STUDIES ON ORGANO-SOLV PULPING OF BAGASSE

A DISSERTATION

submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
PULP AND PAPER TECHNOLOGY

By

RAMNIK SINGH

INSTITUTE OF PAPER TECHNOLOGY
(UNIVERSITY OF ROORKEE)
SAHARANPUR-247 001 (INDIA)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "STUDIES ON ORGANO-SOLV PULPING OF BAGASSE" in partial fulfilment of the requirements for the award of the degree of MASTER OF ENGINEERING submitted at the Institute of Paper Technology, Department of the University of Roorkee, is an authentic record of my own work carried out during the period from July, 1991 to January, 1992 under the supervision of Dr. J.S. Upadhyaya, Reader (Pulp & Paper), at Institute of Paper Technology (University of Roorkee), Saharanpur.

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

Ramnik Singh
(RAMNIK SINGH)

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

(J.S. UPADHYAYA)
Reader (Pulp & Paper)
Institute of Paper Technology
(University of Roorkee)
SAHARANPUR

Dated: Jan. 25, 1992

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Ramnik Singh
(RAMNIK SINGH)

SAHARANPUR

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SYNOPSIS

Chemical pulping technology today is dominated by the kraft process due to its well known advantages. Unfortunately this process is very capital intensive, mainly because of the chemical recovery system required to recycle cooking chemicals and the pollution abatement equipment needed for environmental control.

Pulp makers and researchers in many parts of the world are looking for a number of alternate processes that could help the pulp and paper industry in energy savings, cutting operating costs, lowering chemical requirement and meet the environmental restrictions to mill effluents.

A very promising alternative suggested is Alcohol Pulping or "Organo-Solv Puling".

Much Research and Technology development is done in countries having large resources of softwoods and to some extent on hardwoods. But non-woody fibrous raw materials which form a bulk of raw materials in third world countries have received little attention towards development of suitable technology.

The present study is aimed at to explore the possibility and potential of using Bagasse as raw material for Organo-Solv Pulping. Methanol-Water is selected as cooking liquor and experiments are to be conducted using different catalysts at optimized cooking conditions.

Organo-solv processes are expected to play a significant role in the supply of pulp in near future.

ABSTRACT

The results obtained by the Methanol Pulping(MP) of sugar cane bagasse are discussed. Non-catalized MP process requires high temperature and pressure, but only produces low quality semi-chemical pulps.

The extent of delignification increased with the decrease in methanol concentration. Optimum selectivity in terms of delignification and yield was obtained at 70% methanol concentration. 10:1 was selected as optimum liquor to solid ratio with maximum temperature at 180°C and time at maximum temperature as 3.0 hrs.

Acid catalized MP process are less selective than alkali-catalized ones because of the carbohydrate hydrolysis provoked by the acidic medium.

Paper grade chemical pulps of good strength properties can be obtained by alkali-catalized MP process. Addition of 0.05 % AQ further improved the results. Soda-methanol pulping can be carried out for this purpose with sodium hydroxide savings of 50% or more in comparision with the conventional soda process of bagasse. This is a fact of great importance for small mills without recovery furnace.

Organo-Solv process are expected to play a significant role in the supply of pulp in near future.

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CHAPTER - 1

GENERAL INTRODUCTION

1.1 Role of Organo-Solv Pulping:-

Organo-solv pulping though not a new process, has received new attention since seventies, with a rise in capital investment requirement for the conventional pulping plants. Increasing awareness of pollution caused by conventional process has also drawn the attention of technologists for the development of better process to minimise environmental impact on pollution.

For the past few decades the kraft process has fulfilled the needs of industry for a strong, bleachable paper making fiber. Environmental and economic limitations associated with this process has however, led to the search of alternatives.

Many alternative pulping methods have been explored over the past 100 years, but most have never gone post the laboratory stage of development. Poor pulp quality, chemical losses, and recovery and environmental problems have precluded full scale trials.

Organo-solv pulping has been investigated as an alternative to conventional methods to avoid pollution problems and high capital cost. Organo-solv pulping systems not only can potentially overcome these restrictions but may offer added advantages over the Kraft Process.

1.2 Solvents and Catalysts:-

Organo-Solv pulping in true sense is extraction of pulping raw materials with solvents in combination with or without catalysts.

A number of organic solvents have been proposed for use in Organo-solv delignification either as solvents as such or combined with water. All of these media are good solvents for lignin.

Some of the solvents mentioned in literature, used in organo-solv delignification are as:(1)

1. Methanol
2. Ethanol
3. Butanol
4. Glycerol
5. Glycol
6. Phenol
7. Dioxane
8. Dimethyl-Sulfoxide
9. Formic acid
10. Acetic acid
11. Acetone
12. Ethyl Acetate

In principle, a number of organic solvents may be used in pulping but so far only aqueous methanol and ethanol have shown potential for practical application.

Organo-solv delignifications are commonly carried out at temperatures above 140°C. Consequently delignifications in such high boiling solvents as glycol, phenol etc. can be carried out at ambient pressure. This apparent advantage is, however, more than offset by serious difficulties in solvent recovery. Consequently, solvents with boiling points lower than that of water, such as lower alcohols and ethyl acetate are favoured in Organo-solv methods currently under development. These solvents can be recovered from spent liquors by simple distillation.

Some of the catalysts reported in literature are as:

1. HCl
2. H_2SO_4
3. SO_2
4. Oxalic acid
5. Salicylic acid
6. $AlCl_3$
7. $Al_2(SO_4)_3$
8. BF_3
9. $MgCl_2$
10. NaOH
11. $CaCl_2$
12. $MgSO_4$
13. $MgCl_2$
14. $Ca(NO_3)_2$
15. $Mg(NO_3)_2$
16. Na_2CO_3
17. $NaHSO_3$
18. Ammonia
19. Ammonium Sulfide.

Classification of Organo-Solv Methods:-

Solvent pulping methods can be divided into 'Uncatalysed', 'acid catalyzed' and 'base catalyzed' processes.(1)

In first category pulping is actually promoted by acetic acid released from wood. The rates of acid catalyzed processes appear to be governed by the hydrolysis of α-ether bonds in lignin. Other acid catalyzed reactions that occur in the pulping are complex, including condensation, partial β-ether hydrolysis, release of formaldehyde, free-radical rearrangements. The extent of these reactions is difficult to evaluate, but they are of interest in evaluating the chemical feed stock potential of recovered solvent lignins.

Base-catalyzed solvent pulping such as delignification using NaOH in aqueous methanol, has recently generated increased interest, specifically for pulping softwoods. The chemistry of this process has so far been incompletely characterized. The reaction probably follow a course similar to that of Soda pulping, but with methanol promoting lignin dissolution and reducing condensation.

1.3 Present State of The Art of Indian Pulp & Paper Industry:-

At present, there are about 30 large integrated pulp and paper mills with a total capacity of 14.6 lakh tonnes, besides 275 small paper mills with total capacity of 15.6 lakh tonnes. Quite a few mills are lying closed because of various reasons including management problems, obsolete technology and non-availability of raw materials in the area of location. Out of 275 small paper mills, capacity ranges from 500 to 5000 tonnes per anum. The Development Council for Pulp, Paper and Allied Industries has estimated the demand for paper by the year 2000 to be about 32 lakhs tonnes where as the per capita consumption is tending to be stagnant at approximately 2 Kg. as against more than 200 kg in developed countries. (2)

Raw Material Scene:-

The main sources particularly for the larger mills were forests. Unfortunately, the forest coverage in India now comes down to as low as 16% of the land mass, from 30% in the fifties. The pressure of teeming population coupled with increasing demand for domestic fuel is estimated to reach 230 million tonnes by the turn of the century as against the present availability of only 39 million tonnes. It may be interesting to note that out of the total felling of forests, 86% goes as fire-wood, 11.5 % as timber and building materials and only balance 2.5% goes as pulp wood for paper industry. Because of the ever increasing demand of the paper industry in the country, and the limitation in the availability of raw materials like wood and bamboo, the use of alternate raw materials mainly agricultural residues is increasing day by day. Amongst agricultural residues, rice straw, wheat straw etc. are the more commonly used raw materials where-as bagasse has come into commercial use only recently.

Out of the total demand of two million tons of paper and board, more than 50% is being produced from agricultural resideues mainly in small paper mills,(of 30 tpd capacity).

Pulping:-

There are several pulping processes in use starting from chemical, chemi-mechanical to purely mechanical pulping systems. The alkaline chemical pulping process still remains the bulk of chemical pulping. Although there are several modifications of the alkaline pulping processes, sulphur still remains the most indispensable ingredient in the major pulping processes. Environment aspects are today forcing the pulping industry to devise pulping alternatives which are revolutionary in nature. Since sulphur and chlorine compounds are more harmful to the acquatic life and are malodorous, efforts are being made to find out sulphur-free and chlorine-free pulping and bleaching methods.

In small paper mills, the raw materials are cooked by soda process using sodium hydroxide as cooking chemical for the production of pulp for paper making. During pulping about 50% of the organics of the raw materials get dissolved and goes in the spent liquor generated. Sodium hydroxide used as cooking chemical also goes in the spent liquor in the form of sodium derivatives of the organics mainly lignin. (3)

Chemical Recovery & Pollution:-

Due to non availability of viable chemical recovery unit for small paper mills in the country, huge quantities of the spent liquor generated is being drained which is causing very huge loss of sodium hydroxide presently costing around Rupees 3,000 million a year. In addition to this, the liquor drained is generating very heavy pollution load, since most of the small paper mills are not having effluent treatment facilties.

Considering the above facts it becomes of prime importance to find out pulping procedures which are economically and environmentally viable and to explore the possibility of obtaining bleachable grade pulp.

Annexure-I gives summary of installed capacity of paper and paperboard industries category wise.

.4 Advantages of Organosolv Pulping:-

Interest in organosolv pulping can be traced to the following factors.(4)

Investment costs:-

Modern Kraft pulp mills require a substantial initial investment cost and a large minimum production capacity for economical operation. In contrast, the operation and chemical recovery in organosolv pulping processes is often simple, at least in principle. The relative simplicity of organosolv pulping could make it possible to establish mills with 150-200 ton/day capacity in locations with limited wood supplies.

Environmental factors:-

The chemical pulping industry is facing increasingly stringent environmental limitations on emissions of volatile sulfur compounds in the atmosphere and of chlorinated organics in bleach-plant effluents. The application of organosolv pulping methods may offer a means of curtailing such emissions.

By-product potential:-

The chemical recovery in organosolv pulping processes can isolate lignin as a solid material and carbohydrates as a syrup. Both of these by-products show promise as chemical feedstocks.

In addition to the above mentioned advantages it has been reported that organosolv pulping gives high delignification selectivity and therefore high yield pulp. The process is reported to be suitable for different kind of fibrous raw materials. Water and energy consumptions are also low.

1.5 Objectives of Study:-

(1) Collection of bagasse from U.P.State Corporation, Unit: Saharanpur.

(2) Raw material preparations by isolation of pith from bagasse using combi-
(2) nation methods.

(3) Raw material investigations

(A) Proximate Analysis

(B) Morphological Analysis

(4) Pulping Studies

(A) Choice of Alcohol

(B) Optimization of Pulping Parameters.

a) Temperature

b) Alcohol water composition (V/V)

c) Liquor to solid ratio

d) Time at maximum temperature

(C) Physical properties of pulp obtained at optimized cooking conditions.

(D) Soda cooking and Kraft cooking of Bagasse at specified conditions and their pulp testing for comparision to Methanol Pulp.

(E) Studies on Effect of Different Catalysts:

a) Sulphuric Acid (H_2SO_4)
b) Sodium Hydroxide (NaOH)
c) Anthraquinone (AQ)
d) Calcium Chloride ($CaCl_2$)
e) Magnesium Chloride ($MgCl_2$)

CHAPTER - 2

LITERATURE SURVEY

2.1 Chronological Developments In Organo-Solv:- (5)

Delignification of any kind of lignocellulosic raw materials for the production of pulp and paper or for other purposes with organic or aqueous organic solvents has been known for a long time. In the early 1930's, Kleinert and Tayenthal (1931) studied the action of aqueous alcohol mixtures upon various woods in the temperature range of kraft pulping, with a slow raising to the final temperature. A strong delignification effect was found, mainly when mixtures of water and low weight aliphatic alcohols were used. These preliminary findings were substantiated by other researchers.

Rassow and Gabriel (1931) used ethylene glycol; Aronovsky and Gortner (1936) carried out some experiments with different alcohols and concluded that 1-butanol was the most effective alcohol in removing lignin from wood; Grondal and Zenczak (1950) tried out with triethylene glycol; others like Clermont and Bender (1961) and Bobomolow et al (1979) have used more sophisticated organic solvents such as dimetyl sulfoxide and tetrahydrofurfuryl alcohol respectively.

Independently of the results obtained in all of these experiments, at least one general question has been clearly answered. From the economic point of view, the recovery and recycling of the solvents is of utmost importance due to their high costs, and among all the solvents that have been tested, the alcohols, mainly those of low molecular weight and low boiling point, present the most favorable conditions to be recovered with industrial proved techniques; although some authors, like Aronowsky and Gortner (1936) assert that butanol and isoamylalcohol are more effective solvents than other volatile alcohols.

The way in which each solvent attacks lignin has not been cleared and many hypothesis have been raised. Sarkanen and Schuerch (1957) showed that the so called ethanolysis reaction of lignin acid catalysis involves at least two important reactions. The first implies the introduction of an ethoxyl group into the molecule of lignin, and the second is a true cleavage reaction leading to the liberation of one phenolic hydroxyl and one carbonyl group; which leads to the cleavage of the molecular structure of lignin. To related conclusions reached Arlt and Schuerch (1958), however, they add that the ethoxyl groups were similarly introduced in a reaction which resulted in molecular cleavage. Kleinert (1974) suggested that, although pulping with aqueous alcohol looked like a simple high temperature extraction of the wood, in reality it was a composite phenomenon of degradation, solvation, and solubilization process as had been shown in previous work (Springer and Zoch,1966); also he suggested that the bulk delignification exhibited two distinct phases of approximately pseudo-first order, that resembled those observed in isothermal neutral sulfite pulping (Kleinert, 1967). Also, Kleinert(1967) studied the kinetics of delignification of aspen and beech wood with aqueous solutions of ethanol at temperatures ranging from 180 to 190°C, and found that the results were very similar to those reported previously fro alkaline delignification (Kleinert, 1966) and in which he proposed that two distinct overall mechanisms were involved, each one resembling a first-order reaction pattern. The mechanism with the greater rate constant was found to be related to the bulk delignification, a complex of free radical reactions (Kleinert and Morton, 1962) of the type of a Rice-Herzfeld mechanism (Rice and Herzfeld, 1934) with thermal lignin homolysis as the initiation reaction, and the lower constant to residual delignification. The Arrhenius activation energy of bulk delignification in kraft pulping was about 32,200 cal/mole, whereas that of residual delignification was only about two-thirds of this value, inspite of the fact that lignin solubilization during residual delignification was more difficult than during bulk delignification.

Sarkanen (1980) mentioned that in the earlier studies of delignification of lignocellulosic raw materials with organic or aqueous organic solvents, small amounts of mineral acid were used as catalysts, mainly 0.5% HCl or 0.2% H_2SO_4. Later on it was found that organic acids such as acetylsalicyclic (Schwenzon, 1966) and salicyclic (Nelson, 1977) were probably more efficient catalysts. Another finding was that when sufficient high pulping temperatures (180°C and above) were applied, no addition of catalyst was necessary for satisfactory delignification, at least in the case of hardwoods, as Aranovsky and Gortner (1936), and Kleinert(1974) had sustained; in this case the organic acids released from wood probably acted as acidic catalysts. One fact to be underlined is that hardwood species are pulped with relative ease at 170-180°C, relative to softwoods when a solvent or aqueous solvent mixture is used as a delignifying agent.

The results of the studies headed by Sarkanen and Tillman (1980) which explored the selectivity of delignification of various catalysts in ethanol water systems, using western cotton (Populus trichocarpal) wafers, demonstrated that the selectivity of delignification was strikingly dependent on the way the reaction mixture was brought to the peak temperature showing that longer times were better than shorter ones. Also, the selectivity was found to be independent of the nature of the catalysts, and the temperature seemed to have little effect. According to Sarkanen(1971) the separation of lignocellulosics to their components by organosolv delignification represents, undoubtedly, one of the simplest options for integrated utilization of this biomass and possesses realistic potential for industrial applications.

The influence of pH changes on the yield of pulp, was also studied by Kleinert (1974) adding small amounts of HCl or NaOH to the liquor at 1h cooking time. The results showed that even small HCl additions reduced carbohydrate retention, where-as small NaOH additions increased yield only slightly. The trials, perhaps were suggested by the experiments carried out at the beginning of the 60's by Meyer et al (1961) and Bahlar (1965), studies that were in line with the early findings of Bailey (1940) and Larocque et al (1941).

Thus far, there remains many unanswered questions regarding organic solvent delignification of lignon-cellulosic raw materials. Taking into account the earliest investigations mainly that of Kleinert, already mentioned, and those of Wedeking and Engel (1933), Aronovsky and Gortner (1936), Bailey (1942), Schweers (1974) and Springer et al (1971): Bowers and April (1977) used a 50-50% (volume) of u-butanol and water as delignifying agent, southern yellow pine meal (30-60 Tyler mesh) as raw material and operating temperatures of 174°C and 205°C, concluded that a 50-50 (volume) n-butanol-water solution was an effective delignifying agent for southern yellow pine mainly at 205°C and a residence time of 12 h. Also that wood losses incurred in the experimental program were small and finally that the delignification of this material could be represented by a shrinking-core mathematical model with overall delignification controlled by diffusion through a liquid film and diffusion through a delignified wood zone.

April et al (1979) based on the findings of Wayman and Lora (1978), who demonstrated that the great delignification effect of phenol was ascribed to the fact that aromatic compounds tend to prevent lignin condensation by reacting with electrophilic substances thought to be condensation precursors, used aqueous solutions of n-butanol and phenol to reduce the lignin content in pine meal from 30% by weight to 18% and 3% respectively. The experimental results suggested that a two-step process occurred in dissolving the lignin as mentioned previously.

Sachetto et al (1983) from the BATTELLE-Geneve Centre, developed a process in which they used a convenient mixture of water, acid and phenol in such a way that cooking of the biomass could be carried out under mild conditions (no pressure, 100°C) resulting in a simultaneous dissolution of lignin and of the non-cellulosic carbohydrate. The pulp so prepared could be used as a conventional pulp and also as a dissolving pulp after bleaching.

Continuing with their experiments April et al (1982) supported by the results of Sarkanen et al (1971) and Goldstein et al (1979) who indicated the relative importance of acidity on rate and extent of hydrolysis and showed that the efficiency of lignin removal was directly related to hemi-cellulose, and in some cases to B-cellulose hydrolysis, practiced a prehydrolysis prior to organo-solv pulping in order to remove hemicelluloses. The experimental data indicated that percent lignin in pulp decreased with time, yielding higher lignin removal. This resulted from a lower resistance to solvent penetration as the polisaccharides of the outer hemicelluloses degraded. The delignifying agent was n-butanol-water 50-50% (volume). Over the range studied, the optimum condition for hemi-cellulose hydrolysis without serious degradation of cellulose fibers was found to be 200°C and 150 min. In the same way Hansen and April found that the bulk delignification occurred in two steps which could be describedas first-order kinetics. Isokinetic relationships determined from these rates constants showed that the mechanisms of bulk delignification did not change in various solvent systems. Based on these relationships, first step bulk delignification results in new solvent systems were predicted within 6% of the experimental results and the second step predicted results were within 12% of those experimentally determined.

