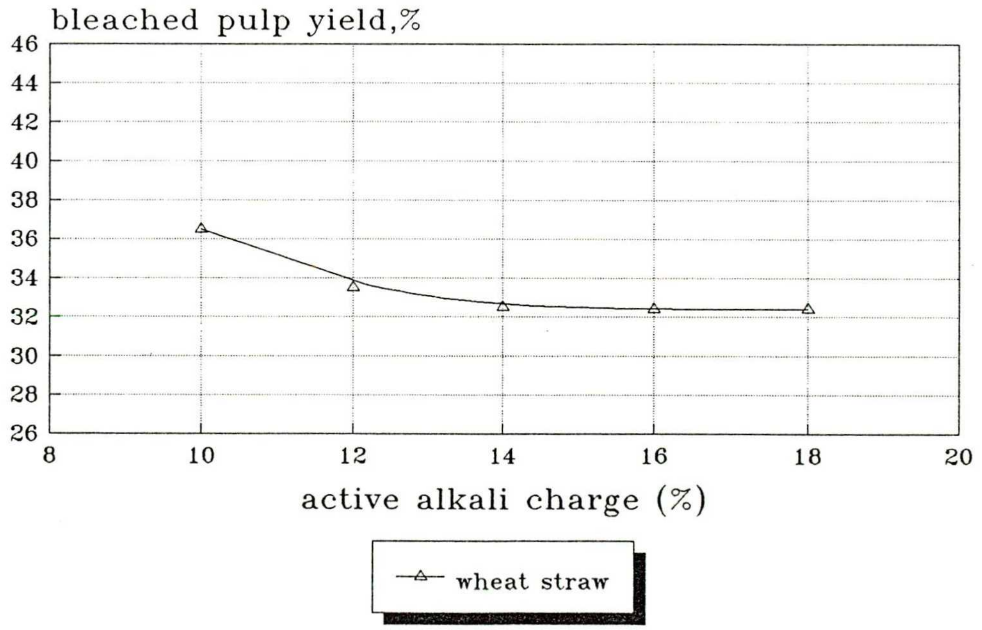
temp.=164 °C, and active alkali=13.24%

Figure 5.7: The effect of active alkali charge upon bleached pulp yield .



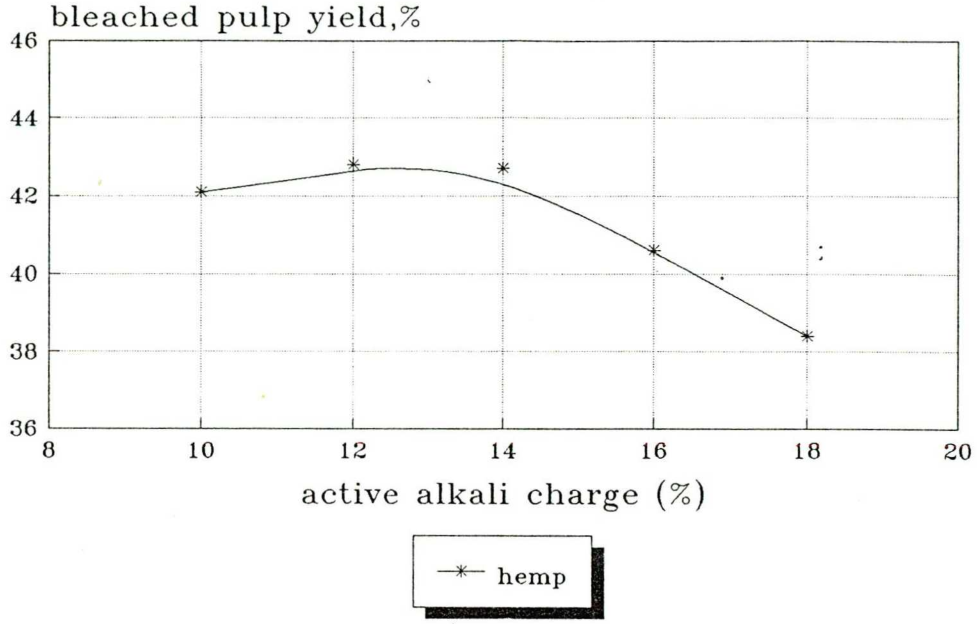
time=1 hour, and temp.=145 °C

Figure 5.8: The effect of active alkali charge upon bleached pulp yield .



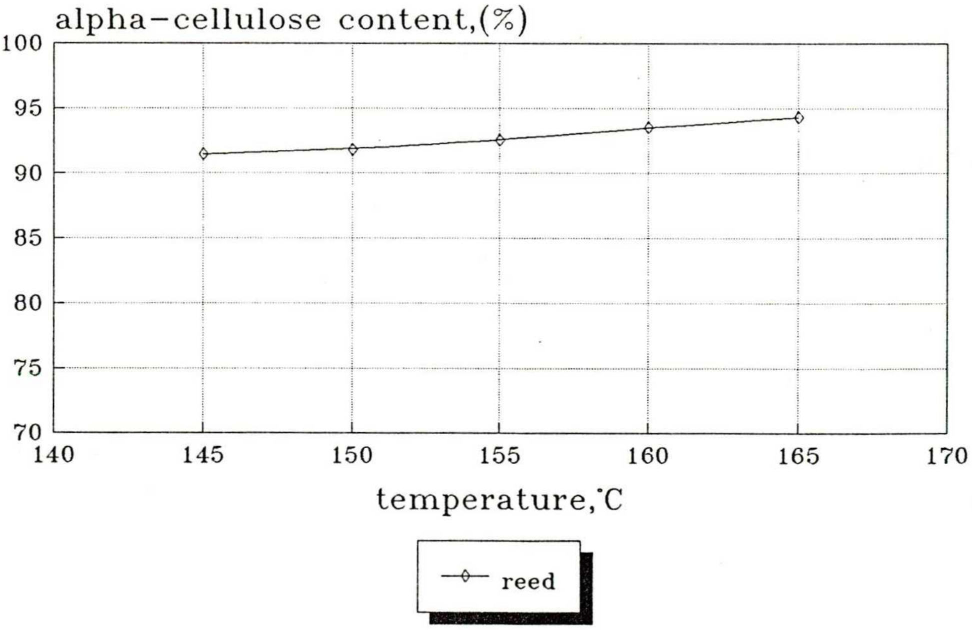
time=3 hour, and temp.=170 °C

Figure 5.9: The effect of active alkali charge upon bleached pulp yield .



