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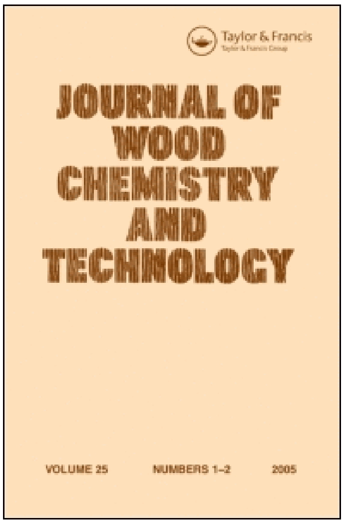

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EFFECT OF ALKALI PRETREATMENT ON EUCALYPT CHIPS ON KRAFT BLACK LIQUOR VISCOSITY AND PULP STRENGTH

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ABSTRACT

Higher viscosity of eucalypt kraft black liquor is apparently caused by a condensation of the polyphenolic extractives with lignin during pulping. Extraction of the chips with 0.1-0.2 N NaOH at 115-125°C for 4 hours is suggested, prior to pulping, for removing most of the tannin-like material constituting about 10% of plantation grown eucalypt (E.Tereticornis hybrid, 8-10 years old). Pulp yield, Kappa number and strength of a control cook with 16% active alkali are maintained with 13-14% chemical charge for the extracted chips. Viscosity data for black liquors at 80 - 100°C for concentrations up to 61% show lower values for extracted chips. The viscosity for 50% black liquor at 100°C decreases by one-third and two-third after pulping chips extracted with 0.1 and 0.2 N NaOH, respectively.

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INTRODUCTION

Plantation grown eucalypts are increasingly used in various countries for producing chemical pulps. Watson and Cohen[1] have surveyed the developments in pulping technology until 1968 for the utilization of native and plantation grown eucalypts. E. grandis, E. tereticornis and E. globulus are used in this country for making paper and rayon grade pulps. This study deals with alkali pretreatment and pulping of E. tereticornis from 8-10 years old plantations in the state of Uttar Pradesh.

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BLACK LIQUOR PROCESSING PROBLEMS

All eucalypt species contain a significant amount of extraneous polyphenolic compounds of varying chemical composition, concentration and distribution dependent upon species, age and growth factors. Plantations supply relatively uniform pulp wood unlike the native mixed mature/over-mature Australian eucalypts rich in polyphenolic extractives (kinos). The plantation grown eucalypts also contain an appreciable concentration of alkali soluble extraneous constituents presumably of monomeric and oligomeric polyphenolic tannin-like compounds.

Wood constituents are selectively solubilised during kraft pulping as sodium salts of degraded polydisperse lignin and polysaccharide degradation products in black liquor. Some polyphenolic extractives will hydrolyse in alkali to form ellagic and gallic acids and other intermediates.[2] The latter may oxidise further or condense with lignin and probably modify the physico-chemical properties of black liquor.

During chemical recovery, black liquor is concentrated in the evaporation plant to 60–64% dissolved solids and burned in the recovery furnace to reclaim pulping chemicals and energy. The concentrated black liquor is introduced as a coarse spray into the recovery boiler and the droplets undergo dehydration, swelling, volatilisation and pyrolysis reactions as they fall towards the hearth bed countercurrent to the hot furnace gases through the reducing atmosphere.

Viscosity of black liquor is an important design or operating parameter governing fluid flow pattern and heat transfer rates in the evaporation plant and spray droplet characteristics in the recovery boiler. Some of the major problems of processing eucalypt black liquors relate to the following aspects:

- inventory of pulping chemicals
- load to recovery furnace
- viscosity (with possible temperature dependent Bingham plastic behaviour above 45%)
- lignin separation as granules or lumps
- shape, size distribution, swelling and combustion characteristics of spray droplets

The higher viscosity of eucalypt black liquor adversely affects the efficient and continuous operation of the recovery section. The evaporation plant often becomes a bottle-neck in chemical recovery and seriously limits pulp production. The above problems are similar to the Australian experiences in processing black liquors from native eucalypts[3,4].