The efforts to delignify wood by base-catalyzed solvolysis in organic solvent, as in the soda process, and in acid-catalyzed solvolytic delignification, have shown to be more effective for pulping hardwood than softwoods as Bailey(1940); Larocque and Maass(1941), Schwenzon (1964) and Nakano et al (1976) have demonstrated. However, among the various solvent systems that have been investigated, the amine compounds fall into a special category since they increase the soda pulping rate of all wood species as can be deducted by the studies of Wise et al (1939) and Bloom and Jahn (1942).

Green and Sanyer (1982) found that the addition of alcohols or amines during alkaline pulping increased the rate and selectivity of delignification above that of conventional soda and kraft processes. Particularly the pulping selectivity increased with increasing concentration of organic component and alkali. At high amine levels the alkali requirements were substantially reduced out, despite the higher hemicellulose stabilization and retention, the cellulose viscosity and pulp mechanical properties deteriorated. In general, low-molecular weight mono or difunctional amines were more effective than higher molecular weight of long-chain-length analogues, and primary amines were better than secondary amines. Also, the low molecular weight alcohols such as methanol, ethanol and methyl cellosolve were more effective than higher alcohols such as n-propanol and n-butanol since the last are only partially miscible in water and formed two phases with different pulping rates leading to non-uniform pulping.

Sachetto et al (1982) proposed a preliminary lay out for an industr-plant. Marton & Granzow (1983) reported experiments carried out with ethanol and NaOH. Biological Energy Corp.(BEC) set up (1984) pilot plant for pulping with alcohol at Valley Forge, Pa. with 14 lb./day capacity. Wood chemist

Raymond A. Young of the University of Wisconsin, Madison, U.S.A. discovered (1986) that water, acetic acid and ethyl acetate create an ideal cooking liquor for pulping. Commissioning of pilot plant (1984) on Methanol pulping (Organocell) at Technocell mill in Pasing. Set up of 33 tpd pilot plant by Repap (new name of BEC) group in 1989 at Newcastle, N.B.,Canada.

Towards commercialisation are Alcell process 300 tpd by Repap, due to start this year and Organocell process by Technocell group plan to switch over 60,000 Tons/year Bayerische Zellstoff mill in Kelheim, Germany from Sulfite process to produce 1,20,000 tons/year of Organocell pulp, due to start late 1992.

2.2 Organosolv Pulping Methods Proposed in the literature.(6)

SOLVENT	%IN H_2O	CATALYSTS	WOOD: LIQUOR	RAW MATERIAL	COOKING TEMP.	KAPPA/YIELD
Methanol	50-100	none HCl, H_2SO_4 Methyl Sulfuric acid $CaCl_2$, $Ca(NO_3)_2$ $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$	1:10	Spruce Pine beech aspen	130-220°C	8-19/59-63% (aspen) 18-65/50-63% (Spruce)
Ethanol	40-60	none HCl, H_2SO_4 aromatic organic acid $NH_3, NaOH, Na_2CO_3$ $CaCl_2, FeCl_3, AlCl_3$ $(NH_4)_3PO_4$ anthraquinone methylanthraquinone	1:6-15	Spruce Pine beech aspen birch eucalyptus poplar red oak sweet gum bagasse rice straw	120-240°C	44/48 % (beech) 27-36/53-58% (aspen) 29-38/49-52% (birch) 85/56 %(spruce)
Propanol	60-80	$CaCl_2$	1:10	spruce	200°C	38-63/45-54 % (spruce)
Propanediol	50	none	not specified	beech	190°C	32-71/39-42 % (beech)
Butanol	30-70	none HCl, H_2SO_4 $NH_3, NaOH, Na_2CO_3$ $AlCl_3$, Alum $FeCl_3, (NH_4)_3PO_4$ aromatic organic acid antraquinone	1:10-15	spruce pine birch poplar sweet gum rice straw bagasse	120-250°C	72-87/70-84 % (pine)
Glycol	20-100	none HCl, H_2SO_4 methylsalicylate salicylic acid sulfonic acids	1:4-6	pine birch eucalyptus straw	100-205°C (also under atmospheric pressure)	9-32/49-54% (eucalyptus) 42-84/48-57% (pine) 27-40*/52-57% (birch)
Tetrahydrofurfuryl alcohol	50-100	none HCl, H_2SO_4 NaOH acetic acid oxalic acid	1:10	spruce pine birch	95-205°C (also under atmospheric pressure)	3-39/49% (birch) 15-39/45-50% (spruce) 29/45%(pine)

Phenol	20-50	none HCl sulfonic acids oxalic acid	1:8-15	spruce pine aspen birch bagasse straw	80-205°C (also under atmospheric pressure)	11/44 % (birch) 13* /51 % (spruce) 27* /46 %(pine)
Cresol	20-80	none cuprous oxide acetic acid anthraquinone	1:7-8	spruce beech birch red lauan	160-190°C	29* /53 % (beech) 22* /49 %(spruce) 15* /49% (spruce)
Formic acid	80	not specified	not specified.	hardwood softwood (not specified)	100°C (atmospheric pressure	60-65/59 % (HW)
Acetic acid	50-95	none HCl	1:4-8	spruce beech aspen	110-220°C	10-30/52-55%(aspen) 16/46%(spruce)
Acetic acid/ Ethyl acetate	26-33/ 33-49	none	not specified	aspen	165-170°C	8-11/48 %(aspen)
Peroxoic acid (N_2O_2+ RCOOH)	80-100	none H_2SO_4	1:4-8	spruce pine birch	70-90°C (atmospheric pressure)	4-23/42-61 % (pine) 5-6/56-62(birch)
Amine	25-90	none anthraquinone	1:1-10	pine beech eucalyptus	165-200°C (also under atmospheric pressure)	16-105/61-69 % (pine)
Dimethylsulfoxide	95-100	HCl H_2SO_4	1:10	spruce beech birch	100-185°C (atmospheric pressure)	8-53* /40-49% (spruce)
Sulfolane	50	H_2SO_4	1:6	aspen	130°-160°	26-39* /52-55 % (aspen)
Dioxane	100	none	not Spf	birch	180°C	67* /54,5 %(birch)
Butylecellosolve	50	none	1:15	pine	175-235°C	71-84/55-78%(pine)
Ethylene-Chlorohydrin	100	none	1:5-7	beech poplar	120-150°C (atm.pr.)	84* /68,5 %(beech)
2-oxacolidinone 2-imidazolidinone	upto 100	none	1:8	spruce	200-250°C	44/not specified (spruce)

* Kappa number has been calculated from the published data assuming that the lignin content of pulp is related to Kappa number by the factor 0.15 which is not necessarily correct for organosolv pulps.

2.3 Organo-solv Technologies Towards Commercialisation:-

Organosolv technology have come out of the laboratory stage of development and a few of them are in progress to be commercialised in near future after successful runs at pilot plant scale.

Some of Organo-Solv Processes at an advanced state of development are as follows:

1. Alcell Process
2. MD-Organocell Process
3. Ester Pulping Process
4. ASAM Process

The Alcell Process:- (7)

After many years of research, development, and pilot-plant experience, Repap Enterprises, Inc. started up a commercially scaled mill at Newcastle, N.B., in March 1989. The mill was built to demonstrate and test a proprietary organosolv pulping method known as the Alcell process. This facility has operated routinely since startup, completing more than 1000 cooks and producing over 5000 tons of pulp from individual species as well as mixtures of hardwoods.

After 18 months of operation, the facility has demonstrated that the Alcell process, a pure organosolv process using simple aqueous ethanol as a pulping liquor, is capable of producing fully bleachable chemical pulps with physical and optical properties equivalent to those of kraft pulp. Mill experience also has verified several other process advantages.

o The process is environmentally benign.

o Efficient recovery of pulping solvent is feasible and practical.

o Economically attractive mills can be built at about one-fourth the size of a modern kraft mill.

o By -products from the process can generate profits.

o The pulps can be bleached to 90% ISO brightness using bleach sequences free of molecular chlorine. (Totally chlorine-free bleach sequences are now under investigation, with promising early results.)

o The pulp can be used without difficulty as a major part of the furnish in quality coated paper manufactured on a full-size modern paper machine and blade coater.

o A pilot plant in Valley Forge, Pa., (14-lb/day pulp capacity) was used to develop the basic operating and design parameters of the process as well as to test its feedstock flexibility. More than 5 tons of Alcell lignin are being produced daily. The lignin has been fully dried, bagged, and sold on a commercial basis as demanded by the marketplace. Evaporated stillage, consisting of syrups mostly of water-soluble hemicellulose saccharides and low-molecular-weight lignin fragments, is also being produced. Furfural, another significant by-product of the process, is recovered and sold on a routine basis.

The experience with the demonstration facility has been so positive that Repap is planning and designing a commercial-scale mill with an approximate capacity of 300 metric tons/day. This mill will incorporate some significant design improvements (e.g., continuous cooking) based on operating experience at the Newcastle facility. Annexure-II gives the expected Alcell mills by 2000 (as claimed by Repap group) (8).

Operating Principles:-

Schematic diagram is given as 2.3 A,(9).

The general operating principles of the Alcell process are described in several patents. The cooking medium is a mixture of water and low-molecular-weight aliphatic alcohols. All of the pulping runs at the Newcastle facility have used approximately 50% (weight/weight) denatured ethanol/water mixtures at temperatures in the range of 195°C. The cooking chemical, ethanol, is recovered primarily by distillation. Thus a relatively simple distillation tower in the Alcell process performs the same function as the recovery furnace, the lime kiln, the causticizers, and other high-cost and high-maintenance components of the chemical-recovery cycle in the kraft process.

No acid or alkali is added to the cooking liquor, which maintains a natural pH of about 4. This acidity derives from the acetic acid released from acetyl groups in the wood during the early stages of the cook. The actual cooking time required is a function of pH, temperature, alcohol concentration and the type of wood being cooked.

The Pulping Cycle:-

The Alcell process is illustrated in Fig. 2.3 B At the Newcastle (10) mill, the pulping cycle begins when about 10 tons of conventionally debarked, chipped, screened, and pre-steamed chips are loaded into a batch digester, which functions as an "extractor" in the Alcell process.

Steam packing of the extractor is an option. After steam has been driven down through the bed of chips to purge air from the vessel, cooking liquor that has been held at full temperature in the primary liquor accumulator (after being used as a secondary liquor in the previous cook) is flashed into the extractor. After pressure equalization, the primary liquor is rapidly circulated through primary liquor heaters and the chip bed in order to bring the chip charge up to cooking temperature as quickly as possible. Once at full temperature, the primary cooking cycle begins and lasts for a predetermined time, usually in the range of one hour. The primary liquor, now loaded with dissolved solids consisting mostly of low-molecular-weight lignin, hemicellulose saccharides, furfural, and acetic acid, is displaced from the extractor into a recovery feed accumulator by secondary liquor that has been held at full temperature in a secondary-liquor accumulator. The secondary liquor contains some dissolved solids, since it was used in the previous cook as a final-wash, or tertiary, liquor. After an appropriate exposure to the chips, the secondary liqour is itself displaced into the empty primary accumulator by fresh tertiary liquor from the tertiary accumulator. The tertiary liquor is then transferred to the empty secondary accumulator. Thus, the chips are exposed to three hot liquors in the process, each having a progressively lower solids content. The first liquor performs mostly cooking, while the last two liquors serve mostly to wash out the dissolved solids from the cooked chips.

Following the transfer of the final tertiary liquor to the secondary accumulator, the extractor is vented to a blow-down condenser, and the condensed vapors are returned to the recovered alcohol tanks for reuse in the process. Finally, the cooked chips are stripped with steam to remove and recover residual alcohol, and the pulp is sluiced from the extractor. The pulp is then screened and cleaned in a conventional manner, thickened, and sent on for bleaching. No brownstock washer is required. The complete cycle can take anywhere from about five hours to more than seven hours, depending on designed conditions.

Lignin and by-products recovery:-

The high-solids primary liqour (black liquor), which was displaced into the recovery feed accumulator at the end of the primary cooking stage, is flashed continuously into an atmospheric pressure flash tank. The overhead vapors are condensed and returned to the recovered alcohol tank for reuse in the process, while the concentrated black liquor is treated to precipitate a major lignin fraction, known as Alcell lignin. This lignin is separated from the liquor and then dried and bagged for sale. A second, less desirable option would be to use the isolated lignin as a sulfur-free fuel to provide process energy.(The lignin, with 11,000 Btu/lb, has a slightly lower heating value than coal.)

The liquor, which contains alcohol, furfural, hemicellulose sccharides, low-molecular-weight phenolic compounds, and other minor components, is pumped to the distillation tower. Ethanol is condensed from the overheads of the tower for reuse in the process; furfural is recovered from side draws on the column; and the stillage is then evaporated, following which it can either be burned to reduce process energy requirements or sent for further processing to recover additional by-products.

Pulp Characteristics:-

Chemical Composition:-

Despite the fact that the physical properties of bleached Alcell pulps are very close to those of kraft pulps sof the same species, there are some distinct differences. Probably because the Alcell process operates under acidic conditions, these pulps appear to have a higher glucan-to-xylan ratio than do draft pulps. Consequently, they have some of the characteristics of high α-cellulose pulps. Presumably, the acidic cooking conditions favor cellulose retention and hemicellulose hydrolysis, the net effect of which is a discernible yield advantage for Alcell pulps over kraft pulps. This yield advantage can be 2% or more with some species.

The lower hemicellulose content has other advantages to the papermaker. In carefully performed trials with certain Alcell pulps, it has been shown that much less hemicellulose is lost in the white water from the pulp during refining than is observed with many market kraft pulps. This advantage can be as high as 1.5% on pulp, giving that much higher yield on the paper machine and lowering the cost for water treatment at the paper mill.

Another reason for the pulp-yield advantage is that very few rejects are observed after pulping. Presumably because of the very low viscosity of alcohol-water mixtures at 195°C, penetration of the cooking liquor into the chip is rapid. No hard chips have been observed, even with large oversized chips, and knots are effectively cooked. This represents another advantage of the Alcell process, since uniform chips size is not important to pulp quality, as it is in the kraft process.

Bleaching Characteristics:-

After efficient washing, the pulp generally has a kappa number in the mid-to high-20s, depending on the wood species. Lower kapp numbers from the cooking stage are possible, but an accompanying loss of strength is common.

These are relatively high kapp numbers as compared with hardwood kraft. Alcell pulps are remarkably receptive to oxygen bleaching. Using conventional oxygen bleaching procedures, pulp kappa numbers have been reduced by 70% with only a few points loss in pulp viscosity. By comparison, under similar conditions, most kraft pulps would lsuffer at least a 50% loss in viscosity.

The reason for this behaviour is not yet understood. However, it might be related to the fact that the pulp is not exposed to sodium ions during the cooking process. There is substantial evidence that bleached Alcell pulps beat faster than many bleached kraft pulps. There is substantial evidence that the brightness of bleached Alcell pulps reverts significantly less than kraft pulps. This may be a function of the lower extractives content of these pulps, which is almost certainly a consequence of being treated with hot organic solvents (ethanol) during the pulping process. Wtih regard to capacity, the general trend is that Alcell pulps have a higher opacity than kraft pulps from the same wood species.

Physical Properties:-

The physical properties of fully bleached Alcell pulps compare favorably with those of kraft pulps from the same species. In the 400-mL CSF range frequently used in papermaking, the Alcell pulps produced from mixed hardwoods show bulk, burst, tensile, and tear properties equal to or better than kraft pulps from the same species. The physical properties of Alcell and kraft market pulps at 400 mL CSF are listed in Annexure-III.

By-Products:-

The Alcell process generates several interesting and marketable by-products. The largest of these is Alcell lignin, which can amount to about 18% by weight of the dry wood charge. The lignin is highly hydrophobic, contains no measurable sulfur and very low ash, and as a consequence is quite distinct from either lignosulfonates or kraft thiolignin. It is a uniform product with a number average molecular weight of about 1000 daltons, a softening point of about 145°C, and a glass transition temperature of about 100°C. The dried and bagged product- available from the Newcastle mill for commercial application and testing - has a moisture content of less than 3% and a medium particle size of 20-40 m. This material is being tested with positive results in numerous applications, including as a partial replacement for phenol formaldehyde resins in the manufacture of building board, as components in rubber compounding, and at the low value end, as an oil or gas replacement in lime kilns. Because it is a new product, we expect to be continually developing the lignin for use in a variety of applications.

Another major by-product of the process is furfural, which is generated naturally in the process and is simply recovered as an impure side draw from the distillation tower. The mill is upgrading this product and selling it as a commodity. Significantly more furfural can be manufactured from the pentose sugars present in the stillage, but this would require additional investment in equipment. It is estimated that a 300-metric-ton/day mill will generate more than 14 million lb/year of furfural from the side draw.

Several other interesting by-products have been identified in the process, and studies are now underway to identify economic means for their recovery and purification.

Environmental Advantages:-

Given today's climate of heightened environmental awareness, the greatest advantage of the Alcell process may be that it has a minimal impact on the environment. The Newcastle plant has proved that the process is odorless, is free from TRS(total reduced sulfur) and methyl mercaptans, is free from liquor dregs and lime grits, and produces minimal amounts of knots and rejects. The major effluent apart from the bleach-plant effluent, is the stillage evaporator condensate, which contains only easily treated BOD (mostly acetic acid, ethanol, and a few other minor organic volatiles). The bleach-plant effluent, as currently anticipated for the 300-metric-ton/day mill, will contain no dioxins or furans, and AOX levels should be well below 1 kg/metric ton of pulp. This would comply with any anticipated effluent limits. Furthermore, an Alcell mill requires far less water than a kraft mill.

Economics:-

Qualitatively, it is clear that without a need for a recovery furnace, lime kiln, causticizers, and brownstock washers, the Alcell process has a substantial capital cost advantage over a comparably scaled kraft mill. This capital cost advantage can be used to reduce the scale of an Alcell mill such that it becomes economically attractive at 300 metric tons/day of pulp capacity or less, depending upon location and project. There are also several operating cost advantages. Without a recovery furnace and other high-maintenance equipment, an Alcell mill should have lower maintenance and operating labor costs and a higher number of operating days per year. Wood costs also are lower, since pulp yield for the Alcell process is higher.

On the other hand, the recovery and sale of lignin and other by-products creates additional demand for externally generated energy, so utility costs for an Alcell mill will be higher. The cost of cooking chemicals(ethanol) for the Alcell process also is higher. However, these two disadvantages should be offset by the value of the generated by-products.

The MD - Organocell Process:-

With DM 45- Million of fundamental research complete, Germany's Organocell is fast moving towards the first large-scale application of its environmentally-friendly solvent pulping process. It is planning to switch over the 60,000- ton/yr Bayerische Zellstoff mill in Kelheim from the sulfite process it uses today to produce 120,000 tons/yr of Organocell pulp. The mill will employ an adaptation of the Organoslv pulping method and is due to start up during 1992. (11)

"Results of the demonstration plant are more than encouraging", agrees managing director of Organocell Gerhard Dahlmann. "The pulp produced is not only of excellent quality, similar to kraft pulp, but its bleaching properties are also outstanding. They have already reached 88°ISO brightness after just three-stage bleaching.