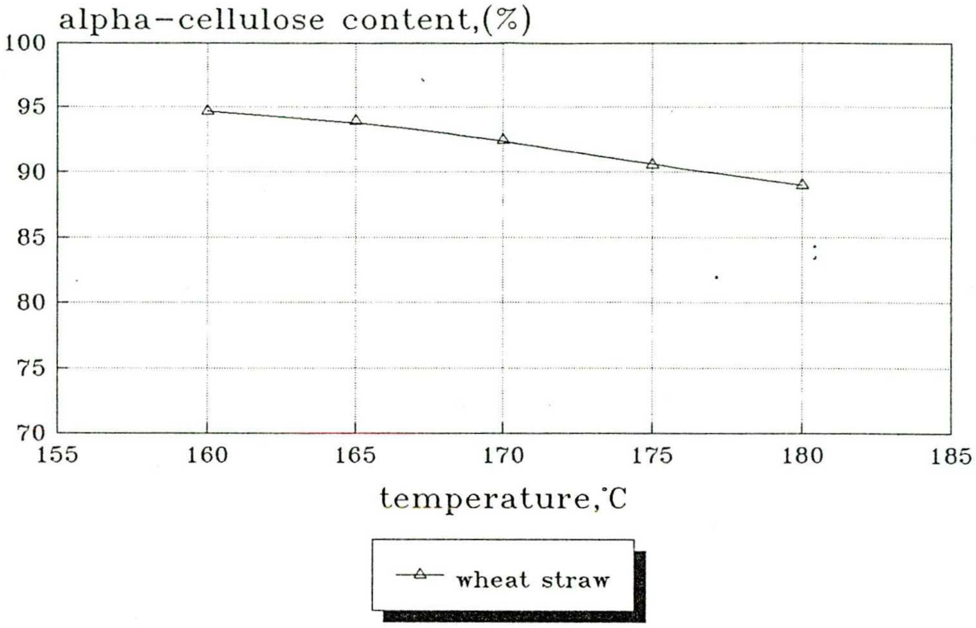
time=3 hour, and temp.=164 °C.

Figure 5.10: effect of temperature upon alpha-cellulose content.



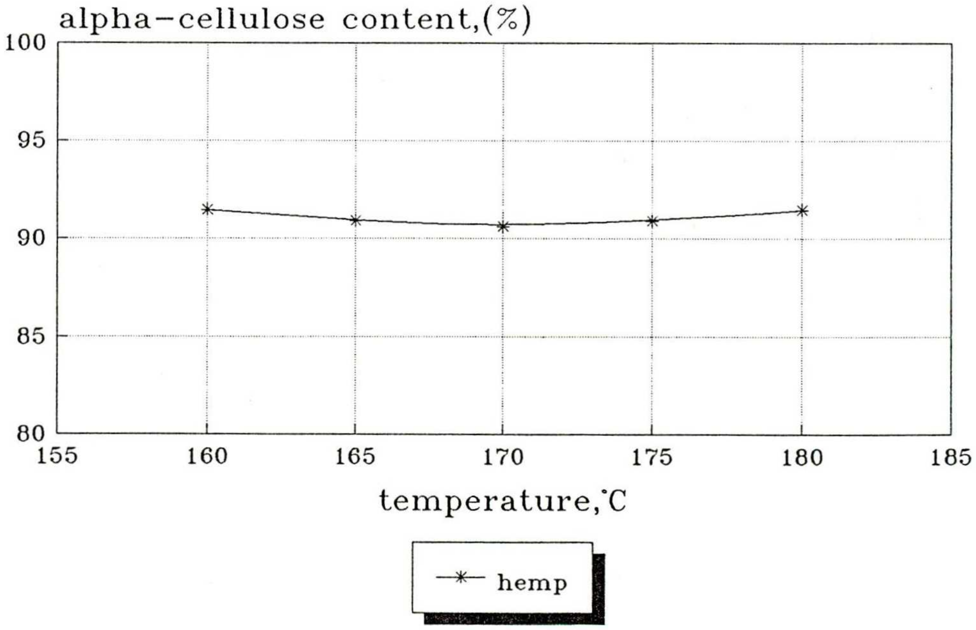
time=1 hour, and active alkali=12%

Figure 5.11:The effect of temperature upon alpha-cellulose content.



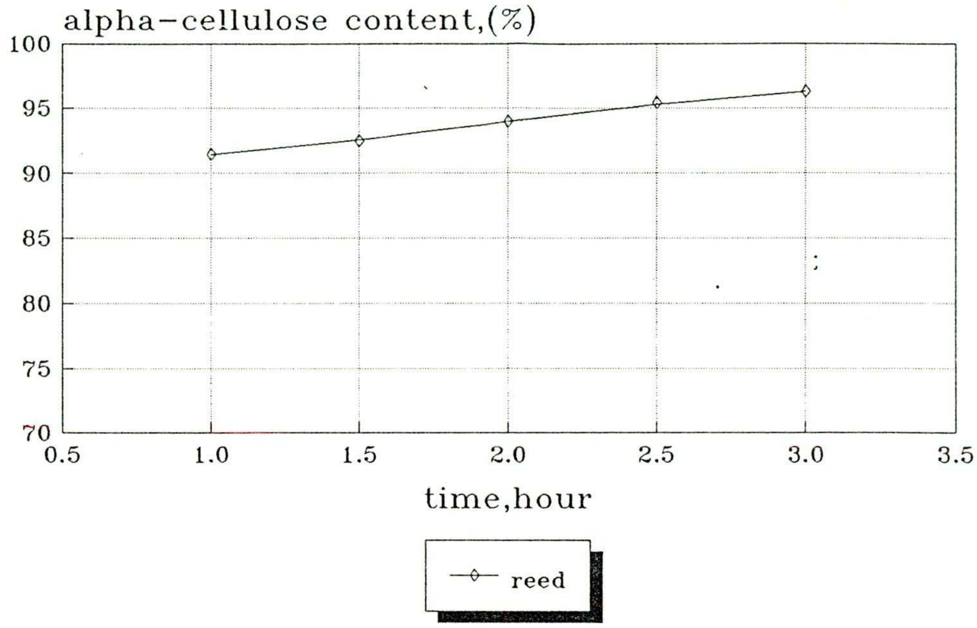
time =3 hour, and active alkali=10%

Figure 5.12:The effect of temperature upon alpha-cellulose content.



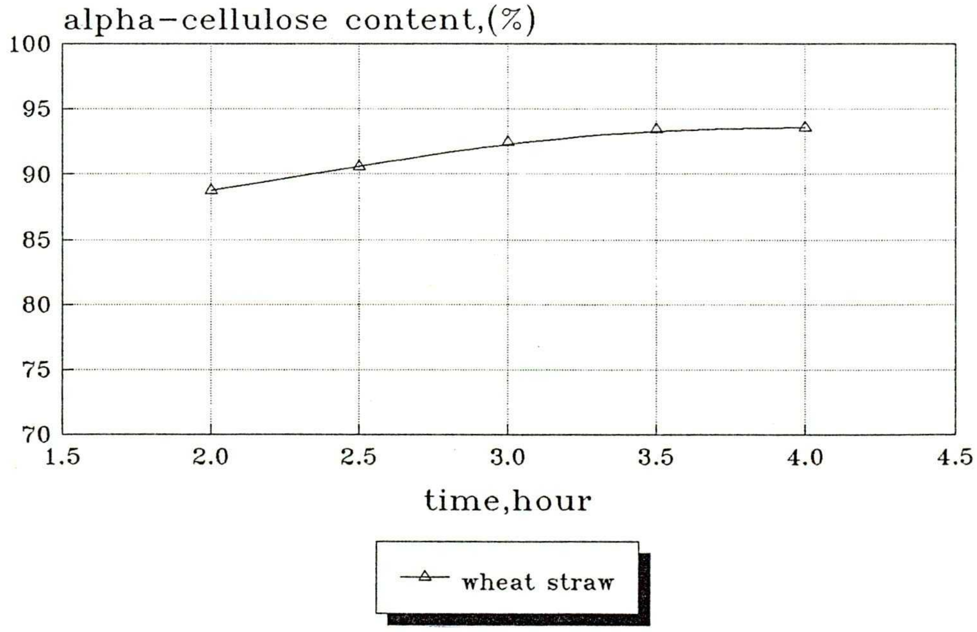
time=3 hour, and active alkali=13.24%

Figure 5.13: effect of time upon alpha-cellulose content.