Typical viscosity data at 40°C for various black liquors (40%)compiled in Table 1 shows the species dependency[5–9]. Figure 1 shows the viscosity data of southern pine and various eucalypt black liquors at 50°C. The graphs show a sharp rise in the viscosity

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TABLE 1

Viscosity of Kraft Black Liquors

Species	Viscosity,cp 40%,40°C,	Organics %	Sample	Ref.
E. deglupta, 3 yr	15	73	A	9
E. deglupta, 13 yr	19	72	A	9
E. deglupta, 19 yr	20	69	A	9
E. Tetradonta	35	70	A	9
E. regnans	10	70	A	9
Mixed eucalypts (mature/overmature)	16-500	70-73	A	9
Mixed hardwoods (upto 28 species)	25-470	76-79	L	9
Southern pine	14	71	C	5
Bamboo	10	57	C	8
Bagasse kraft	92	66	C	8
Bagasse soda	115	59	C	8
E. tereticornis hybrid (8-10 yr)	160	-	L	8
E. grandis (8 yr) (prehydrolysis-kraft)	500	70	C	8
Straw	200	-	C	7

Sample: A - Autoclave, C- Commercial
L - rotary digester (laboratory)

of eucalypt black liquor above 35-45%. Oye and co-workers[9] also have reported abnormally high viscosity values at 20-60°C for black liquor from laboratory pulping of several eucalypt species. While the graphs in Figure 1 are not strictly comparable due to the diversity of species, geographical growth factors and variations in pulping conditions,two of the eucalypt

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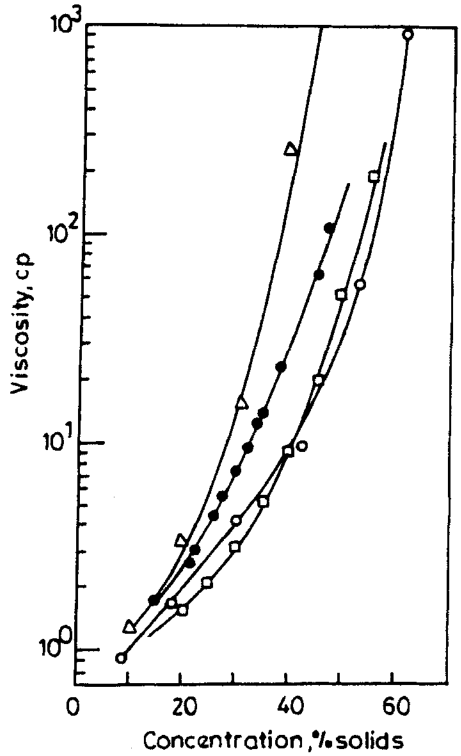

Fig. 1: Viscosity data of various eucalypt and pine black liquors at 50°C

△ Over-mature eucalypt(9)

□ Southern pine (5)

● This work-eucalypt, 8 years

o Eucalypt, 13 years (9)

black liquors possess higher viscosities than the pine black liquor. The over-mature Australian eucalypts show an abnormal increase in viscosity above 50%. Smith[3] also has observed higher viscosities for eucalypt black liquor compared to pine black liquor.

It is believed that the presence of ellagitannins, ellagic acid and gallic acid and their possible conden-

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sation products with polymeric degraded lignins contribute to the relatively large values of viscosity of eucalypt black liquors[3,4]. Kraft black liquors from pulping of softwoods like pine, spruce and fir are relatively free of any processing problem during evaporation and combustion. It would seem logical that removal of the polyphenolic extractives from eucalypts prior to pulping should give a black liquor of satisfactory processing characteristics comparable to the softwood black liquors. The polyphenolic extraneous constituents are alkali labile and it should be feasible to remove them from eucalypt chips by alkali pretreatment prior to normal kraft pulping.

This investigation deals with alkali pretreatment of commercial eucalypt chips and its effects on viscosity of the kraft black liquors and the strength of the corresponding pulps. Oye and coworkers[10] also have reported preliminary results on alkali extraction of over-mature West Australian eucalypts to reduce the viscosity of concentrated kraft black liquors.

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EXPERIMENTAL

Mill chips (40 kg) free of knots and other abnormalities were fractionated manually using square wire mesh screens to obtain the following fractions: (a) −25 + 18 mm (b) −18 + 12 mm and (c) −12 + 6 mm. Fraction (c) was used for tests with 300 g chips (preliminary experiments and Series A) while fractions (a) and (b) were used for trials with 2.5–3 kg chips (Series B).

Alkali Pretreatment

A-Series

Preliminary experiments were done at 100°C in a 3 liter flask equipped with a reflux condenser and a

Parr autoclave (2 liter) was used for subsequent work at 115 and 125°C. The spent liquor was concentrated in a rotary vacuum evaporator to different concentration levels and used for obtaining viscosity data at 50°C with a capillary viscometer.

B-Series

A rotary digester (17 liter) was used to treat chips (2.5-3 kg) with alkali at 115/125°C. The time to temperature was 60-80 min and time at temperature 240 min. Details of the pretreatment conditions are given in Table 2.