"Methanol-based, the process is sulphur free and the limited use of bleaching chemicals means that bleached pulp can be produced with practically no load on the environment. the amount of AOX compounds, for instance, is less than 0.5 kg/ton of Pulp produced".

Pollution problems were precisely the reason why Technocell, a subsidiary of MD Papier, became interested in the Organosolv Pulping Process.

A small pilot plant was started up in 1984 at the Technocell mill in Pasing- one batch digester with a capacity of just 10 kg of pulp. The solvent used in methanol (a non potable alcohol - a distilling licence would be needed for any other).

By 1987, it had become obvious that the process had good possibilities and a larger five-ton/day demonstration line was started up for test and demonstration purposes.

PROCESS:-

In this process wood chips are initially treated with a 50:50 methanol-water solution at 185-195°C and then with a solvent containing 30:70 methanol-water containing 5-10 per cent sodium hydroxide(based on wood) at about 170°C. Both stages are conducted in one continuous digester, separated only by the difference in densities. The total residence time is only 45 minutes. Tests have shown that it can be used for any type of raw material, bagasse, straw, hardwoods, softwoods, including pine etc.

After cooking the pulp is blown and screened, washed and cleaned before bleaching. The process is suitable for producing bleachable pulp with strength close to kraft. The spent liquors from each stage are concentrated in two separate four stage evaporators. Lignin is precipitated from the first spent liquor stream as the methanol evaporates. Because of the high alkalinity in the second spent liquor stream, lignin does not precipitate in the evaporator. Instead the concentrated solution is sent to an electrodialysis cell where caustic is regenerated and lignin is precipitated. Lignin precipitate is filtered and spray dried for sale as a byproduct.(Figure 2.3 C shows the block diagram of Organo-cell process.)

Chemical Recovery:-

Methanol recovery is handled via two four-effect evaporation lines, resulting in high recovery rate of around 50%. Lignin from the first cooking stage is obtained by precipitation, while an electrolysis unit recovers the caustic soda from the second stage. Optimization of the recovery system is still needed and, at Kelheim, the company plans to install a recovery boiler rather than an electrolysis unit.

Limitations:-

It is believed that the requirement for two recovery systems (methanol and caustic) diminishes the capital cost advantage of this process versus kraft, bringing its suitability for small scale chemical pulping operations into question. Better information on process economics is required.

Because of heavy capital and operating costs, however, this process is not likely to become a viable alternative to the kraft process for market pulp. In central European countries, such as Germany, Austria and Switzerland,(12) where new kraft mills may not be accepted, the process has possible applicatioon.

Ester Pulping:-

Wood Chemist Raymond Young of the University of Wisconsin, Madison, U.S.A. has discovered that water, acetic acid and ethyl acetate create an ideal cooking liquor for pulping. By adjusting the ratios sof these ingredients and through precise control of cooking time and temperature, a paper grade quality, high strength pulp can be produced with an acceptable yield.

Young and Biodyne, a Neenah, Wisconsin based research firm, are developing an ester pulping pilot plant which will produce 10 to 15 tpd of pulp. Young believes that if the pilot plant results are positive, many companies will be retrofitting their mills to use the new process. The payback period could be between 10 to 20 years.(13)

Process:-

In ester pulping, the solvent is a 33:33:33 mixture of ethyl acetate, acetic acid and water. Typical pulping temperatures are in the range of 170-200°C for hard woods and 190-200°C for soft woods. Cooking times normally are 0.5-2 hours for hard woods and 1-2 hours for soft woods. (14)

Pulp Characteristics:-

According to proponents of this process, aspen ester pulps are equal in tensile strength to kraft pulps but somewhat lower in tear. They also claim that bleachable softwood pulps can be produced by this method. Ester pulps in general exhibit an extremely low bulk. The process offers flexibility and can produce pulps with a range of properties for a variety of purposes.

Chemical Recovery:-

Esters were chosen because they readily separate into two liquid phases when combined with water: an organic and an aqueous phase. This separation provides a means to economically recover the cooking chemicals.

The recovery system is designed to include liquid-liquid phase separators, a filter or centrifuge to remove and recover the lignin, distilation columns to remove and recover volatile organic chemicals such as alcohols and esters, an extraction column for acetic acid separation, and burning systems to handle sugars, lignin and concentrated organic chemicals. A nonsulfur pristine lignin is recoverable and could be used for other commercial purposes, while the volatile organic provide excellent synthetic fuels.

Advantages of Ester Pulping:-

(As claimed by Dr. Young)

1. Stronger Pulp
2. Reduced cooking time
3. Lower cooking temperature
4. Higher Yield
5. Simpler chemical recovery
6. Lesser pollution.

Annexure-IV & V give the Ester Pulp properties.

The ASAM Process:- (Alkaline Sulphite Anthraquinone Methanol)

The ASAM system is currently being developed by R. Patt and is being implemented on a pilot- plant scale.

Patt Claims this process produces pulps as strong as kraft with higher yields and significantly higher brightness.

The ASAM Process is an attractive alternative to the kraft process if it can be successfully proven on a commercial scale, but this is unlikely to occur for atleast 5-10 years. Feldmuhle has buit a 5 t/d pilot plant covering pulping, bleaching and chemical recovery at its Baienfurt mill in co-operation with Kraftanlagen Heidelberg. The plant was commissioned in October 1989 and the technical assessment is likely to be finalised soon.(15)

PROCESS:-

In ASAM pulping, a mixture of 20% sodium sulphite, 5% sodium hydroxide and 0.2% anthraquinone (all expressed as % on wood) is used in liquor containing 35% methanol. Pulp produced by the method has low residual lignin, high brightness and yield, strength superior to kraft. The process is suitable for hardwoods as well as softwoods and the resulting pulps can be bleached with conventional or with chlorine free sequences.

There is no information on the intended recovery process. With the need of a recovery process for alcohol solvent as well as caustic and sulphite, it is doubtful that this process economic on a small scale.

2.4 MECHANISM OF THE PROCESS:

Alcohol-water delignification is a complex process involving degradation, solvation, and solubilization process. Some reactions of lignin degradation may be homolytic, as indicated by the free-radical content of lignin preparations isolated from the black liquor. However, the changes in carbohydrate retention are strongly pH-dependent. Also, loss of hemicelluloses can be described to hydrolysis reactions. A solatile pulping agent will rapidly distribute through the raw material, producing uniform delignification. Lignin degradation is primarily a function of temperature and residence time, whereas solubilization depends upon pore size and pore distribution. Therefore, factors, that remove hemicellulose also influence delignification.

Due to low surface tension, organic solvents can penetrate faster (16) into the cell wall and thus hydrolysis of lignin carbohydrate bonds. This hydrolysis of lignin-hemicellulose bond leads to the degradation of lignin. Delignification with Methanol is effective in separating the cellulosic raw material into its three main components. Hemicelluloses are soluble in aqueous phase, lignin is soluble in the organic phase and cellulose is separated as a solid.

Benzyl-alcohol group of lignin was expected to occur during alkali-methanol cooking. The presence of alkali seems to be necessary to the cleavage of the B-aryl ether of lignin in ethanol-water pulping. Very little is known about the behaviour of the B-aryl ether upto date, which is one of the major linking principles, occuring in a frequence of 48 to 60% in lignin. The concentration of NaOH needed to hydrolyze the B-aryl ether linkage in ethanol water pulping is much lower than one in soda pulping. (17)

It seems that the presence of alcohol favours the cleavage of the B-aryl ether linkage of lignin as we have observed that yield was increased when the concentration of Methanol was raised. Methanol is supposed to have an ability to protect guaicol from undergoing further reactions, such as condensation.

2.5 Chemicals Generated During Alcohol Pulping: Characteristics and Applications:- (18)

The characteristics and applications of some of the by-products obtained in the organosolv pulping of mixed hard woods are discussed.

The by-product obtained in largest quantity is the lignin recovered by precipitation. This lignin is low in sugars and ash, and has low molecular weight and low glass transition temperature. It can be used without modification as partial replacement for phenol formaldehyde resins in the manufacture of structural wood panels, and as a tackifier in rubber production. In addition, since this lignin has several functional groups that permit derivatization, it can be considered a chemical intermediate for the manufacture of other products.

Other by-products include furfural, sugars and water soluble lignins. Furfural is generated spontaneously during pulping and is recovered as a concentrated stream as part of the recovery of the alcohol used for pulping. Additional amounts of furfural can be generated from the pentose sugars that are produced during pulping. These sugars can also be used as fermentation substrates and to produce xylitol. Another by-product discussed here is a water soluble, very low molecular weight lignin fraction. This is primarily syringl in nature and has the potential of playing a role in phenolic adhesives.

Process Description:-

The process has been described in detail in the literature and only a brief description will be given here to review how the by-products are obtained at the Demonstration Plant. In the extraction section of the Demonstration Plant wood chips are initially loaded into a 53 cubic meter extractor (Figure 2.5A).

After preheating and removing air from the vessel with low pressure steam the chips are extracted in three stages with countercurrent flow of solvent at around 195°C. At the end of the third extraction the relatively clean solvent remaining in contact with the pulp is drained, the extractor is vented and then steam-stripped until only trace amounts of solvent remain. The pulp is then discharged from the extractor by sluicing, screened and cleaned and sent for bleaching.

While the extraction section is batch, solvent and by-products are recovered continuously (Figure 2.5).B).

In the lignin recovery section the spent liquor obtained in the extraction section is flashed to atmospheric pressure, and then dilutd to precipitate the lignin. The lignin is recovered as a cake by solids/liquid separation and then is dried to obtain a powder product. The solution obtained after lignin recovery contains dilute alcohol, sugars, furfural, acetic acid and low molecular weight lignin fragments that were not captured in the precipitation procedure. This stream is fed to the alcohol recovery section, where a 1.2 meter diameter, 27 meter high distillation tower recovers alcohol as a head product for reuse in the process. A fraction rich in furfural is obtained as a side draw in the tower. The stillage from the tower contains the wood sugars, low molecular weight lignins and acetic acid.

Lignin:

Properties:-

Typical chemical and physical properties of the lignin produced in the Demonstration Plant are shown in Annex-VII.

The product is characterized by its low molecular weight and its high purity as indicated by its low level of sugars and ash. This organosolv lignin has low solubility in water under neutral or acid conditions. It is soluble in dilute alkaline solutions and in polar organic solvents. The organosolv lignin has a lower glass transition than the commercially available kraft tested.

The elemental analysis of the lignin (Annex-VII) shows that it has higher carbon, lower oxygen and slightly lower methoxyl content than lignin in wood.

The higher carbon and lower oxygen are indicative of some degree of side chain rearrangement and/or self-condensation.

Applications:-

Strategy for lignin utilization has been initially to take advantage of the properties of the material and try to use it without modification or derivatization. Most of product development efforts have been focused on the replacement of phenol-formaldehyde resins used as binders in wood composites. Extensive lab and pilot scale evalutions have shown that it i possible to partially replace phenol-formaldehyde resins used in the manufacture of plywood and oriented strand board by unmodified ALCELL lignin. This has recently been confirmed in mill trials in which plywood and waferboard panels equivalent to the controls were successfully manufactured using binders in which ALCELL lignin replaced 15-20 % of the phenolic resin. ALCELL lignin has also been evaluated as tackifying resin for rubber manufacture. The product has good tackifying properties and exhibits some synergism when used in conjunction with a commercial tackifier. It contributes superior green strength and its dynamic mechanical properties are favorable as indicated by the higher rebound vs compared with commercial tackifying. In addition it appears to have some antioxidant properties.

Other applications that are under study include lignin use as a binder for fiberglass insulation, its incorporation in polymer systems aimed at reinforcing paper products and at increasing their water resistance, and its use in other areas where phenol-formaldehyde resins are used.

Lignin derivatization will play a role in the development of these additional applications. Unmodified ALCELL lignin is a reactive material that can be made more reactive through derivatization. A lignin with enhanced number of aliphatic hydroxyl groups can then be used to participate in further reactions.

Furfural:

Under the pH and temperature used during the extraction stages some of the pentose sugars that are dissolved are converted to furfural. Furfural generated in the process is recovered at a concentration of 60-70 % as a side draw in the distillation tower used to recover the pulping solvent. It can be easily upgraded to 85-90% by water extraction, and distilled further if required. Since additional quantities of furfural could be manufactured from the pentose sugars present in the stillage stream, an ALCELL mill has the potential of being a significant factor in the furfural market.

Stillage:-

The stillage obtained in the solvent recovery tower contains wood sugars, some low molecular weight lignins, acetic acid, ash, and other minor components.

The sugars are mostly xylose, some of them still in oligomeric form; they are generated under the conditions of acidity prevailing during pulping. As observed, xylose production reaches a maximum in the early stages of the cook and then declines as the dissolved sugars are converted to furfural. Because of its pentose sugar content, the stillage is potentially a substrate for acid catalyzed dehydration to generate additional quantities of chemicals such as furfural or xylitol. Fermentation may offer opportunities to convert this material to acetone, butanol, ethanol, or single cell protein.

The lignin present in the stillage stream corresponds to lignin fragments that were not captured by the precipitation process used to recover the bulk of the lignin due to their low molecular weight and water solubility. Several different fractions have been isolated from the stillage using different procedures. In general these fractions are characterized by a low molecular weight fraction (Number Average Molecular Weight in the range of less than 500) and a low glass transition temperature in the range of 24-60°C.

Our preliminary applications work has indicated that these materials can play a role in phenolic adhesive systems for wood and also in uses for which water solubility during processing is desirable.

Remarks:-

The lignin obtained by this organosolv pulping process is characterized by its low molecular weight, high purity, low glass transition temperature and relatively high decomposition temperature. It has a high proportion of aromatic hydroxyl groups. Other features include carbonyl groups, aliphatic hydroxyls (mostly primary), carboxylate groups and double bonds in the side chain. Mill scale trials have shown that the material can be used as a partial replacement for phenol formaldehyde resins used in plywood, oriented strand board and other applications. It has also been shown that the lignin can be used in rubber as a tackifier with antioxidant properties. The material is reactive and therefore offers opportunities for other applications through chemical modification.

The process also produces a water soluble, very low molecular weight lignin fraction. This is predominantly syringyl type and may have application in the adhesives industry.

Pentoses are produced during pulping and are partially converted to furfural. The furfural formed in this manner can be easily recovered at a high concentration in the same distillation column used for the recovery of the pulping solvent.

CHAPTER - 3

EXPERIMENTAL METHODOLOY

3 A MATERIALS AND METHODS:

3·1 A Raw Material Used:-

Bagasse, a reside left over after extraction of juice from sugarcane (Sacharrum Offcinarum) is a highly potential, renewable raw material source for this industry. It has the advantage of being readily available at central places, namely sugar mills, which are easily accessible. Further, the development of technology for making different grades of pulp and the number of varieties of paper from this raw material as well as incentives being given by Govt. of India by way of central excise relief have given an impetus for using Bagasse for pulp and paper making extensively.

Availability:-

While India is doubtless famished in forestry, it is largest sugarcane growing country in the world. On less than 2.5% of land cultivation, India grows and harvest about 190 million tonnes of cane every year. Only 45% of the cne presently produced which is the sugar mills, where after saving 10% for seed etc., 35% of cane produced is crushed. Due to variation of fibre content in sugar-cane from 13% to 16% of cane in Northern and Southern regions of our country, the production of wet bagasse varies from 26% to 36% based on sugar cane crushed, OR 33% of the cane crushed. The balance 55% of the cane produced is used by Gur and Khandsari units from where bagasse is not available as it is used as fuel. Therefore about 22.0 million tonnes of bagasse at about 50% moisture content is being produced annually from the sugar mills in india.

Even if 10% of this bagasse is made available to paper Industry. It would be possible to have additional paper production as much as 0.7 million tonnes. Utilization of bagasse in India is increasing both in small pulp mills as well as integrated paper mills.

Advantages of bagasse as a raw material:-(18)

A. Available at one place namely sugar mills.

B. Best amongst all non-wood fibrous raw materials in terms of fibre length and alpha cellulose content.

C. Silica content is manageable in pulping operations.

D. Recovery of chemicals from spent liquor has been established.

E. Viscosity of concentrated black liquor is not a serious unmanageable problem.

F. Scrutiny of proximate chemical analysis of various fibrous raw materials reveals that bagasse has all the requisite for economic manufacture of paper.

Due to the favourable economics of bagasse pulp production, it is expected that its use will spread more widely in all sugar producing countries than the use of other non-wood fibres.

Annexure-VIII gives leading countries in production capacity for bagasse pulp.

Annexure-IX gives typical uses of bagasse pulp in various grades of paper and paper board.

3.2 A Raw Material Preparation and Analysis:-

The air dried bagasse was collected from local unit of state sugar corporation. The total pith content was determined by TAPPI useful method UM 3-1981. The air dried bagasse was mechanically depithed and the amount of pith so removed was determined. The mechanically depithed bagasse was further treated in a hydrapulper at 5% consistency for 10 minutes and the amount of pith removed by wet depithing method was also determined. The total amount of pith, pith removed by dry depithing method as well as by wet depithing method, alongwith the amount of pith still associated with bagasse, are reported in Table - 3.2 A (i).

The whole bagasse, depithed bagasse and pith were chemically analysed by TAPPI standard method. The chemical composition of different fractions of bagasse including whole bagasse, separated fiber (depithed bagasse) and pith is given in Table - 3.2 A (ii).

The morphological studies of different fractions of bagasse was done by Bereau of Indian Standard method IS 5285-1969, and the dimensional characteristics of bagasse fractions are given in Table - 3.2 A (iii).

3.3 A Experimental Procedure:-

First of all, it was planned to optimize the cooking parameters of pulping with suitable organic solvent without any catalyst. For the optimization of cooking parameters, bombs of 1 litre capacity each were used. The digester is capable of accomodating 4 bombs during single run. During cooking, each bomb was filled with 75 gms of O.D. bagasse and the required amount of cooking liquor was added to it. The bombs were inserted inside the digester and it was filled with tap water upto a level slightly above the upper head of bomb.

The pulp obtained was washed on a 300 mesh washing screen with water and then refined in the laboratory refiner. The details of digester and refiner are given under Equipment Specification chapter.

The pulp obtained after disintegration was dried seperately and the total pulp yield was calculated on O.D. weight basis in each batch.

Determination of Kappa Number of Pulp was done using Tappi Standard T236-OS-T6. To check lignin content, Klason's lignin was determined and a factor of 0.16 was established to be multiplied with Kappa Number to give approximate lignin content of pulp.

3.4A EQUIPMENT SPECIFICATION:

Rotary Autoclave:-

The rotating autoclave consists of a digester body framed with drive and electric equipment. The autoclave rotates at 2 r.p.m. The electrical equipment includes six equipment placed on digester body, energy regulator maximum thermostate, slip rings and necessary circuit breaker on the digester head there are manometer, theremometer, needle valve and safety valve. The digester body is insulated and covered externally with stainless steel plates.

Technical Data:

Make	:	WEVERK
Length	:	890 mm.
Width	:	1090 mm.
Height	:	1165 mm.
Maximum working Pressure.	:	15 Kg/cm^2
Digester Volume	:	15 litres
Driving motor	:	0.25 H.P. 1400 r.p.m.
Element	:	4 KW

Materials : All parts in contact with digester liquor area made of acid proof Steel.

Net Weight : 280 Kgs.

Laboratory Raffinator type D:-

Made - DEFIBRATOR AKTIEBULAG, STOCKHOLM.