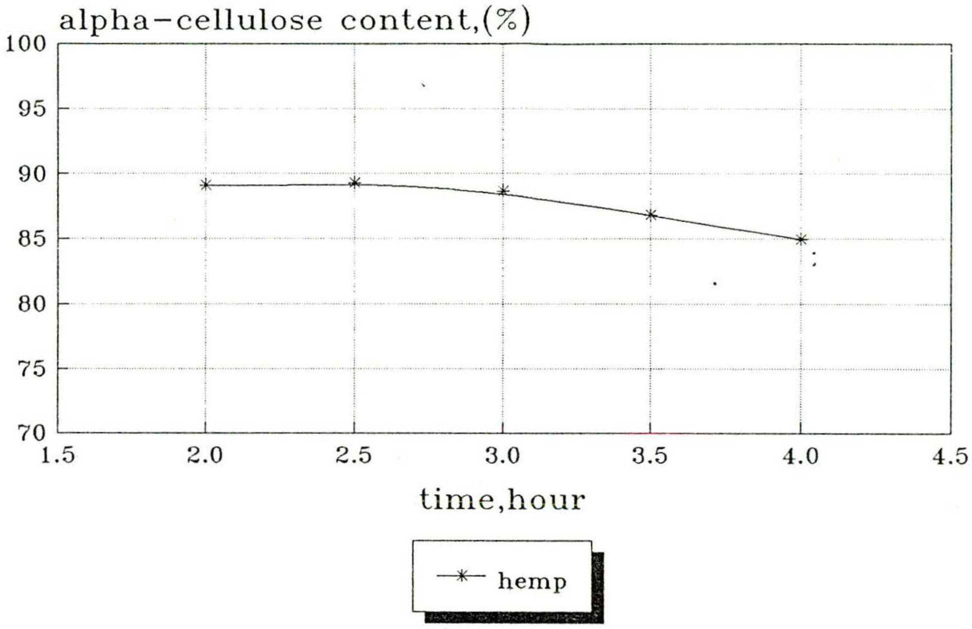
temp.=145 °C, and active alkali=12%

Figure 5.14:The effect of time upon alpha-cellulose content.



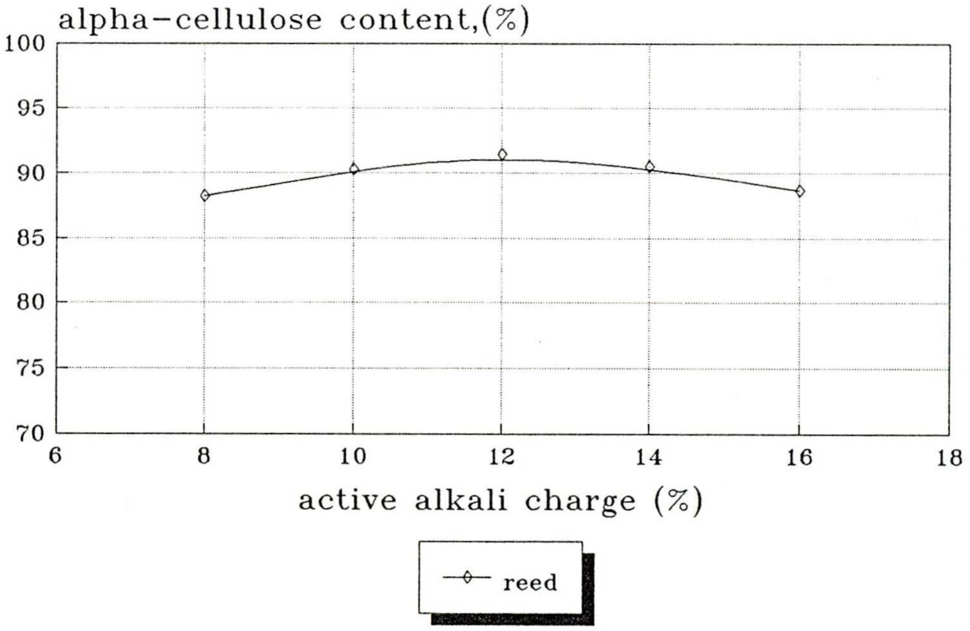
temp.=170 °C, and active alkali=10%

Figure 5.15:The effect of time upon alpha-cellulose content.



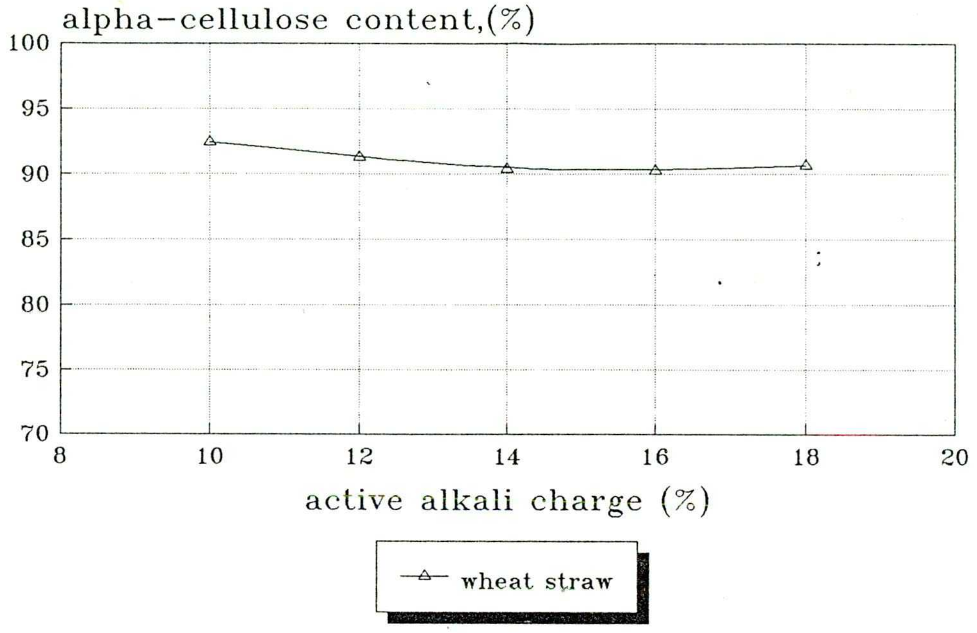
temp.=164 °C, and active alkali=13.24%

Figure 5.16: effect of active alkali charge upon alpha-cellulose content.