Pulping

Pulping was done in Parr autoclave or rotary digester using original and extracted chips and the conditions adopted are given in Table 2. Pulp yield and Kappa number or permanganate number were determined for all the runs. The black liquor was concentrated to 50-60% in a rotary vacuum evaporator and used as stock solution for obtaining viscosity data. A range of capillary viscometers (Cannon Fenske type) were used for all the determinations above 70°C for the concentration range of 10-60%. Pulp from the rotary digestions beaten to 40 °SR in a Valley beater was used for strength evaluation.

Proximate Analysis

Debarked logs (diam. = 7-20 cm, length = 140 cm) picked at random from the mill wood yard were cut to small pieces in a saw mill and the sawdust was collected, air dried and screened to obtain the -40+60 mesh fraction. Extractive free wood meal was prepared by sequential treatment with 0.5% NaOH, acetone and water and used for proximate analysis by Tappi standard procedures.

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TABLE 2

Experimental Conditions for Alkali Pretreatment and Kraft Pulping of Eucalypt Chips

Condition	Prelim. expts.	Series A	Series B
1. ALKALI PRETREATMENT			
Chip size, mm	-12 + 6	-12 + 6	-25 + 18
			-18 + 12
Chips, kg (o.d.)	0.3	0.3	2.5-3
NaOH Conc., N	0.05-0.5	0.1,0.2	0.1, 0.2
Temp., °C	100	115, 125	100, 115
Time, hr	24, 48	4	4
Liquor:chips,g/g	5:1	5:1	3.5:1-4:1
Equipment	3-lit Flask	2-lit Autoclave	17-lit Rotary digester
2. PULPING			
Temp.,		170	170
Sulfidity, %		20	20
Time to temp., min		90	90-120
Time at temp., min		60	60
Liquor:wood, g/g		5:1	3:1-4:1
Chemical charge (% as Na_2O)			
(a) Normal chips (control)		16	16
(b) Pretreated chips			
0.1N NaOH		14	14
0.2N NaOH		13	13

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RESULTS AND DISCUSSION

Alkali Solubles

The proximate analysis[11] in Taole 3 shows that about one-sixth of the wood meal corresponds to the extraneous constituents, which normally consist of tannin-like polyphenolic compounds, resin and fatty acids and other soluble polysaccharides. Hot water and alkali solubles correspond to 5 and 13-18% respectively. The tannin-like components presumably polymerise during acid hydrolysis of the polysaccharides for lignin determination and add to the Klason lignin residue. The Klason lignin contents of the original and alkali extracted residues are 34-36 and 24-27% for -40 + 60 mesh fraction; the corresponding values for the fine fraction (-60 mesh) are 39 and 21%. The difference (10-18%) in the Klason lignin contents of the original and alkali extracted wood meals approximately corresponds to the alkali solubility values and may be considered as an index representing the polyphenolic extractives[10]. The latter is present to the extent of 18% in the fine wood meal (-60 mesh) and 10% in the -40 + 60 mesh fraction. Thus pretreatment of eucalypt chips with alkali prior to pulping should remove the polyphenolic tannin-like extractives and eliminate or reduce possible condensation reactions during delignification.

Alkali Pretreatment

A summary of the pretreatment conditions and results is given in Table 4. The yield of extracted chips was 75-97% depending upon the severity of the extraction conditions. The yield was 87-97% with relatively mild conditions representing the predominant removal of the extraneous constituents corresponding

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TABLE 3

Proximate Analysis of Eucalypt Wood Meal[11]

Constituent (o.d. basis) %	Sample A[1] (-40 + 60) mesh	Sample B[1] (-40+60) mesh	Sample B[1] (-60) mesh
Wood Meal			
1. Solubilities:			
Water (cold)	-	5.1	2.9
Water (hot)	4.6	5.8	5.2
Ethanol	5.1	3.1	3.6
Methanol	6.2	3.9	4.4
0.5% NaOH	13.3	10.1	16.3
1.0% NaOH	-	12.5	18.3
Acetone[2]	3.6	3.2	2.1
Total extractives[3]	16.4	12.9	18.0
2. Klason lignin	33.5	35.9	39.1
Extractive Free Wood Meal			
Klason lignin	23.7(28.5)[4]	26.6(30.5)	20.7(25.3)
Holocellulose	58.8(70.8)	61.1(70.2)	61.1(74.5)
α-Cellulose	41.4(49.8)	42.7(51.9)	42.5(49.1)
Pentosan	13.7(16.5)	14.7(16.9)	13.1(16.0)