The laboratory raffinator is a disc refiner with special cast-iron discs, diameter 200 mm, the upper cone of which is fix and the lower one rotating. The machine is intended for refining fiber pulps for wood fiber board, cardboard, paste-board and paper.

The raffinator can either be handled manually, or equipped with a suitable charging pump. The fiber pulps are brought to the centre of the grinding disc through a funnel. The rotating disc is driven in counter clock wise direction by V-rope drive. This disc is pressed upward by spiral spring which is fixed between the stand and a ring. The ring can be screwed on cage enabling a variation of the spring pressure and thus the grinding are done. The rotating grinding disc can be brought in direct contact with the fix one by the spring pressure. In order to render possible an adjustment of the disc clearance wanted there is a collar, internally threaded which is screwed on cage, externally threaded. The horizontal position of the fix disc can be adjusted by means of three set screws. The disc clearance can be checked by a distance gauze on three points round the periphery of the grinding discs by unscrewing the plugs.

The adjustment of the disc clearance is made on following way:

Collar is screwed down on cage in such a way that the grinding discs are narrowly touching each other. This can be observed if the grinding disc is turned at some time by pulling the V-rage limit a scraping sound is heard, when the discs touch each other. This position the zero position is read on the graduation of the collar. The value of disc clearance desired is added to the zero position and the Collar is turned to the graduation line for the value wanted, where by cage as well as the lower grinding disc, fastened on same, are pressed down.

Motor Data:

One 3 phase induction motor

5.5 KW.

380/220 V, 50 cycles, 2900 r.p.m.

Limitations of Study:-

- Chemical recovery aspects of alcohol used for cooking could not be studied experimentally due to non-availability of suitable equipment. For this study an attached condenser with the digester is required to recover the vapours generated.

- During pulping studies, the comparision of results at different cooking parameters are done using Yield and Kappa Number only. It was found out of the scope of the study to undergo sheet making and testing for every cooking parameter, due to lack of time and manpower. However, sheet properties are tested at optimum cooking parameters found and with best catalyst.

- Pulping experiments could not be tried at higher temperature ranges ($>$ 200°C) due to limitations with the digester.

3 B PULPING STUDIES:-

After literature survey it was concluded that although there are a number of organic-solvents proposed but Ethanol and Methanol are found to be most potential ones due to their easy recovery i.e. by simple distillation.

3.1 B Choice of Alcohol:-

A comparative study of Ethanol and Methanol pulping was done at following fixed conditions.

Alcohol : Water - 50:50

Liquor : Solid - 10:1

Maximum Temp. - 180 C

Time to reach Max.Temp.- 1.25 hr.

Time at Max.Temp. - 1.5 hr.

Table 3.1B gives the results obtained, and respective graph shows comparison.

Further studies were carried out using Methanol as Cooking Liquor.

.2 B) Optimization of Pulping Parameters:-

The optimization of delignification conditions were carried out with Methanol.

a) Temperature:-

In optimizing temperature, the other parameters were set as follows:

Liquid to solid ratio = 10 :1

V/V concentration of Alcohol = 50:50

with water.

Time to reach Max. Temp. = 1.25 hr.

Time at Max. Temp. = 1.5 hr.

Results obtained are shown in Table 3.2B(i) and Graph.

b) Alcohol Water Composition(V/V):-

In obtaining the solvent composition, the other parameters were set as follows:

Liquor to solid ratio = 10 : 1

Maximum Temperature = 180°C

Time to reach Max. Temp. = 1.25 hr.

Time at Max. Temp. = 1.5 hr.

Results obtained are shown in Table 3.2B(ii) and Graph.

c) Liquor to Solid Ratio:-

For obtaining bath ratio, the other parameters were set as follows:

Alcohol water composition(V/V) = 7:3

Maximum Temperature = 180°C

Time to reach Max. Temp. = 1.25 hr.

Time at Max. Temp. = 1.5 hr.

Table- 3.2 B (iii) and respective graph shows the results obtained.

d) Time at Maximum Temperature:-

To optimize this parameter, the other conditions were set as follows:

Alcohol Water Composition (V/V) = 7 : 3
Liquor to solid ratio = 10: 1
Maximum Temperature = 180°C
Time to reach Maximum Temperature = 1.25 hr.

Table- 3.2 B (iv) and respective graph show the results obtained.

3.3 B Soda Cooking and Kraft Cooking of bagasse with and without AQ dosage (0.05 %) at Specified conditions:-

In order to compare results of Methanol cooking with the conventional alkaline pulps, Soda & Kraft Cooking was done for the same raw material.

Soda Cooking Conditions:

Active Alkali = 15 % (as Na_2O)
Bath Ratio = 1 : 4
Maximum Temperature = 160°C
Time to reach Max.Temperature = 1.25 Hr.
Time at Max. Temperature = 1.0 Hr.

Table 3·3 B(i) gives the results obtained.

Kraft Cooking Conditions:

Active Alkali = 15 % (as Na_2O)
Sulphidity = 20 %
Bath Ratio = 1 : 4
Maximum Temperature = 160°C
Time to reach Max. Temperature = 1.25 Hr.
Time at Max. Temperature = 1.0 Hr.

Table 3·3 B(ii) gives the results obtained. Graph 3.3 B gives the comparision of yield & Kappa No. of Methanol(non-catalysed at optimum conditions)-Soda- Kraft. In order to compare Pulp obtained from Methanol cooking with best catalysts, Soda and Kraft cooking was done with 0.05 % AQ.

3.4 B Studies on Effect of Different Catalysts:-

Following parameters were used for cooking as fixed conditions:

Alcohol water composition (V/V) = 7 : 3
Liquor to Solid ratio = 10: 1
Maximum temperature = 180°C
Time to reach maximum temperature = 90 min.
Time at maximum temperature = 2.0 Hrs.

Following catalysts were tried. Their resulsts are shown in respective tables and graphs.

		Result shown in Table & Graph No.
a)	Sulphuric Acid (H_2SO_4)	3.4 B (i)
b)	Sodium Hydroxide (NaOH)	3.4 B (ii)
c)	Anthraquinone (AQ)	3.4 B (iii)
d)	Calcium chloride ($CaCl_2$)	3.4 B (iv)
e)	Magnesium Chloride ($MgCl_2$)	3.4 B (v)
f)	Magnesium sulphate ($MgSO_4$)	3.4 B(vi)

The compairson of Soda and Kraft Cook with AQ 0.05% to Methanol Cook with best catalyst is shown in graph 3.4 B (vii).

3 C PULP SHEET MAKING AND TESTING:-

The unbleached pulp obtained was treated in PFI mill to 40°SR.

60 GSM sheets were made in British Sheet former. After conditioning of sheets, the properties were checked as per Tappi standard methods.

Sheet properties of Methanol Pulp (non-catalyzed) at optimum conditions are compared to Soda Pulp Properties. Table 3 C(i) shows this comparison.

Finally sheet properties of Methanol Pulp with best catalyst is compared to Soda Pulp with AQ dosage (0.05%). Table 3 C(ii) shows the results obtained.

CHAPTER - 4

RESULTS AND DISCUSSIONS

o The results of proximate chemical analysis of bagasse clearly revealed that the alpha cellulose content is higher in depithed fiber and ash content is higher in the pith fraction. Pentosan content is almost 50% higher than in hardwoods and exceeds by three to four times that present in soft woods. Lignin content is about 75% that of softwoods and about equal to that of hardwoods, indicating the possibility of producing high yield pulp from depithed bagasse under optimum conditions.

o In dimensional characteristics, the bagasse fibers are similar to those of hardwoods but are shorter than those of the coniferous woods.

o Pulp obtained from non-catalyzed cooking with Ethanol and Methanol are of semi-chemical type, since it reported high yield and high Kappa No.

o Methanol was selected for further studies because Ethanol will not be suitable in Indian practice due to following reasons:-

a) It is costlier.
b) It has restrictions of Central Excise.
c) It is of inflammable character and has higher fire hazarding tendency.

o With increase in temperature, the delignification is higher as Kappa No. is reduced but yield is adversely affected probably due to increase in peeling reaction at higher temperature.

180°C was selected as maximum temperature for further studies.

- Alcohol concentration affected the acidity of the liquors and this was found to influence the extent of delignification. Lower alcohol concentration favoured faster delignification by virtue of a higher hydrogen ion concentration. Yield of pulp decreased with a decrease in alcohol concentration. At higher pH (pure methanol or methanol water 9:1) delignification is very slow even at higher temperature and does not produce acceptable pulps.

- 70% methanol concentration provides a good compromise for a reasonable rate of delignification while retaining good yield.

- Lower liquor to wood ratio also resulted in higher acidity but this did not translate into enhanced delignification, probably due to some higher deposition.

- 10:1 was selected to be best liquor to solid ratio.

- Methanol pulp (non-catalyzed) require higher time at maximum temperature. As shown in Table 3.2 B (iv) and in respective graph that 32.8 Kappa No. can be achieved with 3.0 hr. cooking at maximum temperature.

- Optimum conditions for Methanol (Non-catalyzed) cooking are:-

  Alcohol water composition (V/V) = 7:3
  Liquor to solid ratio = 10:1
  Maximum Temperature = 180°C
  Time at Maximum Temperature = 3.0 hr.

For study with catalysts, 2.0 hr. time at maximum temperature was selected.

- Acid is found harmful to delignification Kappa no. sizes rapidly with the increase of acid concentration. Yield loss is also there. However, as already discussed addition of acid as catalyst may be helpful in very small dosage to reduce the pH when higher concentration of alcohol is used.

- Addition of Sodium hydroxide to Methanol-water mixture increases the selectivity of the system with respect to lignin, giving pulps with good yield, low Kappa No. According to mechanism studied from literature, the effect of NaOH can be ascribed to a further cleavage of the products of the Methanol reaction and to a conversion of these by-products of the lignin to its more soluble sodium derivatives. The synergistic effect of alkali and alcohol degrades even the condensed lignin into fragment and high yield, low Kappa No. could be obtained.

- Addition of Anthraquinone(AQ) in small dosage (0.05%) further improved the results. The effects of AQ in alkaline solution over the kinetics of the reaction that breakdown the lignin macromolecule are well known. Its presence in the Methanol water-NaOH system is more effective.

- Addition of Calcium Chloride improves the delignification, but yield is adversely affected. Magnesium Chloride seems to be even more attacking as yield is very low. Addition of Magnesium Sulphate also could not produce acceptable pulp.

- The main strength properties of the methanol water pulp were measured [Table- 3 C (i)]. Tear resistance appears even better than that of Soda pulp, where as Tensile strength and Burst index are lower. The density of the MeOH Organo-solv pulp is lower than that of Soda pulp. It is evident that pulps of lower density are usually exhibiting better drainage performance on the paper machine at a given Schopper-Riegler No. This might prove to be of great interest in straw pulping.

- Physico-mechanical properties of Methanol- NaOH-AQ pulp sheets are in acceptable range [Table- 3 C (ii)]. The AQ additive decreased the tear strength of Soda pulp but was not found in Methanol Pulping.

CHAPTER - 5

CONCLUSIONS

Non Catalyzed pulping with Methanol does not produce a well delignified pulp in normal cooking conditions restricting the suitability of this process only to the obtention of semi-chemical pulp. However, with severe conditions i.e. higher temperature ranges ($>$ 180°C) and higher time period (3 Hr. or more) at maximum temperature can result in pulp of suitable Kappa no. while maintaining acceptable yield.

Acid is harmful to delignification, Kappa No. rises rapidly with increase of acid concentration and yield decreases. This happens probably due to carbohydrate hydrolysis provoked by the acidic medium.

Sodium hydroxide has a good catalytic effect on delignification. Presence of NaOH enhances the delignifying ability of Methanol probably through a further cleavage of the products of Methanol reaction.

Calcium Chloride, Magnesium Chloride and Magnesium Sulphate could not produce pulps with acceptable yield. Among all the catalysts tried NaOH with 6 % dosage was found to be the best. Addition of Anthraquinon(AQ) in small dosage(0.05%) further improved the results. AQ significantly increased the delignification effect of Soda and Methanol pulping, especially of Methanol pulping.

Physical properties of Methanol pulp (non-catalyzed) are lower than Soda pulp. However the properties of Methanol-NaOH-AQ Pulp exhibits quite acceptable quality for paper making. The AQ addition decreased the tear strength of soda pulp but was not found in Methanol pulping.

Methanol pulp with Sodium-hydroxide 6% as catalyst gives better strength properties and 50% or more saving of sodium hydroxide as compared to conventional Soda pulp. This is a fact of great importance for small capacity mills without recovery furnace.

CHAPTER - 6

FURTHER WORK

Following points need further studies.

- Study of Chemical recovery aspects of alcohol used for cooking.
- Overall cost economics study of Organo-Solv Pulping.
- Studies on recovery of valuable by-products and their possible uses for consumption in market.
- ~~Study on Pollution aspects of Organo-Solv.~~

TABLE - 3.2 A (i)

Studies on depithing of bagasse for pulping.

Sl.No.	Particulars	Percentage
1.	Total amount of pith	32.0 %
2.	Pith removed by dry depithing method.	8.27 %
3.	Pith removed by wet depithing method.	4.58 %
4.	Total amount of pith removed.	12.85 %
5.	Amount of pith still associated with bagasse.	19.15 %

TABLE - 3.2 A (iii)

Dimensional Characteristics of Bagasse

Cellulosic Material	Length (mm)			Diameter (u)			Ratio of average length to diameter.
	Min.	Avg.	Max.	Min.	Avg.	Max.	
Sugarcane fibers	0.80	170	2.80	10.2	20.2	34.1	85:1
Parenchyma	-	-	0.84	-	-	140	-
Vessel Segments	-	-	1.35	-	-	150	-

TABLE - 3.2 A (ii)

Proximate Chemical Analysis of Bagasse.

			Whole Bagasse	Depithed Bagasse (Fiber)	Pith
1.	Ash	%	3.1	2.5	6.4
2.	Hot Water Solubles	%	2.6	0.8	2.1
3.	Alcohol-Benzene Solubles	%	4.2	1.7	2.6
4.	1% NaOH solubles	%	29.6	26.3	35.3
5.	Lignin	%	20.6	19.7	20.3
6.	Pentosan	%	25.8	26.6	27.4
7.	Hollo-Cellulose	%	74.9	77.5	73.6
8.	Alpha Cellulose (Corrected)	%	37.2	41.8	31.7

TABLE- 3.1. B

CHOICE OF ALCOHOL

(Comparision of Ethanol and Methanol Pulping)

Fixed Conditions:

Alcohol to Water ratio = 50 : 50
Liquor to Solid ratio = 10 : 1
Maximum Temperature = 180°C
Time to reach Max.Temp. = 1.25 hr.
Time at Max. Temp. = 1.5 hr.

Organic Solvent	Lignin to Solid ratio.	Alcohol water Compo-	Maximum Temp. °C	Total Yield (%)	Kappa No.	Lignin (%)
Ethanol	10:1	50:50	180	72.1	78.5	12.56
Methanol	10:1	50:50	180	66.3	69.2	11.0

TABLE- 3.2 E (i)

EFFECT OF TEMPERATURE

Fixed Conditions:

Liquor to Solid Ratio = 10 : 1

V/V Concentration of Alcohol = 50 : 50
with water.

Time to reach Max.Temp. = 1.25 Hr.

Time at Max. Temperature = 1.5 hr.

Max.Temp. °C	Total Yield (%)	Kappa No.	Lignin (%)
160	70.4	76.2	12.19
180	66.8	62.5	10.00
200	60.4	50.2	8.03

TABLE- 3.2 B (ii)

EFFECT OF ALCOHOL COMPOSITION (V/V)

Fixed Conditions:

Liquor to Solid ratio = 10 : 1

Maximum Temperature = 180°C

Time to reach Max.Temp. = 1.25 hr.

Time at Max.Temp. = 1.5 hr.

Alcohol-water Composition (V/V)	Total Yield (%)	Kappa No.	Lignin (%)
80 : 20	69.2	64.3	10.28
70 : 30	67.8	56.4	9.02
50 : 50	62.5	60.2	9.63

TABLE - 3.2 B (iii)

EFFECT OF LIQUOR TO SOLID RATIO

Fixed Conditions:

Alcohol Water composition (V/V) = 7 : 3

Maximum Temperature = 180°C

Time to reach Maximum Temperature = 1.25 hr.

Time at Maximum Temperature = 1.5 hr.

Liquor to Solid ratio	Total Yield	Kappa No.	Lignin (%)
4 : 1	64.1	63.5	10.16
7 : 1	65.3	60.2	9.63
10 : 1	68.2	56.1	8.97

TABLE-3.2-B-(iv)

EFFECT OF TIME AT MAXIMUM TEMPERATURE

Fixed Conditions;

Alcohol water composition(V/V) = 7:3

Liquor to Solid ratio = 10:1

Maximum Temperature = 180°C

Time to reach Max. Temp. = 1.25 hr.

Time at Max. Temp. Hr.	Total Yield (%)	Kappa No.	Lignin (%)
1	74.1	68.2	10.91
2	65.3	49.5	7.92
3	58.6	32.8	5.24

TABLE- 3.3 B (i)

SODA AND SODA-AQ PULPING OF BAGASSE

Fixed Conditions:

Active Alkali = 15 % (as Na_2O)

Bath Ratio = 1 : 4

Maximum Temperature = 160°C

Time to reach Maximum Temperature = 1.25 hr.

Time at Maximum Temperature = 1.0 hr.

Sl.No.	Dose of AQ %(on O.D.) bagasse basis)	Total Yield	Kappa No.	Lignin (%)
1.	0.0	43.5	21.6	3.45
2.	0.05	44.8	18.7	2.99

TABLE - 3.3 B (ii)

KRAFT AND KRAFT-AQ PULPING OF BAGASSE

Fixed Conditions:

Active Alkali = 15 % (as Na_2O)
Sulphidity = 20 %
Bath Ratio = 1 : 4
Maximum Temperature = 160°C
Time to reach Max. Temp. = 1.25 hr.
Time at Maximum Temp. = 1.0 hr.

Sl. No.	Dose of AQ % (on O.D. bagasse basis)	Total Yield (%)	Kappa No. No.	Lignin (%)
1.	0.0	46.1	20.8	3.32
2.	0.05	46.8	19.2	3.07

TABLE- 3.4 B (i)

EFFECT OF SULPHURIC ACID (H_2SO_4)

Fixed conditions:

Alcohol water composition (V/V) = 7 : 3

Liquor to solid ratio = 10 : 1

Maximum Temperature = 180°C

Time to reach Maximum Temp. = 90 min.

Time at Maximum Temperature = 2.0 Hr.

H_2SO_4 (% on O.D. Bagasse)	Total Yield (%)	Kappa No.	Lignin (%)
0.05	54.2	50.3	8.04
0.10	52.6	56.8	9.08
0.15	48.5	64.3	10.3

TABLE- 3.4 B (ii)

EFFECT OF SODIUM HYDROXIDE (NaOH)

Fixed Conditions:

Alcohol water composition (V/V) = 7 : 3

Liquor to solid ratio = 10: 1

Maximum Temperature = 180°C

Time to reach Maximum Temp. = 90 min.

Time at Maximum Temperature = 2.0 Hr.