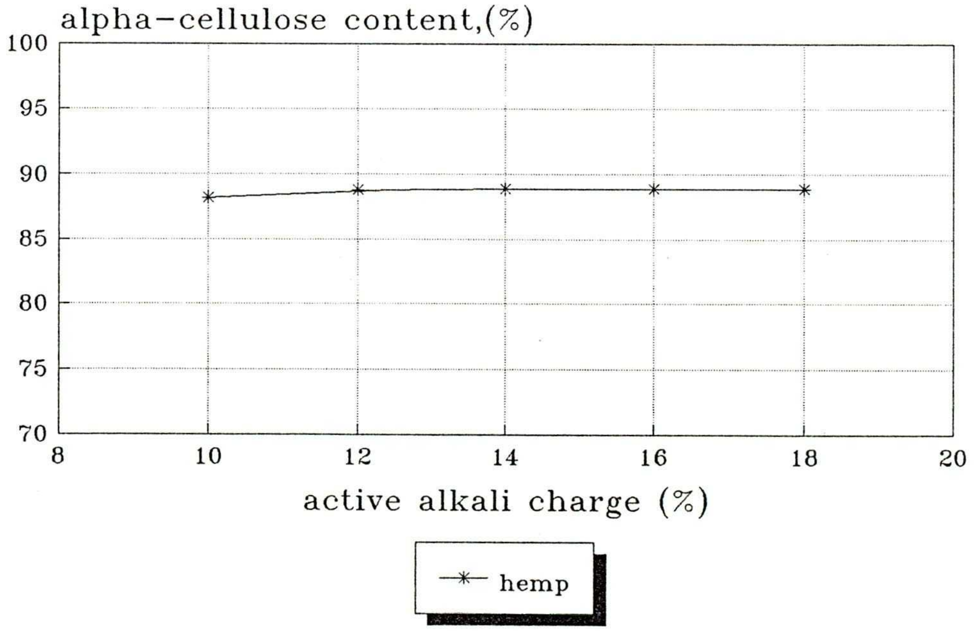
time=1 hour, and temp.=145 °C

Figure 5.17: The effect of active alkali charge upon alpha-cellulose content.



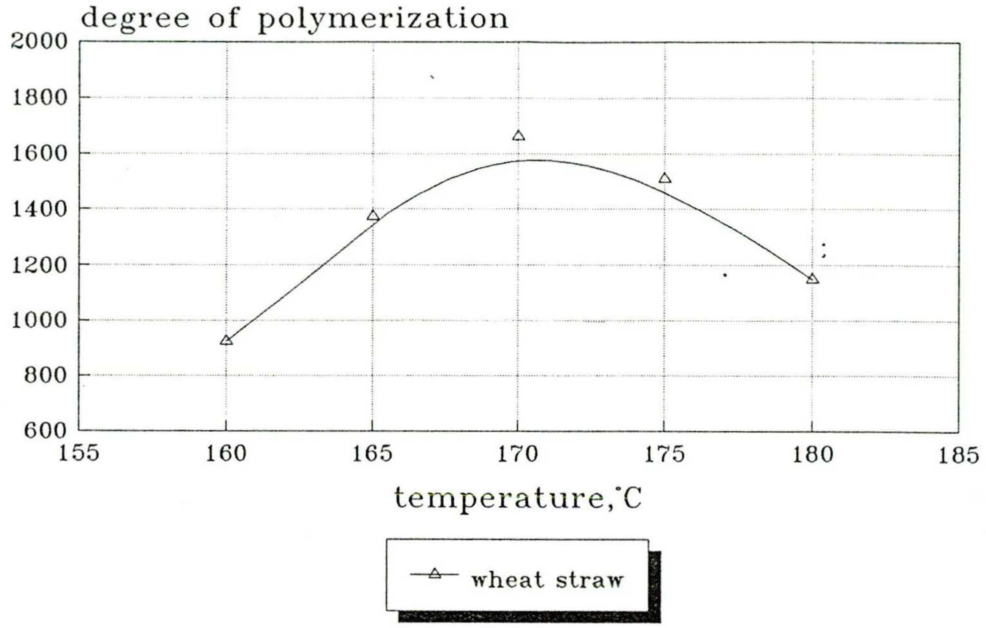
time=3 hour, and temp.=170 °C

Figure 5.18: The effect of active alkali charge upon alpha-cellulose content.



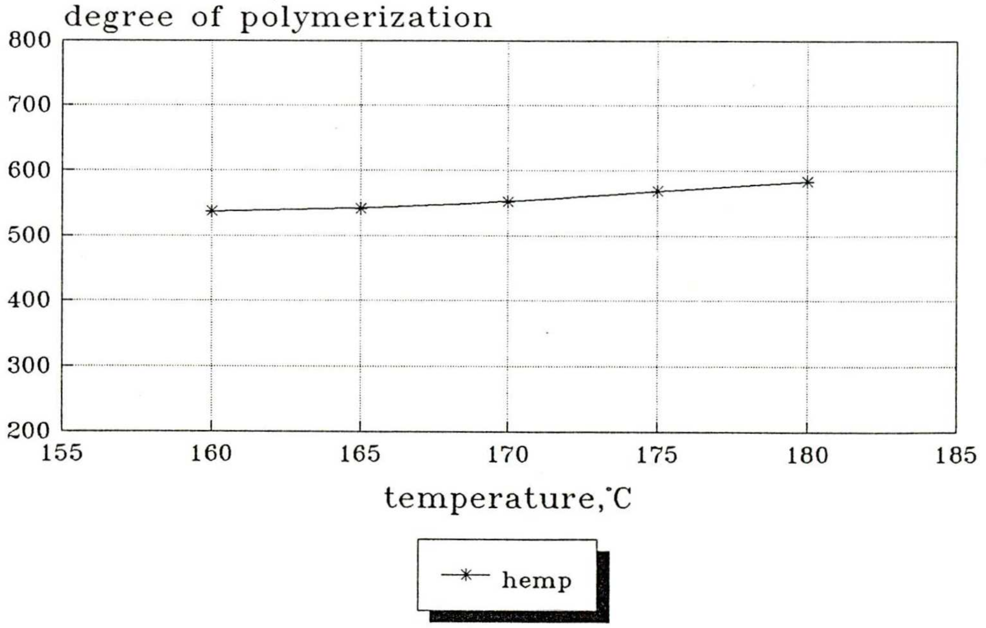
time=3 hour, and temp.=164 °C

Figure 5.19: effect of temperature upon degree of polymerization.



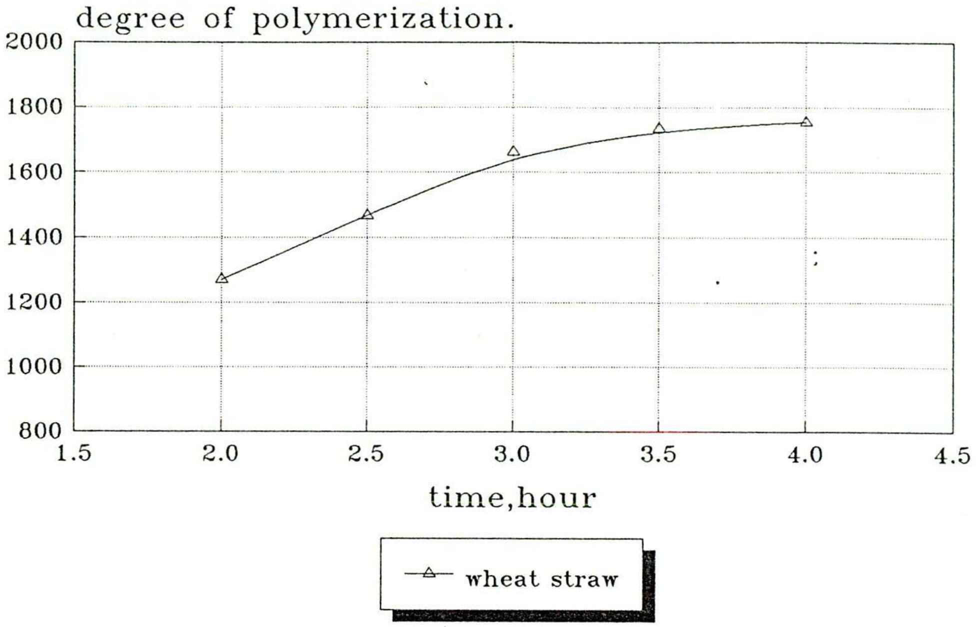
time=3 hour, and active alkaki=10%

Figure 5.20: effect of temperature upon degree of polymerization.