NaOH (% on O.D. Bagasse)	Total Yield (%)	Kappa No.	Lignin (%)
2	62.8	51.3	8.21
4	60.1	42.2	6.75
6	56.2	28.5	4.56

3.4 B (iii)
TABLE-

EFFECT OF ANTHRAQUINONE (AQ)

Fixed Conditions:

Alcohol water composition (V/V) = 7 : 3

Liquor to solid ratio = 10 : 1

% of AQ on O.D. Bagasse = 0.05

Maximum Temperature = 180°C

Time to reach Maximum Temperature = 90 min.

Time at Maximum Temperature = 2.0 Hr.

NaOH (% on O.D. Bagasse)	AQ (%)	Total Yield (%)	Kappa No.	Lignin (%)
2	0.05	63.9	45.2	7.23
4	0.05	61.2	36.3	5.81
6	0.05	57.6	25.2	4.03

TABLE- 3.4 B (iv)

EFFECT OF CALCIUM CHLORIDE ($CaCl_2$)

Fixed Conditions:

Alcohol water composition (V/V) = 7 : 3
Liquor to solid ratio = 10 : 1
Maximum Temperature = 180°C
Time to reach Maximum Temp. = 90 min.
Time at Maximum Temperature = 2.0 Hr.

$CaCl_2$ (% on O.D. Bagasse)	Total Yield (%)	Kappa No.	Lignin (%)
0.5	53.2	49.6	7.93
1.0	48.4	41.2	6.59
2.0	40.3	30.6	4.89

TABLE- 3.4 B (v)

EFFECT OF MAGNESIUM CHLORIDE ($MgCl_2$)

Fixed Conditions:

Alcohol water composition (V/V) = 7 : 3

Liquor to solid ratio = 10 : 1

Maximum Temperature = 180°C

Time to reach Maximum Temp. = 90 min.

Time at Maximum Temperature = 2.0 Hr.

$MgCl_2$ (% on O.D. Bagasse)	Total Yield (%)	Kappa No.	Lignin (%)
0.5	51.5	47.2	7.55
1.0	45.2	40.1	6.41
2.0	38.6 34.6	26.5	4.24

TABLE- 3.4 B (vi)

EFFECT OF MAGNESIUM SULPHATE ($MgSO_4$)

Fixed Conditions:

Alcohol water composition (V/V) = 7 : 3

Liquor to solid ratio = 10 : 1

Maximum Temperature = 180°C

Time to reach Maximum Temp. = 90 min

Time at Maximum Temperature = 2.0 Hr.

$MgSO_4$ (% on O.D. Bagasse)	Total Yield (%)	Kappa No.	Lignin (%)
0.5	59.1	50.4	8.06
1.0	50.3	46.3	7.41
2.0	39.5	40.2	6.43

TABLE- 3 C (i)

Physical properties of unbleached Methanol Pulp (Non-catalyzed) at optimum conditions compared to Soda-Pulp properties:-

Property °SR	Methanol Pulp	Soda Pulp
°SR	40	38
Apparent Density(g/cm^3)	0.62	0.66
Tensile Index (Nm/g)	46	52
Burst Index (KPam^2/g)	2.2	2.5
Tear Index (mN m^2/g)	3.1	2.9

TABLE- 3 C (ii)

Physical properties of unbleached Methanol Pulp with NaOH(6%) and AQ(0.05%) to Soda Pulp with AQ(0.05%).

Property	Methanol-NaOH-AQ Pulp	Soda-AQ Pulp
°SR	39	40
Apparent Density (g/cm^3)	0.58	0.63
Tensile Index (Nm/g)	51	54
Burst Index (kPa m^2/g)	2.6	2.4
Tear Index (mN m^2/g)	3.4	2.5

ANNEXURE- I

SUMMARY OF INSTALLED CAPACITY OF PAPER AND PAPER BOARD INDUSTRIES CATEGORY-WISE AS ON 1ST JANUARY,1991

No.	Category	No. of Units		Annual Installed Capacity(in Tonnes)		Monthly Installed Capacity(In Tonnes)	
		1990	1991	1990	1991	1990	1991
	I	31	31	14,81,100	15,65,423	1,23,425	1,30,452
	II	24	29	3,79,100	4,66,500	31,592	38,875
	III	88	94	7,30,040	7,69,990	60,837	64,166
	IV	110	120	3,70,850	4,00,580	30,904	33,382
	V	58	53	88,469	81,554	7,372	6,796
	TOTAL :	311	327	30,49,559	32,84,047	2,54,130	2,73,671

CATEGORY -I: : Mills having capacity above 20,000 tonnes per annum.

CATEGORY -II : Mills having Capacity from 10,000 to 20,000 tonnes per annum.

CATEGORY -III : Mills having capacity from 5,000 to 10,000 tonnes per annum.

CATEGORY -IV : Mills having capacity from 2,000 to 5,000 tonnes per annum.

CATEGORY -V : Mills having capacity 2,000 tonnes & below per annum.

ANNEXURE - II

EXPECTED ALCELL MILLS BY 2000

HARDWOOD	
Increased BHKP requirements	17 million metric tons
Alcell, 50 %	8.5 million metric tons
Number of new Alcell mills	85
SOFTWOOD	
Increased BSKP requirements	13 million metric tons
Alcell, 15%	2 million metric tons
Number of new Alcell mills	20
Total new Alcell mills	105

Source: Repap Enterprises Inc.

ANNEXURE - III

PHYSICAL PROPERTIES OF ALCELL COMPARED TO KRAFT

		Alcell Pulp	Commercial kraft pulp
Tensile	(km)	7.47	7.40
Tear	($mN.M^2/g$)	7.20	6.75
Burst	($kPa.m_2/g$)	5.08	5.18
Brightness	(ISO)	88.7	89.6

ANNEXURE - IV

COMPARISON OF ASPEN PULP PROPERTIES FROM VARIOUS PROCESSES

	Ester 1	Ester 2	Alcohol	Sulfite	Kraft
Yield %	55.3	64	53	44	54
Kappa No.	15	23	24	20	12
Freeness mLCSF	430	397	...	450	465
Burst factor	37	33	30	31	51
Tear factor	61	47	56	47	107
Tensile, km	8.7	7.1	5.6	5.9	8.7
Bulk, /g	1.20	1.34	1.50	1.36	..
Reference	...	7	12	...	7

ANNEXURE - V

ESTER PULPING OF VARIOUS HARDWOODS AND SOFTWOODS

Species	Yield, %	Kappa No.
	HARDWOODS	
Aspen	55	13
Oak	46	11
Birch	49	16
Eucalyptus	46	20
	SOFTWOODS	
Spruce	44	29
Pine	42	22

ANNEXURE - VI

TYPICAL PROPERTIES OF MIXED HARDWOOD ALCELL LIGNIN

Ash, %	less than 1
Moisture, %	less than 3
Wood Sugars, %	less than 0.5
Acid Number	20-25
Specific Gravity	1.27
Glass Transition Temperature, °C	90-100
Softening, ring and ball, °C	145
Heating Value, J/kg	4.6×10^7
Heating Value, Btu/lb	11,000
Number Average Molecular Weight	less than 900
Weight Average Molecular Weight	less than 2,000
Median Particle size, microns	20-40

ANNEXURE - VII

ELEMENTAL ANALYSIS OF TYPICAL ALCELL LIGNIN

Carbon	65.93
Hydrogen	5.73
Oxygen	28.34
Methoxyl	18.99

ANNEXURE - VIII

LEADING COUNTRIES IN PRODUCTION CAPACITY FOR BAGASSE PULP AND PERCENTAGE OF WORLD TOTAL CAPACITY FOR EACH COUNTRY

	1985		1987		1990	
Country	Cap. 1000 MT	% of world total	Cap. 1000 MT	% of world total	Cap. 1000 MT	% of world total
1. Mexico	408	17.9	292	12.6	292	11.7
2. China	351	15.4	420	18.1	525	21.1
3. Peru	308	13.5	296	12.8	296	11.9
4. Indonesia	183	8.0	183	7.9	183	7.4
5. Taiwan	135	5.9	150	6.5	150	6.0
6. Argentina	135	5.9	135	5.8	135	5.4
7. Venezuela	125	5.5	140	6.0	140	5.6
8. Cuba	108	4.7	108	4.7	108	4.3
9. Brazil	99	4.3	78	3.3	78	3.1
10. Colombia	93	4.1	93	4.0	154	6.2
11. South Africa	90	4.0	99	4.3	99	4.0
12. Iran	60	2.6	60	2.6	60	2.4
13. Pakistan	30	1.3	30	1.3	30	1.2
14. India	30	1.3	90	3.9	90	3.6
15. Iraq	27	1122	27	1.2	27	1.1
16. Thailand	24	1.0	45	1.9	50	2.0
17. Philippines	22	1.0	22	0.9	22	0.9
18. Egypt	18	0.8	18	0.8	18	0.7
19. Bangladesh	15	0.7	15	0.6	15	0.6
20. Ecuador	15	0.7	15	0.6	15	0.6
Subtotal for Ist 20 countries	2276	99.8	2316	99.8	2487	99.8
Estimates total all countries	2281	100	2321	100	2492	100

ANNEXURE – IX

TYPICAL USES OF BAGASSE PULP IN VARIOUS GRADES OF PAPER AND PAPERBOARD

		Bagasse Pulp %
I.	Bleached Bagasse Mechanical, Chem-mechanical and/or Thermo-mechanical pulps Newsprint	
	Mechanical-Type Printing	75-80
	Papers	50
	Tissue	50
II.	High Yield Unbleached Bagasse Semichemical Pulp	
	Corrugating Medium	75-100
III.	Unbleached Bagasse Chemical Pulp Multi-wall Bag Paper	40(upto 60 for Cluppak)
	Test Linerboard	40-60
	Wrapping Paper (-B Grade)	75
	Fruit Wrap and Tissues	60-90
	Glassine and Greaseproof	50-90
IV.	Bleached Bagasse Chemical Pulp	
	Printing and Writing Papers	80-100
	Write-lined Combination Board (liner portion)	50
	Food and Milk Bottle Board and Bristol Board	75-90
	Fruit Wraps and Tissues	60-90
	Glassine and Greaseproof	50-90

Fig. 2.3 A SCHEMATIC DIAGRAM OF ALCELL PROCESS

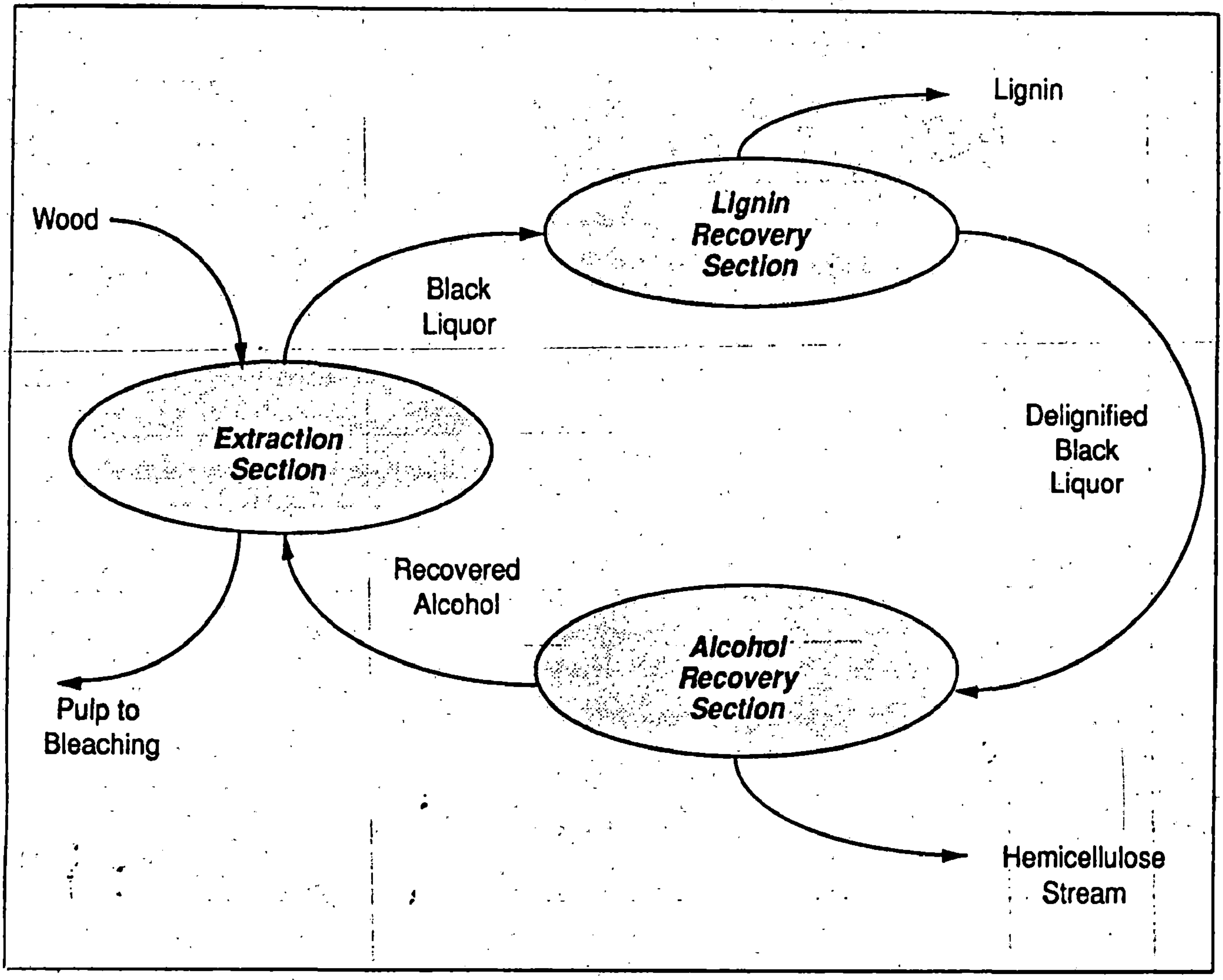


Fig. 2.3 B BLOCK DIAGRAM OF ALCELL PROCESS

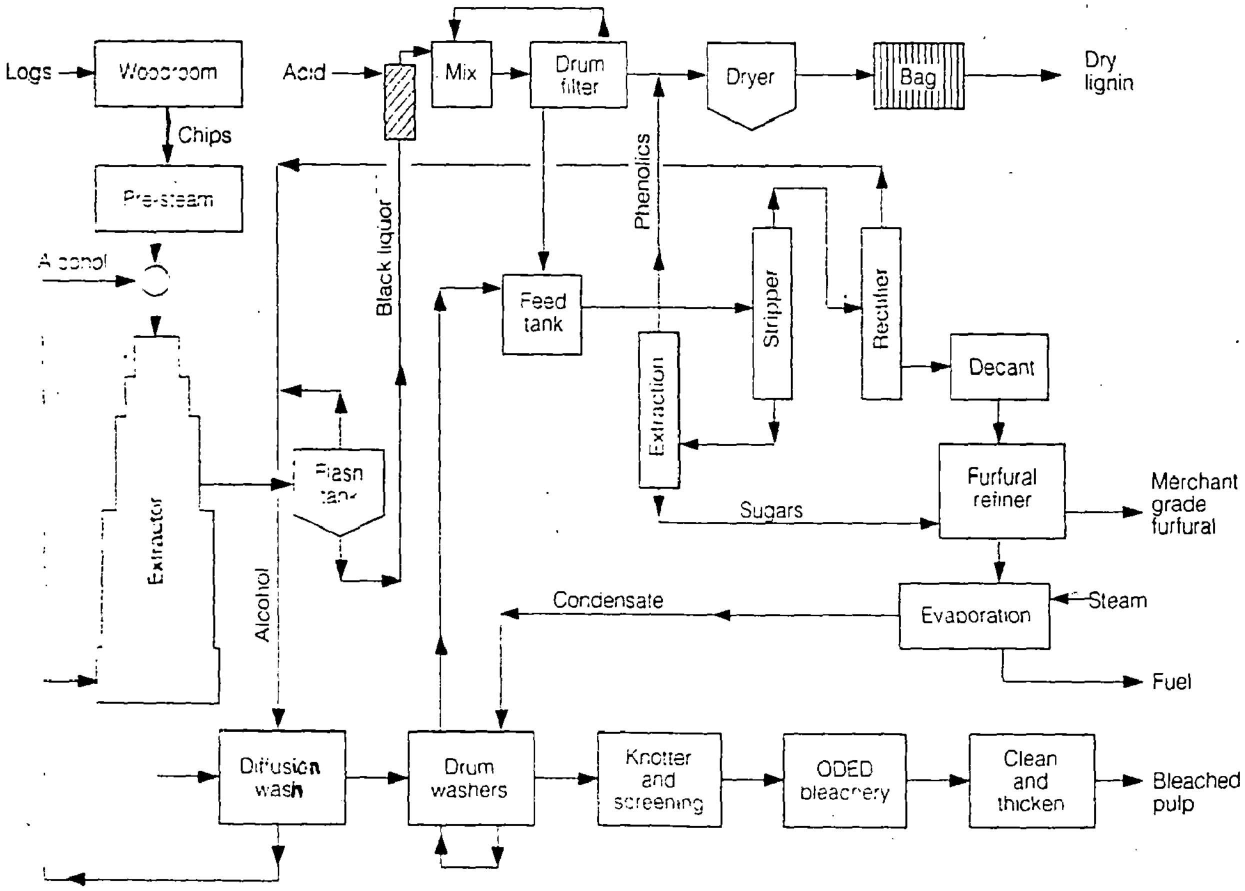
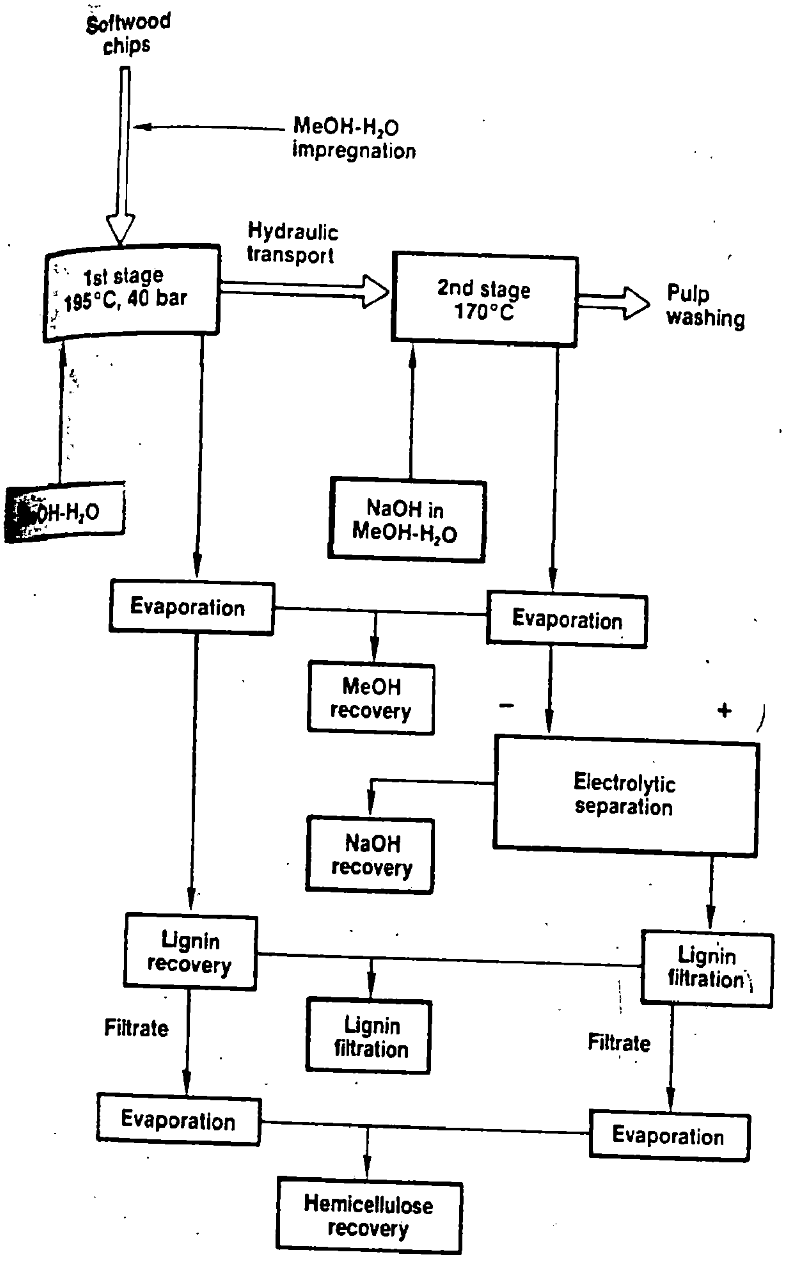