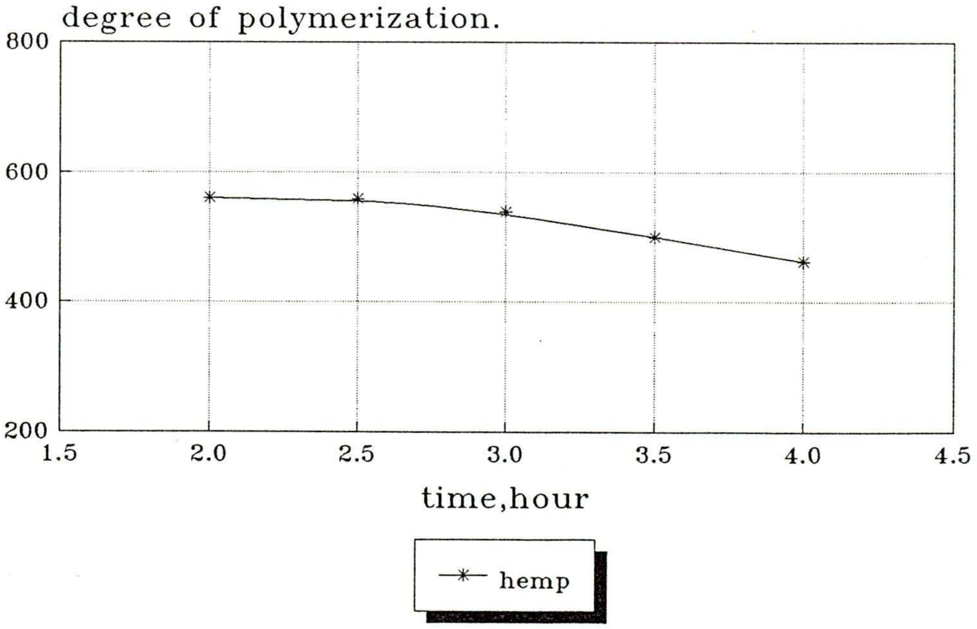
time=3 hour, and active alkali=13.24%

Figure 5.21:effect of time upon the degree of polymerization.



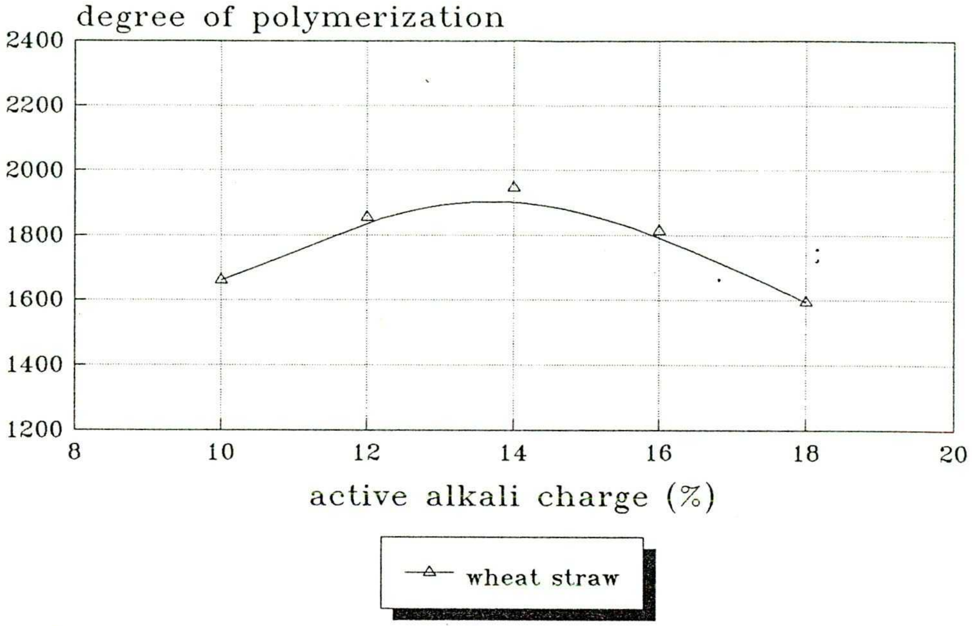
temp.=170 °C, and active alkali=10%

Figure 5.22: effect of time upon the degree of polymerization.



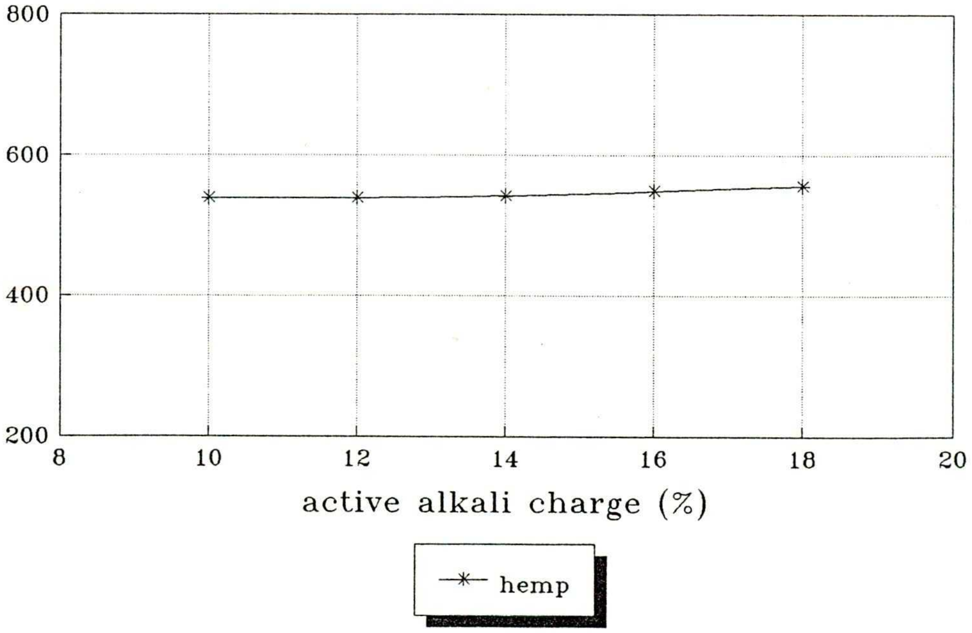
temp.=164 °C, and active alkali=13.24%

Figure 5.23: effect of active alkali upon degree of polymerization.



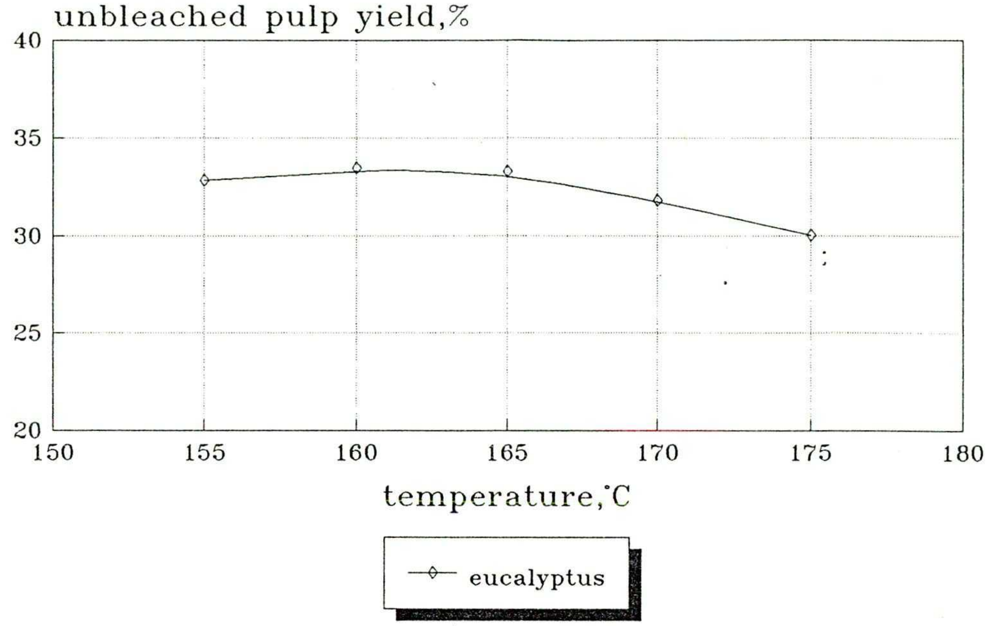
time=3 hour, and temp.=170 °C

Figure 5.24:effect of active alkali upon degree of polymerization.



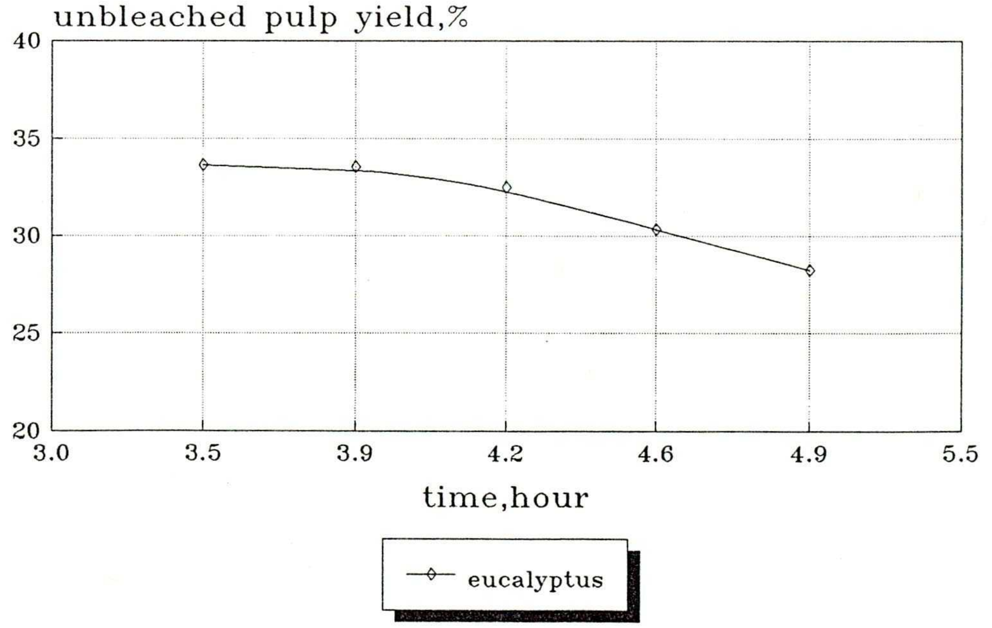
time=3 hour, and temp.=164 °C

Figure 5.25:The effect of temperature upon unbleached pulp yield.



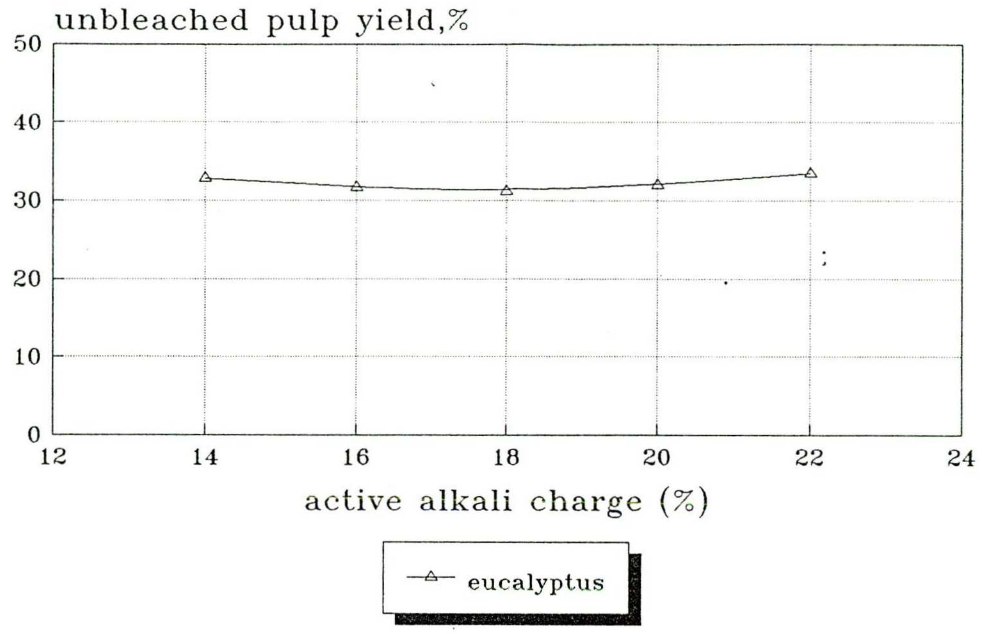
time=3.9 hour, and active alkali=22%

Figure 5.26:The effect of time upon unbleached pulp yield.