Fig. 2.3 C BLOCK DIAGRAM OF ORGANO-CELL PROCESS



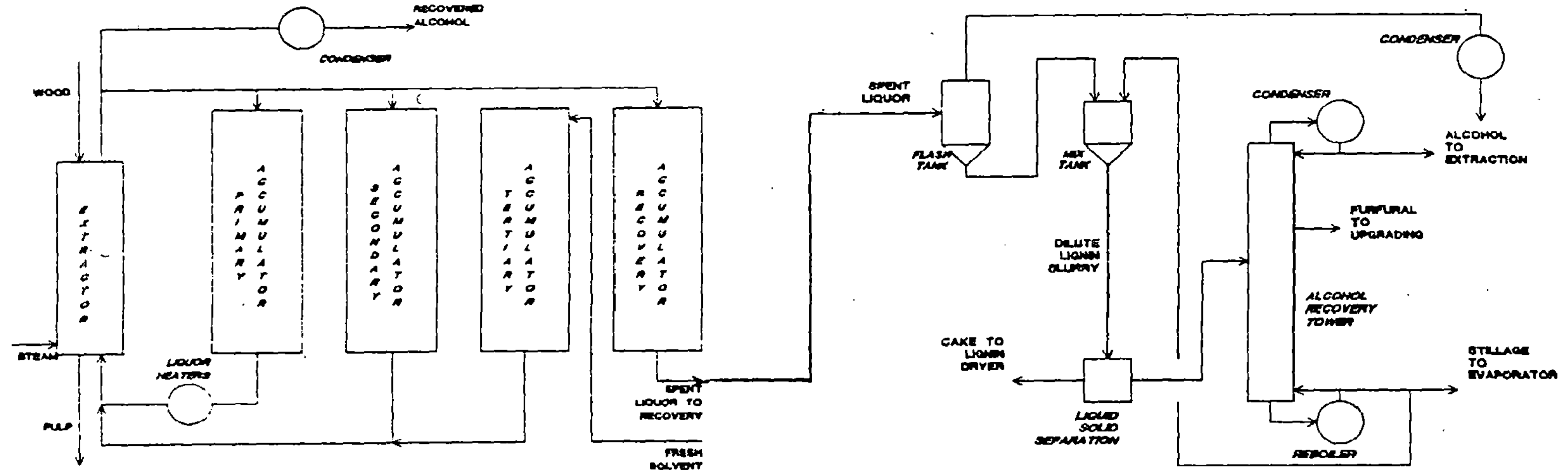
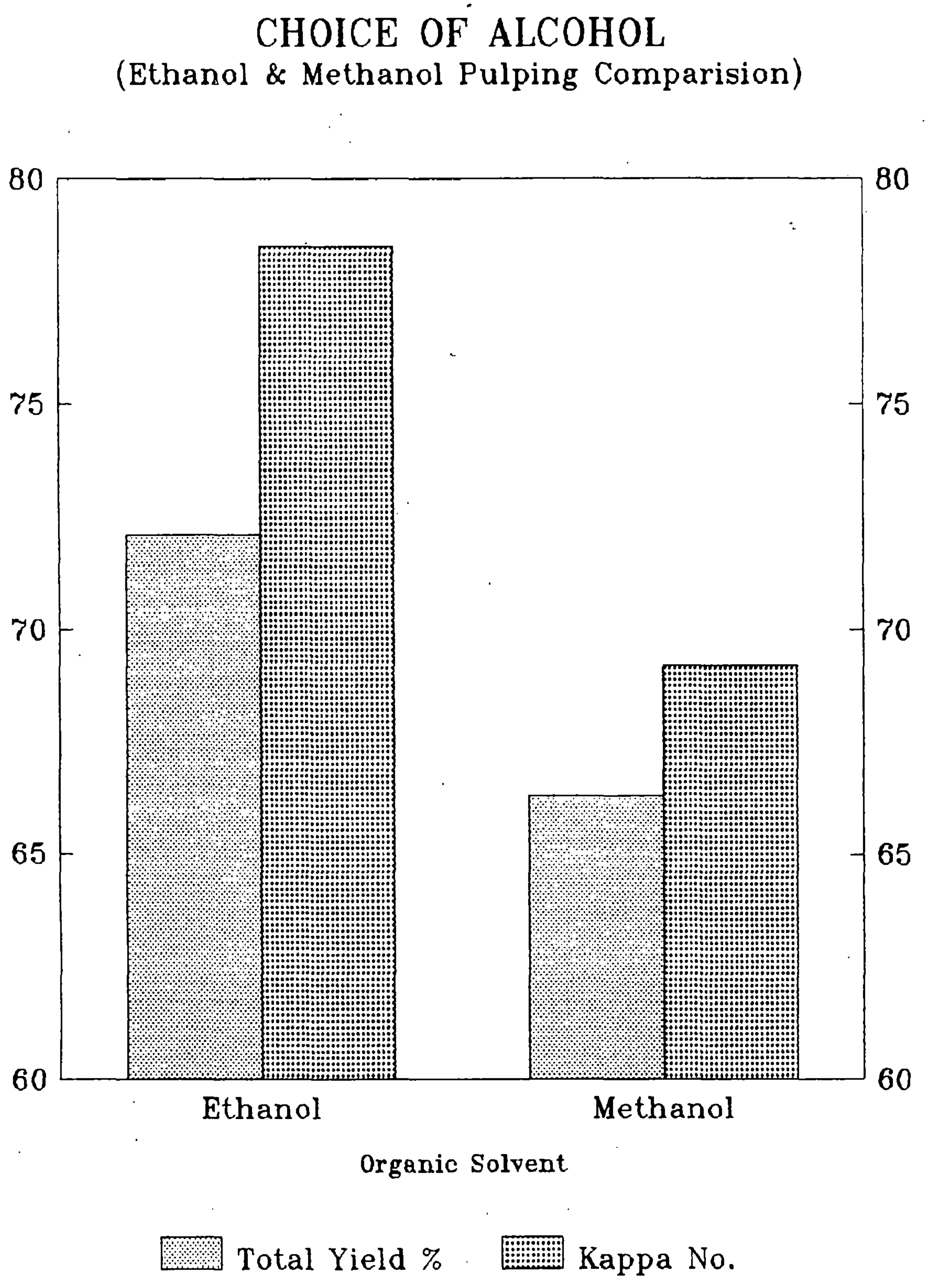


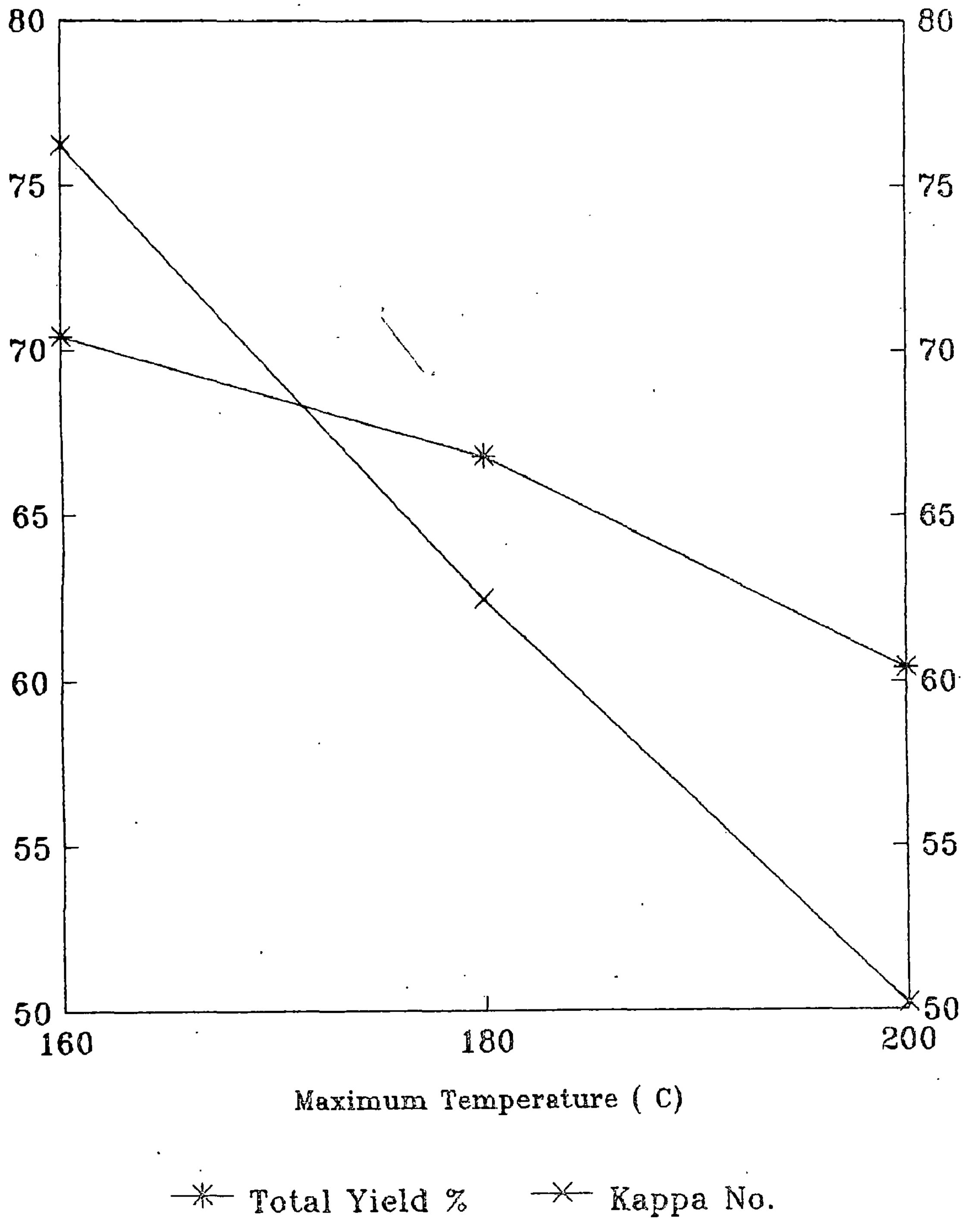
Fig. 2.5 A ALCOHOL AND BY-PRODUCTS RECOVERY

GRAPH 3.1 B

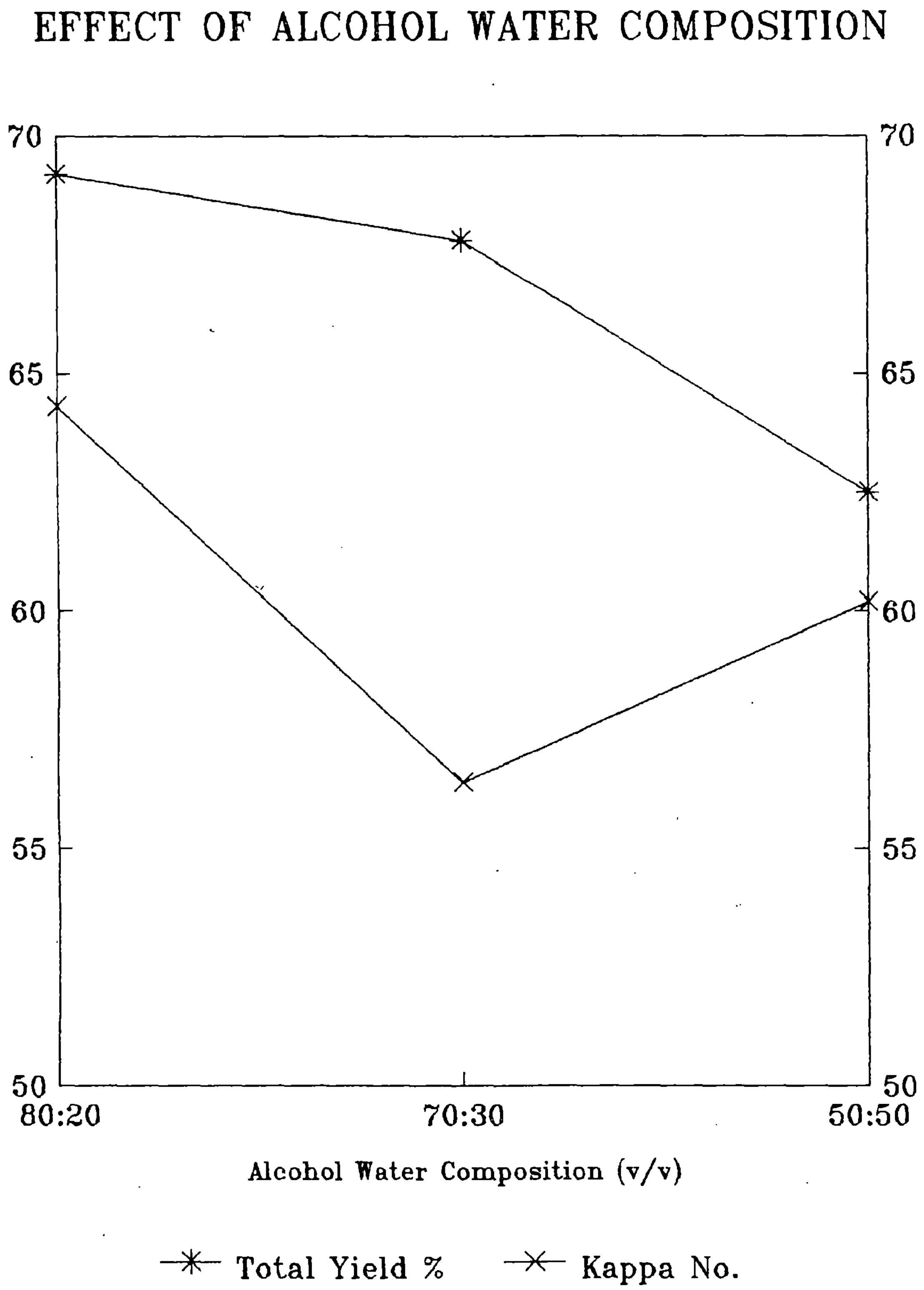

CHOICE OF ALCOHOL
(Ethanol & Methanol Pulping Comparision)
80
75
70
65
60
80
75
70
65
60
Ethanol
Methanol
Organic Solvent
Total Yield %
Kappa No.

GRAPH 3.2 B (i)

EFFECT OF TEMPERAATURE

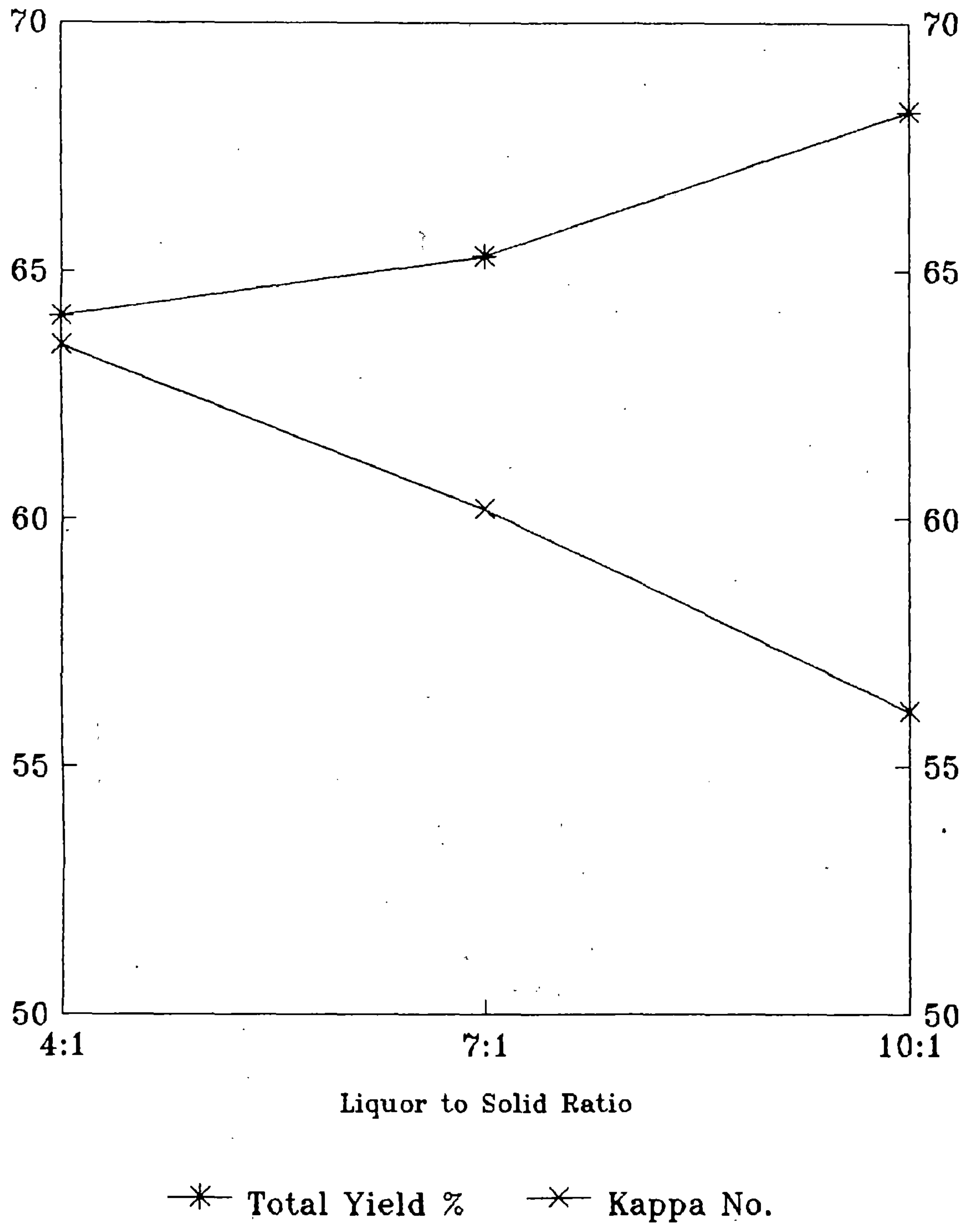


GRAPH 3.2 B (ii)