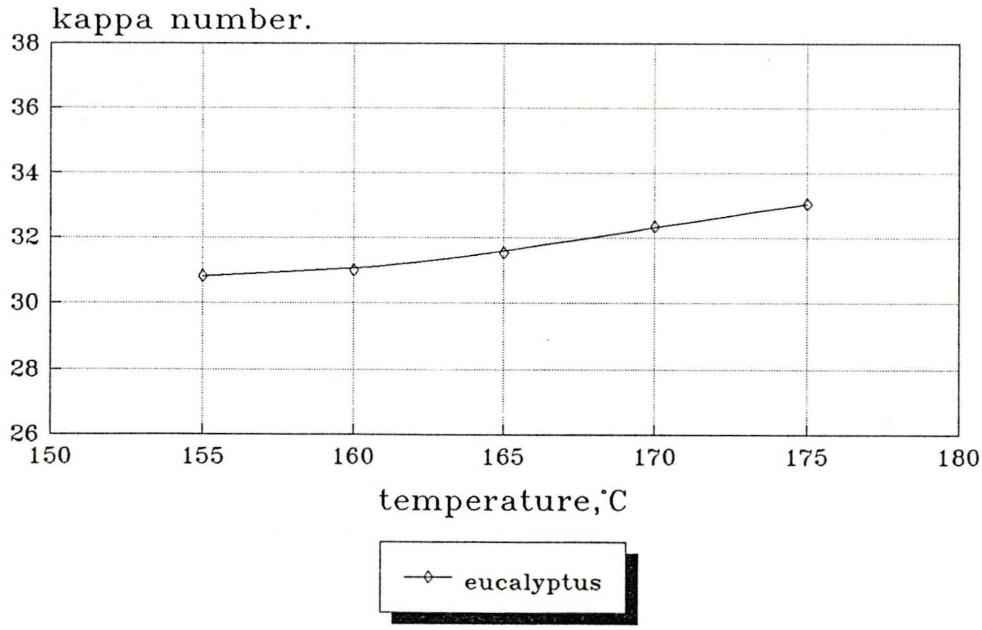
temp.=167 ˚C, and active alkali=22%

Figure 5.27: The effect of active alkali charge upon unbleached pulp yield .



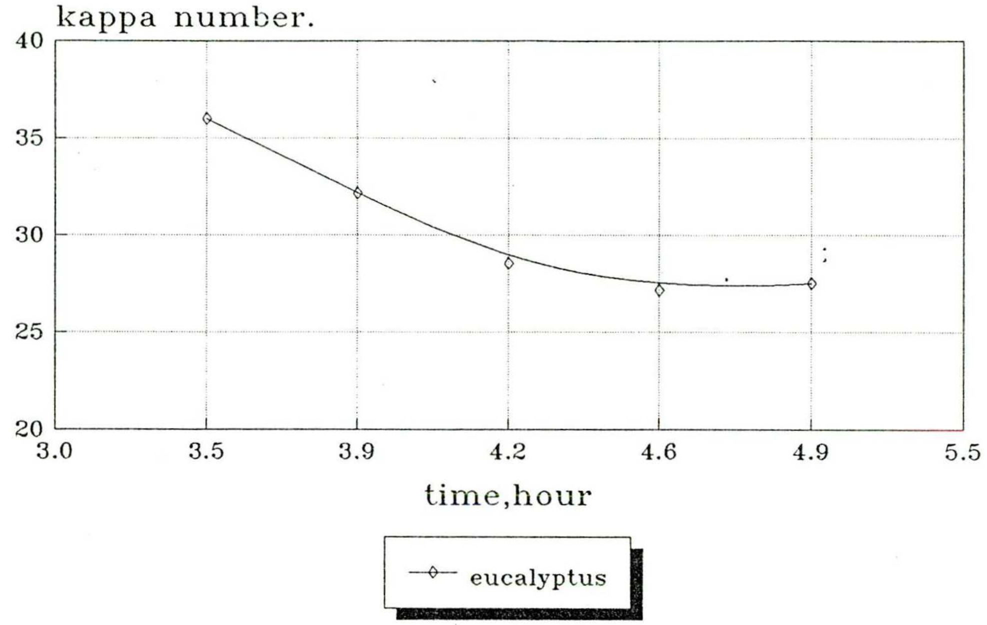
time=3.9 hour, and temp.=167 °C

Figure 5.28: effect of temperature upon kappa number.



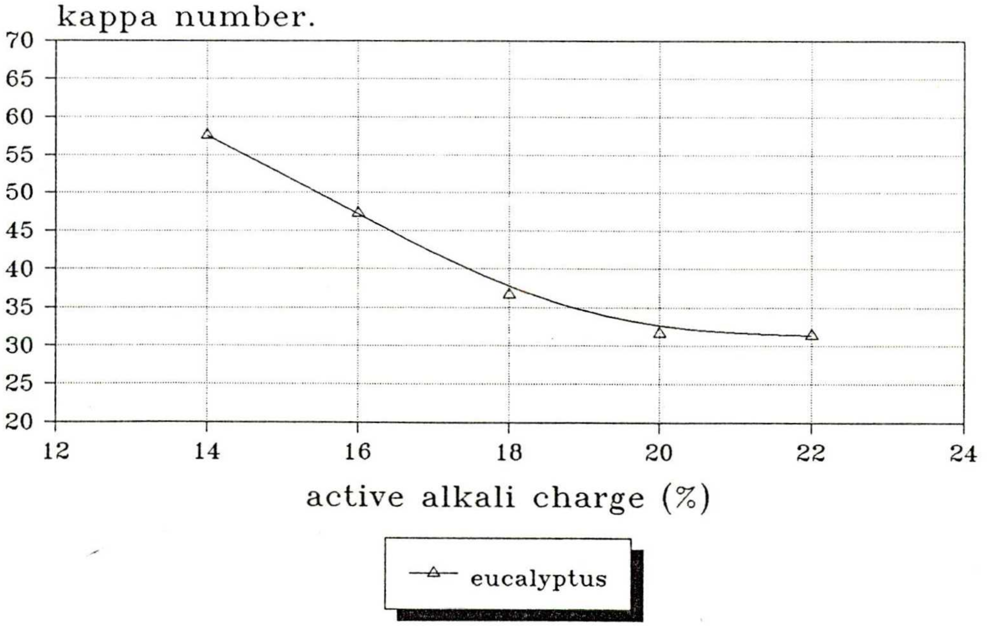
time=3.9 hour, and active alkali=22%

Figure 5.29: effect of time upon kappa number.



temp.=167 'C, and active alkali=22%

Figure 5.30: effect of active alkali charge upon kappa number.



time=3.9 hour, and temp.=167 'C

Figure 5.31:effect of temperature upon the nitrogen content of reed and eucalyptus pulps nitrated for optimum durations