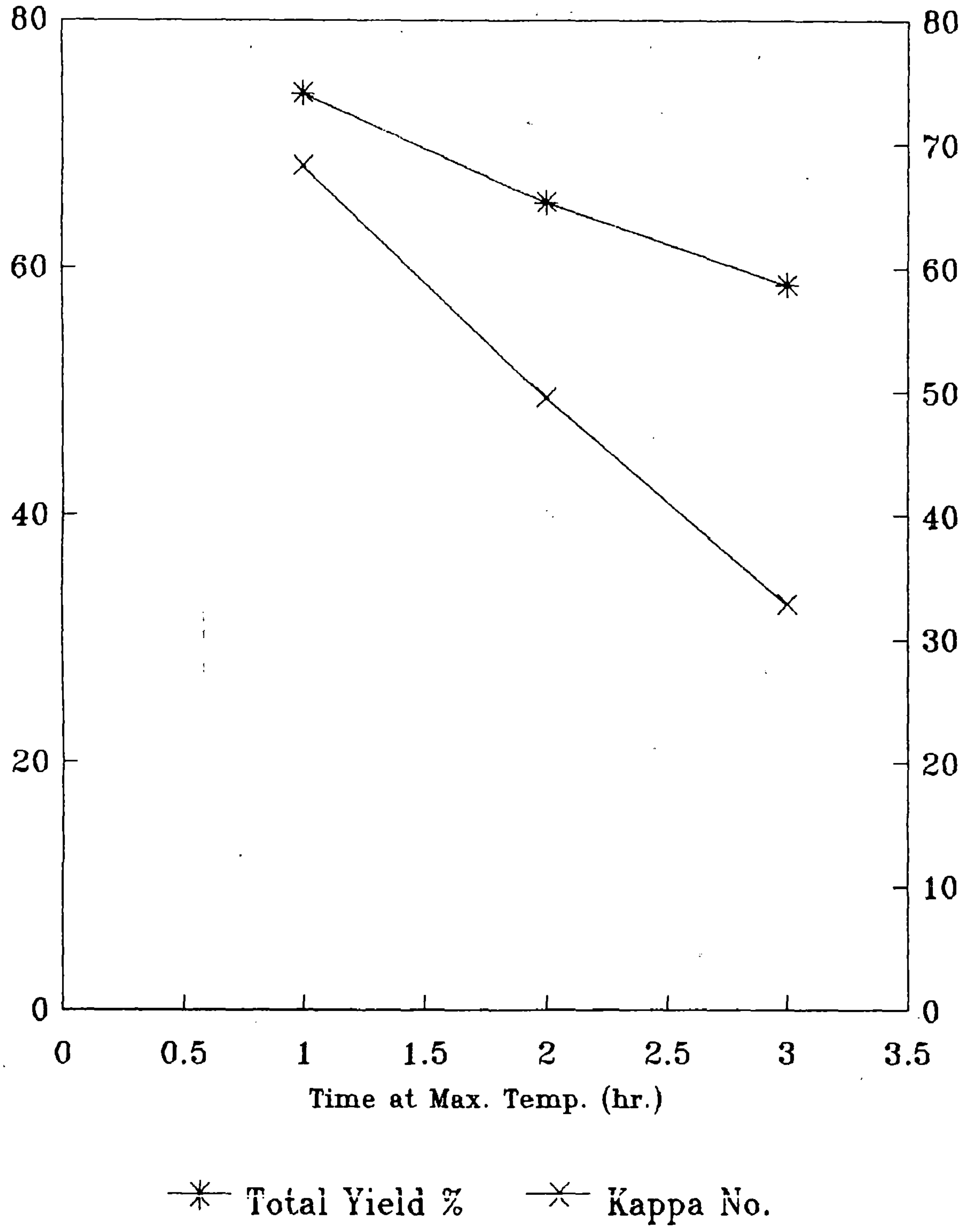

EFFECT OF ALCOHOL WATER COMPOSITION
70
65
60
55
50
70
65
60
55
50
80:20
70:30
50:50
Alcohol Water Composition (v/v)
Total Yield %
Kappa No.

GRAPH 3.2 B (iii)

EFFECT OF LIQUOR TO SOLID RATIO



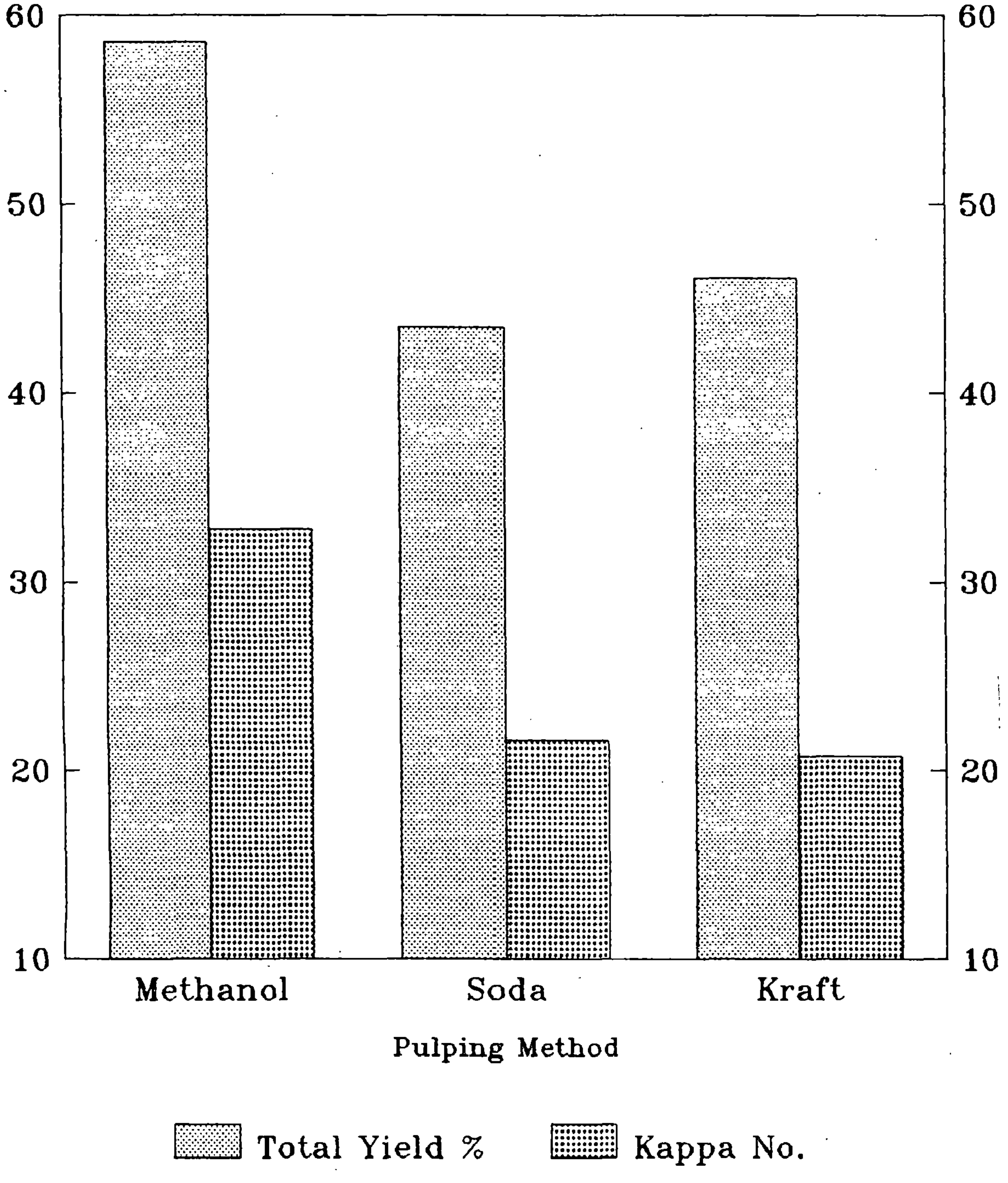
GRAPH 3.2 B (iv)



EFFECT OF TIME AT MAX. TEMPERATURE

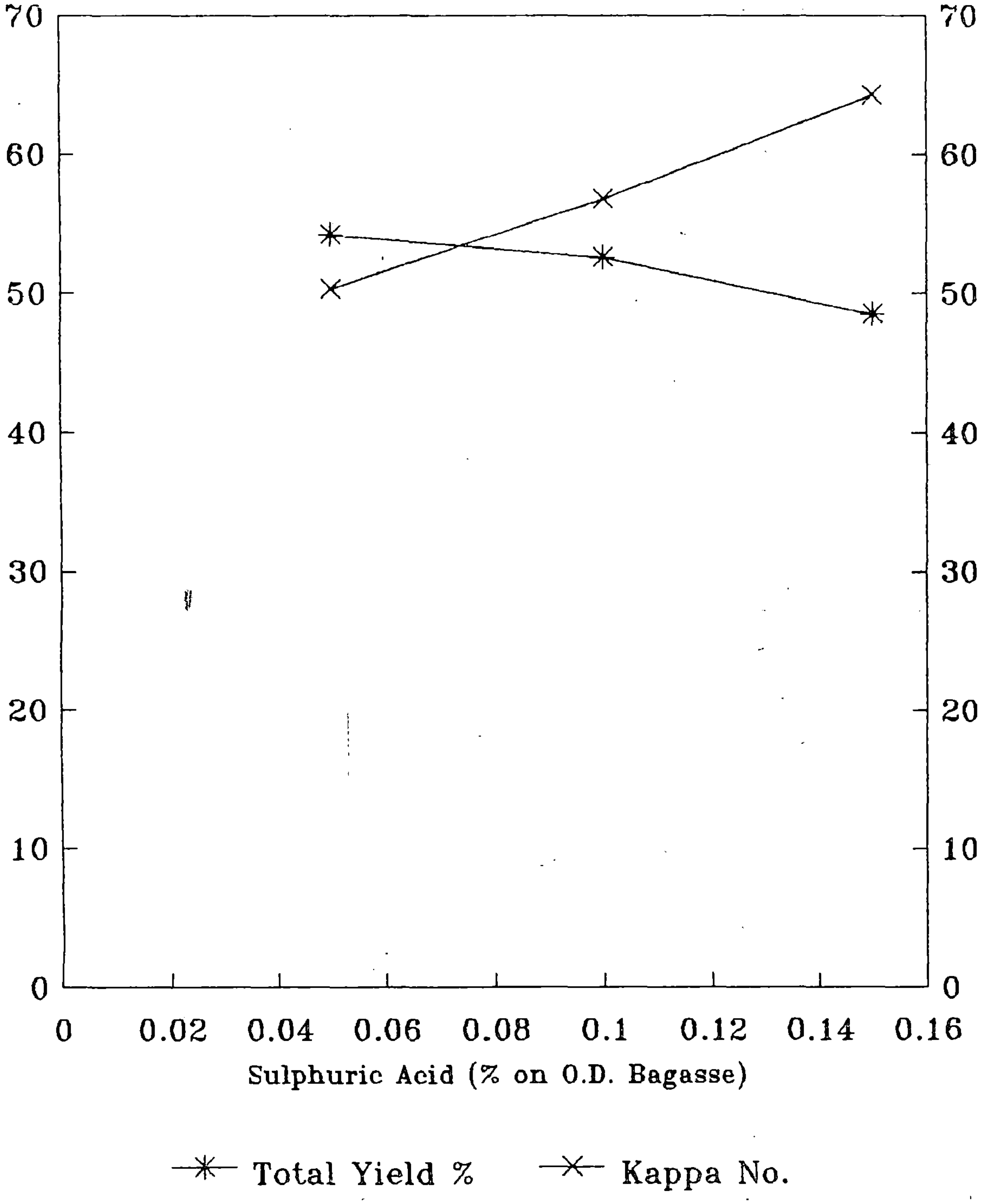
GRAPH 3.3 B

COMPARISION OF METHANOL-SODA-KRAFT PULP
(Methanol Cooking at Optimum Conditions)



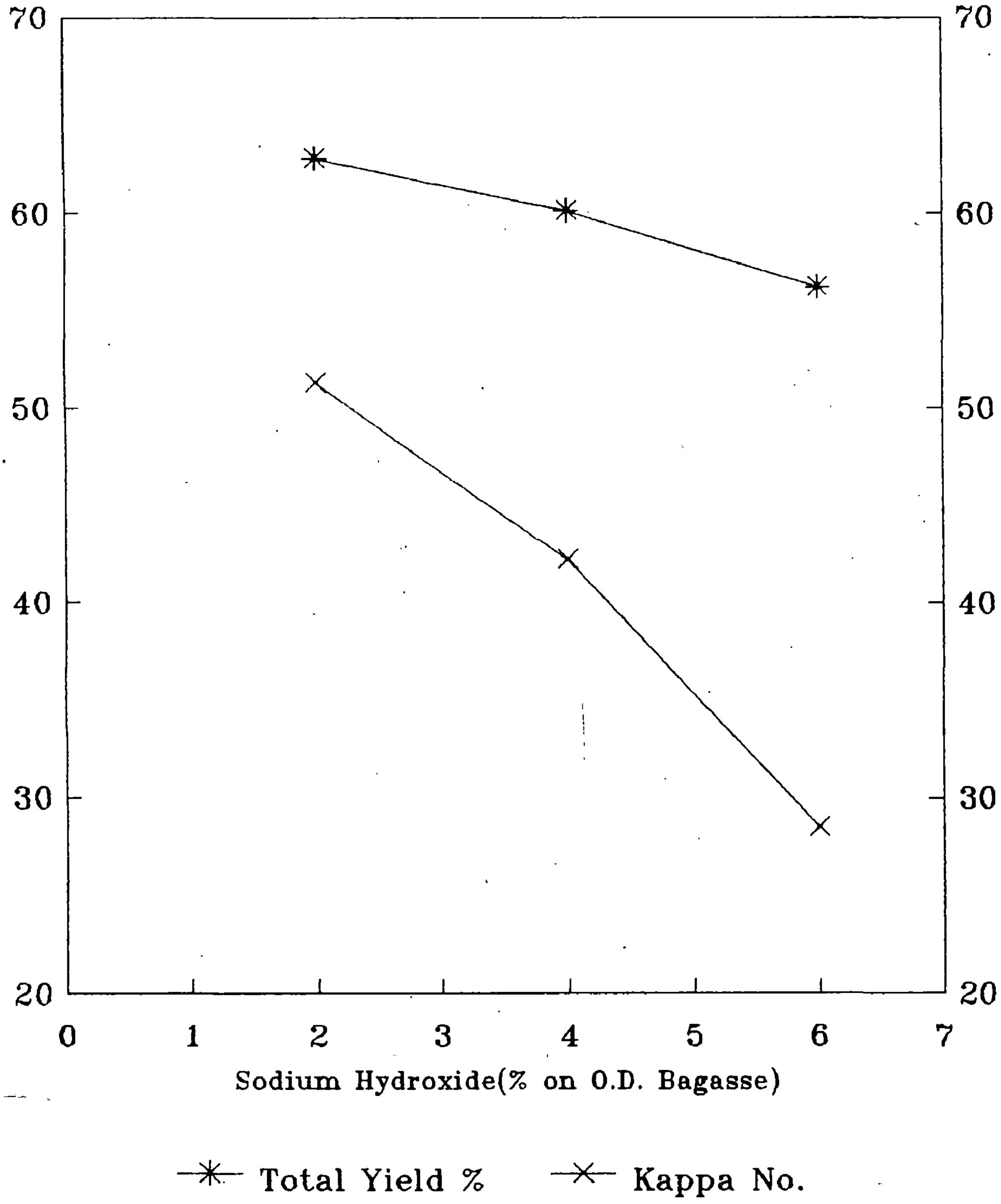
GRAPH 3.4 B (i)

EFFECT OF SULPHURIC ACID



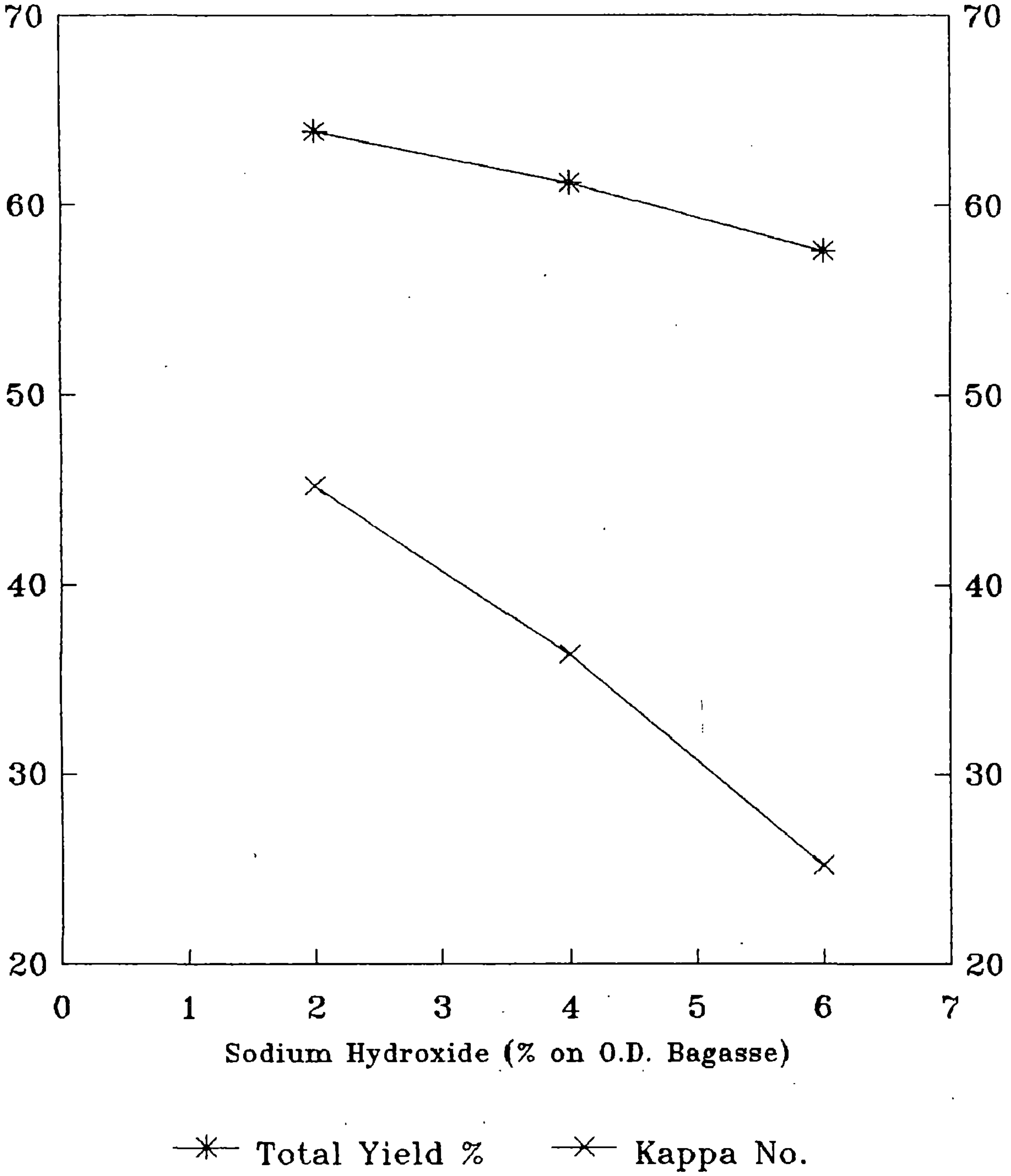
GRAPH 3.4 B (ii)