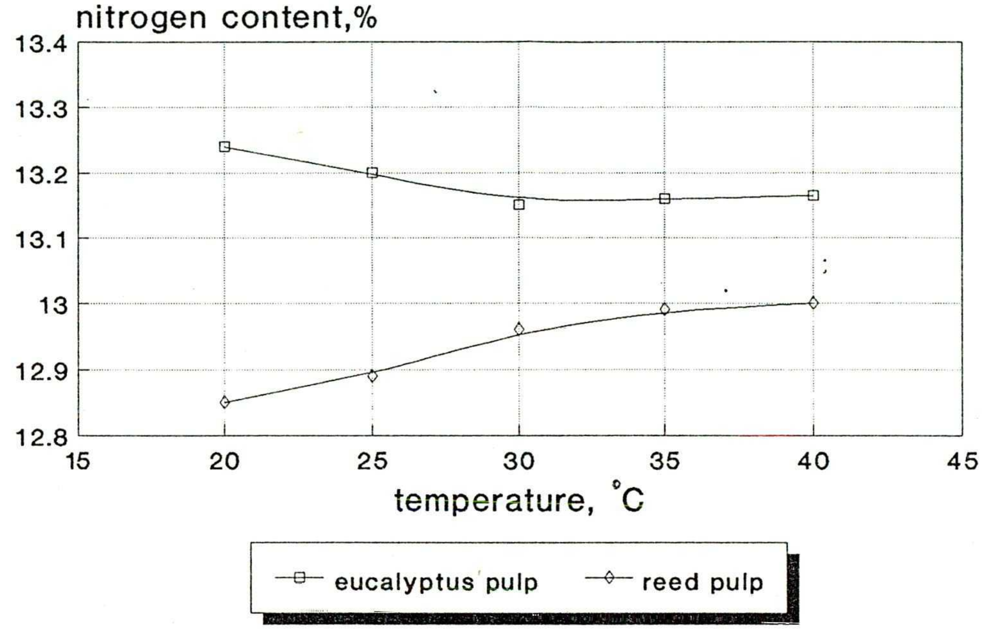
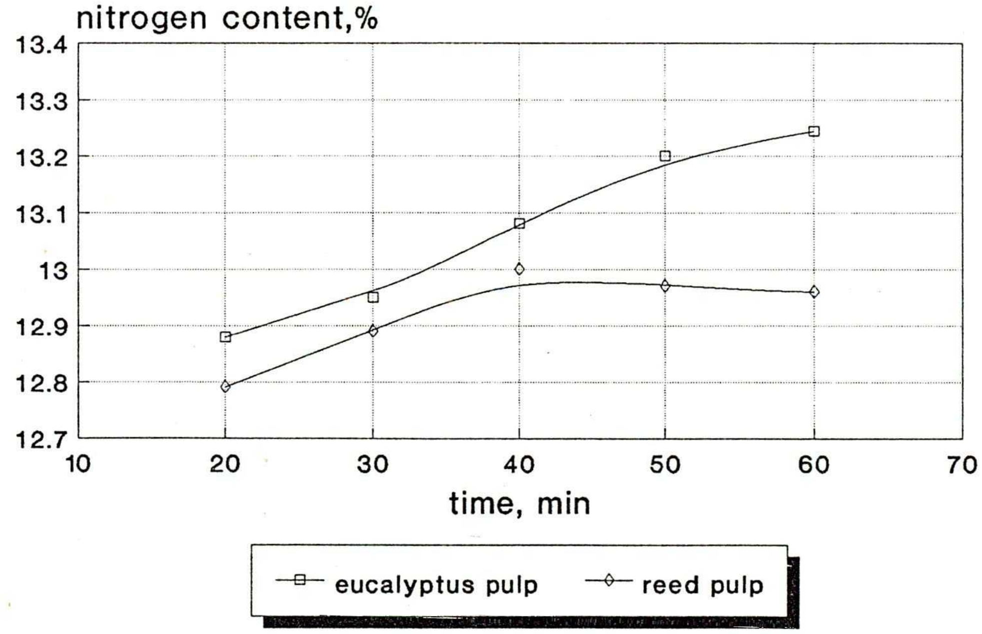


Figure 5.32:effect of reaction time upon nitrogen content of reed and eucalyptus pulps nitrated at optimum temperature.



5.4 CONCLUSIONS

Based upon disclosed results the following can be concluded:

- Maximum bleached pulp yields become apparent by pulping at (145, 170, 164) °C, for (1, 3, 3) hours, and with an active alkali charge of (12%, 10%, 13.24%) for reed, wheat straw and hemp respectively.

- Maximum unbleached pulp yield for eucalyptus becomes apparent by pulping: at 167 °C, for 3.9 hours, and with an active alkali charge of 22%.

- By applying the selected highest values of the different process parameters in pulping, the following order of sequence occurred in their detrimental effect on:

a. Bleached pulp yield:

1. For reed : temperature> duration of pulping> active alkali charge had increasing effect on the bleached pulp yield.
2. For wheat straw: temperature > active alkali charge > longest duration had increasing effect on the bleached pulp yield.
3. For hemp : temperature > active alkali charge > duration of pulping.

b. Unbleached pulp yield:

- For eucalyptus: duration of pulping> temperature> no change occurred in the full range of pulping active alkali charge.

- Order of sequence of the highest values of the selected process parameters on the alpha-cellulose content:

1. For reed: duration of pulping> higher temperature decreasing effect on the alpha-cellulose content> no chnge occurred in the full range of pulping active alkali charge.
2. For wheat straw: temperature > duration of pulping > active alkali charge.
3. For hemp: duration of treatment, neither temperature, nor active alkali charge changed the alpha-cellulose content.

- Bleached pulp yield of reed (55.21%) definitely exceeded that of wheat straw (36.32%), and of hemp (40.99%), while alpha-cellulose content of all plants cellulose pulps are about the same (90%-93%).

- Pulping temperature sensitively influences the DP of wheat straw pulp cellulose. It is likely that at higher temperature the increase in the rate of dissolution of hemicellulose and low molecular fractions of cellulose was significantly exceeding that of the rate of cellulose degradation.
  The independence of hemp pulp cellulose DP of the pulping temperature might be due to partly the lower starting DP (less sensitive at that range of molecular mass to hot alkaline degradation) and partly to the instant solubility of hemicellulose and already depolymerized cellulose still at 160 °C). The DP of wheat straw pulp cellulose is sensitively increasing with the longer duration of pulping.
  The rate of dissolution of hemicellulose and already depolymerized cellulose is exceeding the rate of cellulose degradation in the studied range of time of pulping. Due to significantly higher initial (pulping for less than two hours) depolymerization of cellulose and/or less sensitive types of hemicellulose in hemp, might be the reason of practical independence of the DP of hemp pulp cellulose of the duration of pulping. The DP of wheat straw pulp cellulose is sensitive to the active alkali charge of pulping. With lower active alkali concentrations, DP is increasing, due to the fast dissolution of low molecular depolymerized products and to the simultaneous slow cellulose degradation. Higher alkali concentration, however, generates faster depolymerization on cellulose, therefore the DP is decreasing.
  The initially more depolymerized hemp pulp cellulose became practically stable to further alkaline depolymerization.

- Kappa number of eucalyptus cellulose pulp was increased with a temperature increasing by 6.45%. This was due to the condensation of lignin groups at a high temperature pulping. While different trend of kappa number behaviour occurred in the increasing of duration of pulping and active alkali charge. 25.67% and 43.86% delignification rate occurred when increasing the duration of pulping and active alkali charge respectively.

- By applying the selected highest values of the different process parameters in nitration,the following order of sequence occurred in their detrimental effect on nitrogen content:

1. For reed: duration of nitration> temperature.
2. For eucalyptus: duration of nitration > temperature, temperature had decreasing effect while duration of nitration had increasing effect on nitrogen content

- Alpha-cellulose content of the dissolving pulp close to 90% (but defnitely less than 97%) still permits the production of CN of acceptable commercial value.

- Cellulose nitrate production up to a N-content of 13.1% does not depend too much the initial average molecular mass of the dissolving pulp cellulose (viscosity values from 116.80 through 1496.41 mPa.s).

- Neither the intial molecular mass of the dissolving pulp nor the N-content of the CN seem to be in close correlation with the ethyl alcohol-dimethyl ether solubility of the latter one.

- Dissolving pulps made of reed, eucalyptus, wheat straw, and hemp meet the requirements of the adequate raw materials for the production of cellulose derivatives.

- The central composite rotatable experimental design proved to be proper tool for optimizing the most significant process controlling parameters for the reproducible formation of the wanted products.

- Validity of the calculated process variables could be verified by new pulping experiment performed under the obtaintd optimum conditions. The difference between the experimentally obtained and the calculated bleached pulp yield was insignificant.

REFERENCES

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