EFFECT OF SODIUM HYDROXIDE



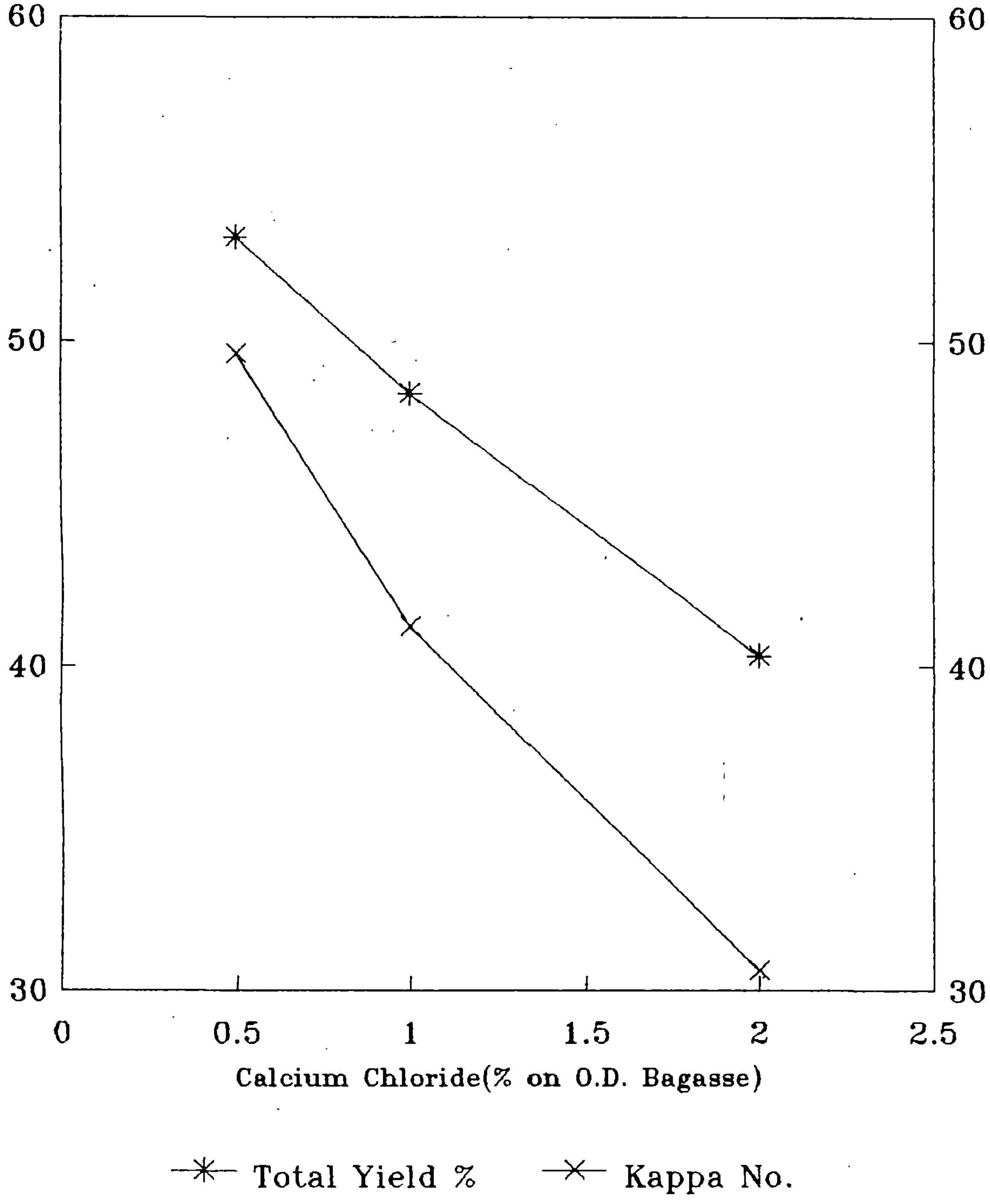
GRAPH 3.4 B (iii)

EFFECT OF ANTHRAQUINONE(AQ)
(AQ = 0.05 %)



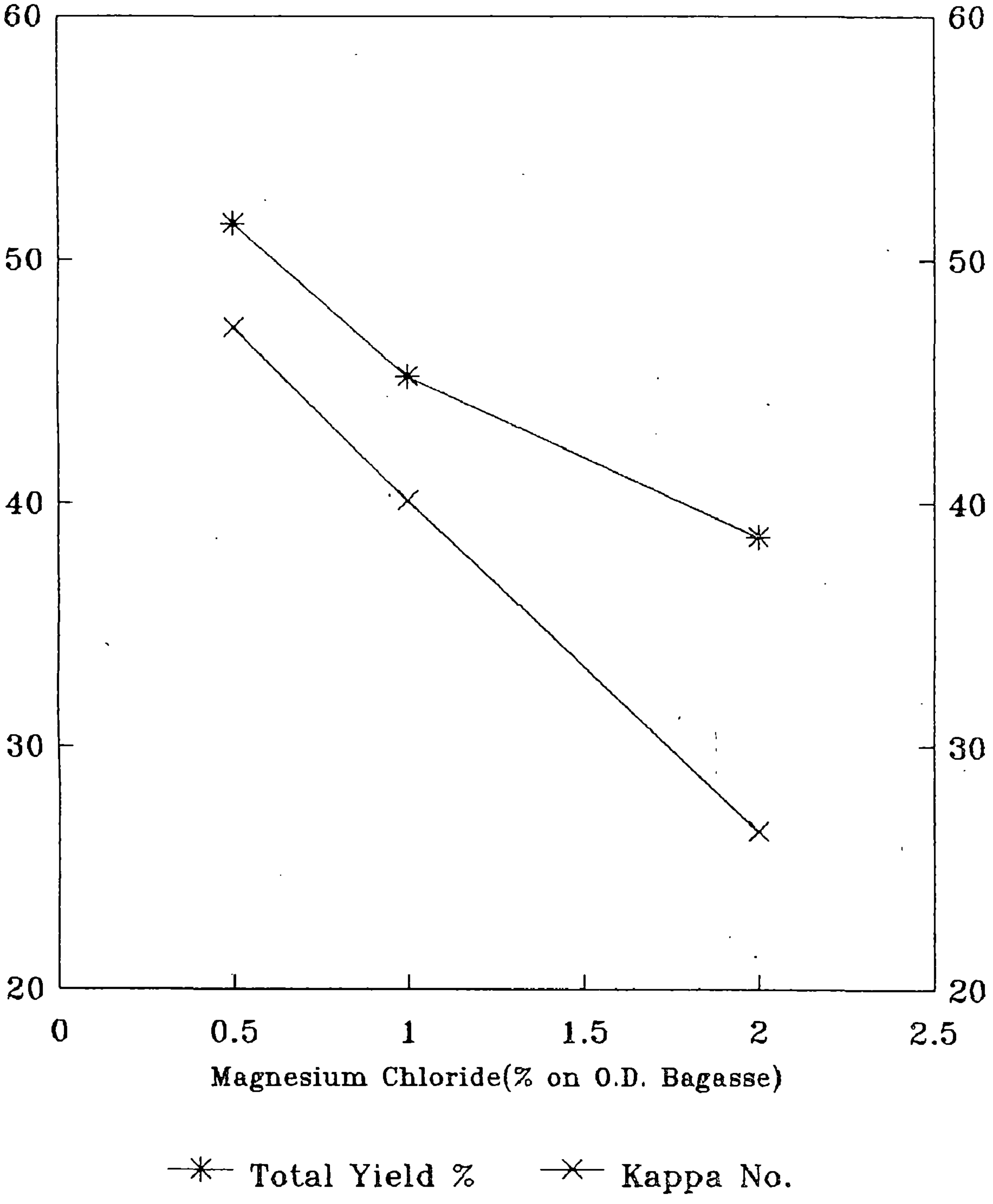
GRAPH 3.4 B (iv)

EFFECT OF CALCIUM CHLORIDE



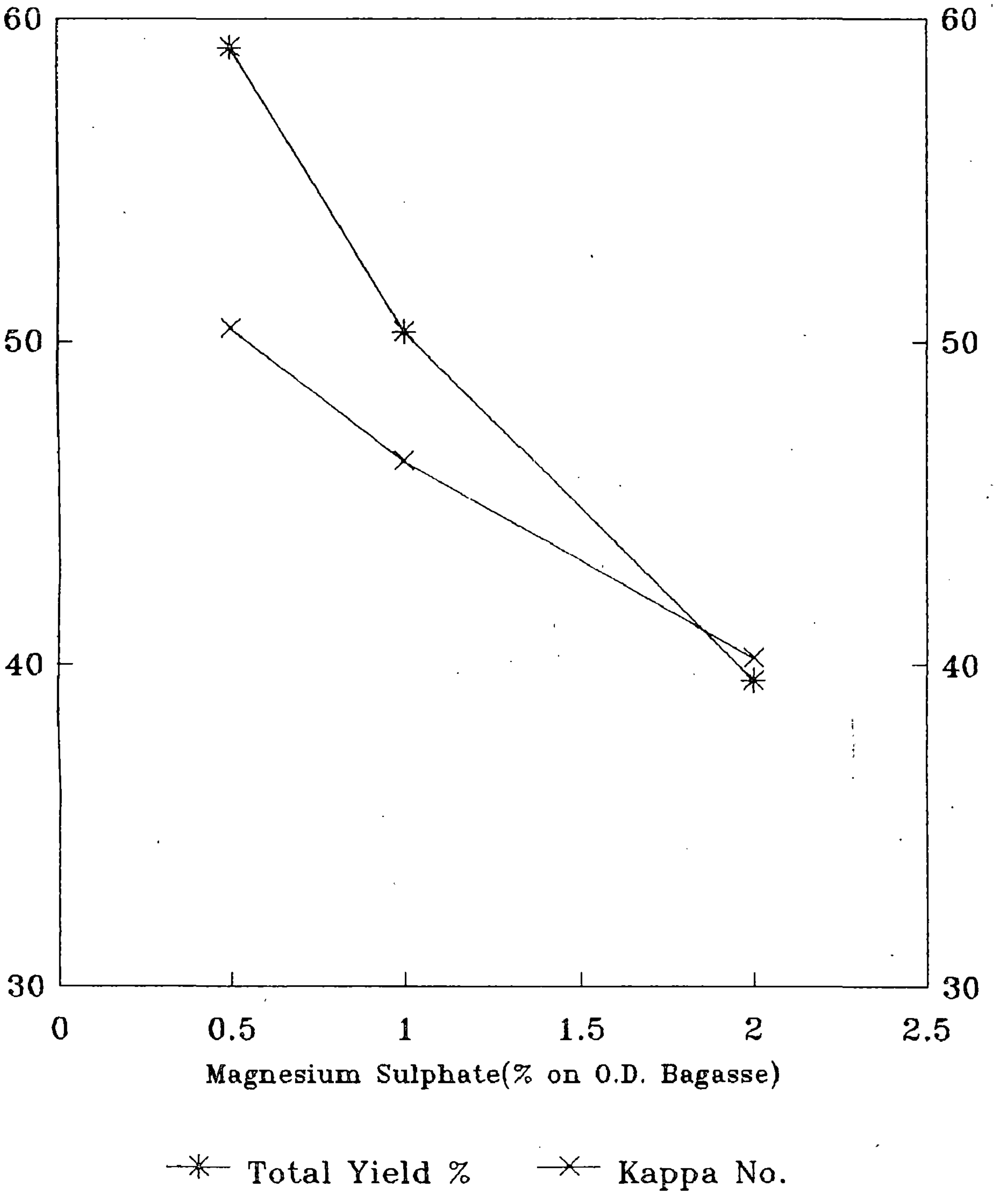
GRAPH 3.4 B (v)

EFFECT OF MAGNESIUM CHLORIDE



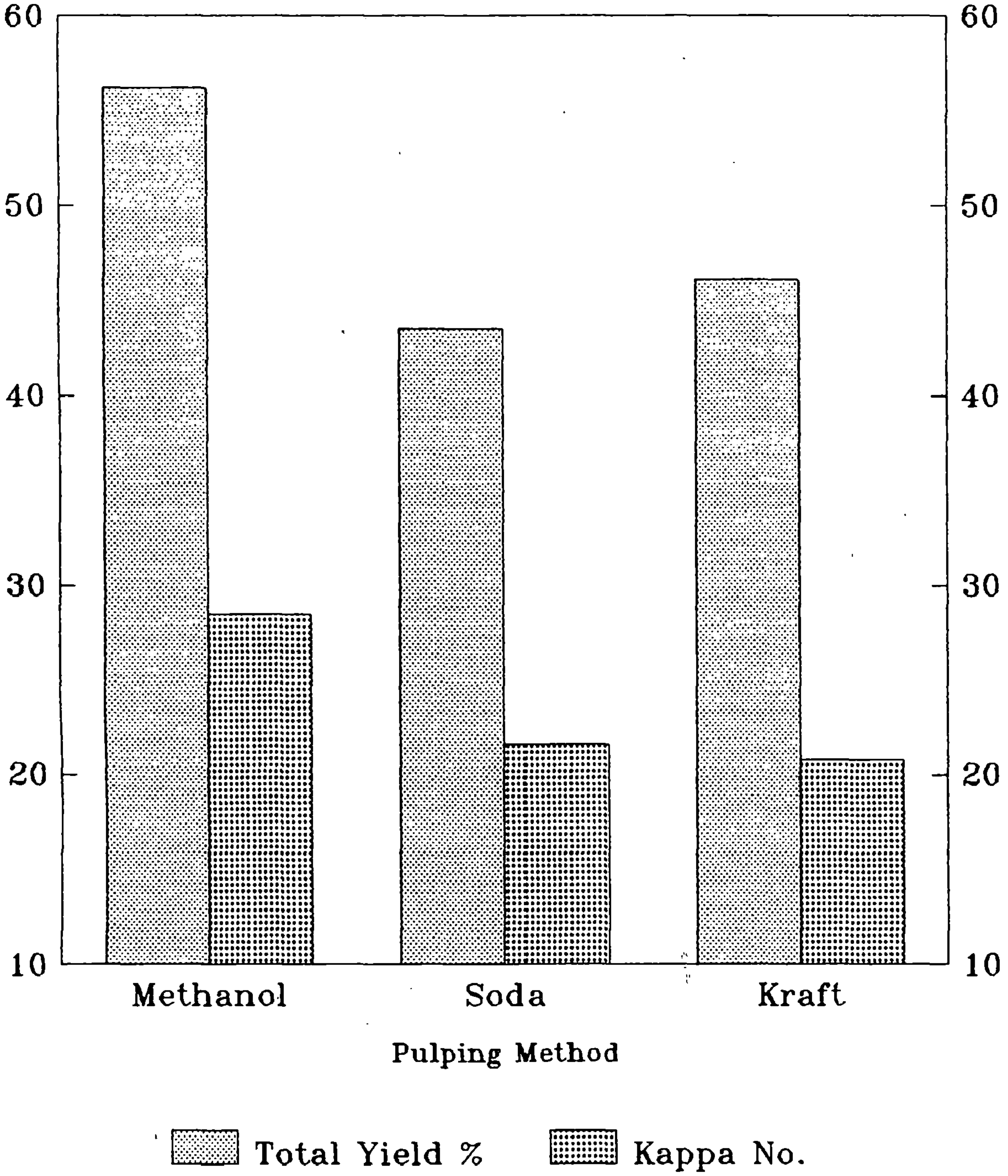
GRAPH 3.4 B (vi)

EFFECT OF MAGNESIUM SULPHATE



GRAPH 3.4 B (vii)

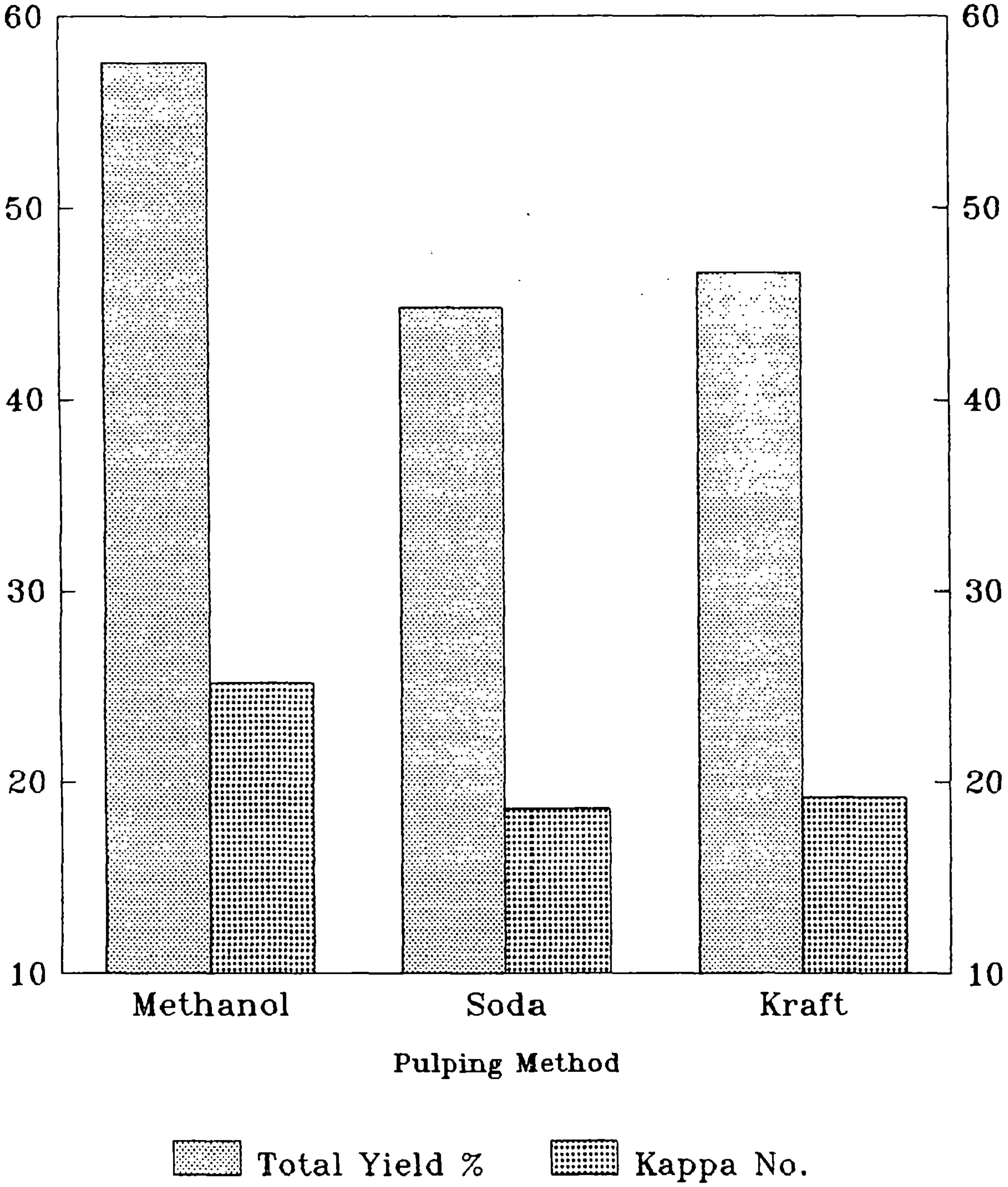
COMPARISION OF METHANOL-SODA-KRAFT PULP
(Methanol Cooking with 6% NaOH)



GRAPH 3.4 B (viii)

COMPARISION OF METHANOL-SODA-KRAFT PULP

(All width AQ Dosage 0.05%)



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