1 Samples A and B collected in April 1976 and April 1978 from 6 and 10 logs respectively.

2 After alkali extraction

3 Extraction sequence: 0.5% NaOH, acetone, hot water

4 Numbers in parenthesis represent extractive free basis

std. dev.- Klason lignin (0.6), Holocellulose (1.3)

TABLE 4

Effect of Alkali Pretreatment Conditions on the Yield of Eucalypt Chips

Run no.	Extraction conditions			Spent liquor	Yield
	NaOH Normality	Time hour	Temp. •C	conc. %	%
1	0.05	24	100	0.5	96.6
2	0.05	48	100	-	95.2
3	0.125	24	100	0.8	94.6
4	0.125	48	100	0.9	91.3
5	0.25	24	100	-	89.0
6	0.25	48	100	3.0	87.0
7	0.50	24	100	4.7	77.0
8	0.50	48	100	5.2	75.6
9	0.10	4	115	-	94.1
10	0.10	4	125	-	93.0
11	0.20	4	115	-	92.3
12	0.20	4	125	-	91.8
13	0.10	4	100	1.4	96.3
14	0.20	4	100	2.4	94.4
15	0.10	4	115	1.8	95.0
16	0.20	4	115	2.8	92.0

Series A: Runs 1-12, Series B = Runs 13-16

Runs 9-12 in autoclave and Runs 13-16 in rotary digester

to the solubility in alkali observed in proximate analysis. The yield of pretreated chips decreased to about 75% on prolonged (24-48 hour) treatment at 100°C with 0.5 N NaOH with the partial degradation of polysaccharide constituents, especially hemicellulose. The proximate analysis of four alkali pretreated chips (0.1/0.2N NaOH, 115/125°C, 4 hr) showed essentially no

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change in α-cellulose content (average - 42.2%). The yields obtained from pretreatment of a larger batch (2.5 kg) of chips based on spent liquor analysis are in good agreement with the results of autoclave determinations. The amount of alkali (as Na_2O) used in Series A and B was 0.7 - 7.5% and 1-2.5% (o.d. chips basis), respectively.

Viscosity of Spent Pretreatment Liquors

Viscosity data at 50°C for spent liquors of alkali extraction at 100°C summarised in Figure 2 shows the dependence on alkali concentration, dissolved solids in extract and extraction time. At lower concentrations, alkali is consumed in dissolution of polyphenolic compounds which presumably retain their oligomeric or condensed structure and contribute to a higher viscosity of the spent solution. An increase in alkali concentration would tend to favour the hydrolysis of condensed tannin-like materials and result in a lower viscosity of the spent liquor. It is also observed that, in all cases, at a given alkali concentration, a shorter extraction time gave a lower viscosity at a given extract concentration. Alkali is depleted with longer durations and partial recondensation of the dissolved fragments probably contributes to the observed higher viscosity. The extent of delignification reactions, though not measured, would be rather small. The spent liquor organics would consist mainly of extraneous components and an increasing proportion of hemicellulose fragments depending upon the alkali concentration used for extraction.

Pulping

Alkali extracted chips were pulped using the conditions shown in Table 2 and the results are summa-

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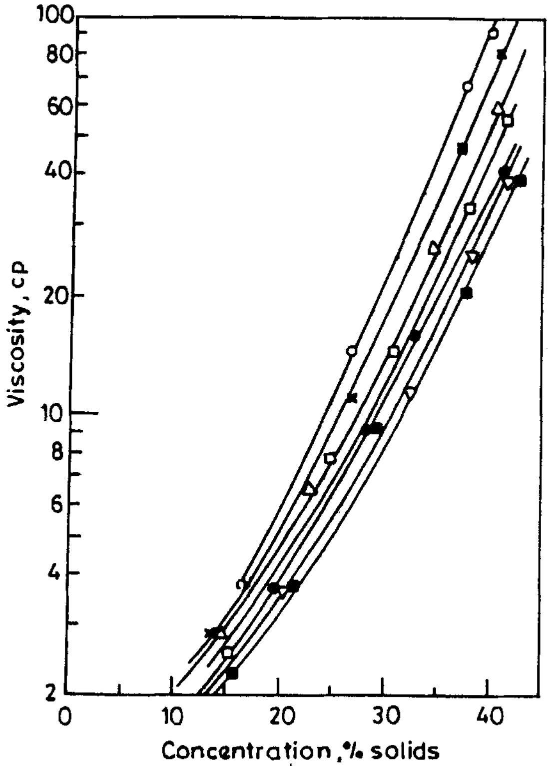

Fig. 2: Viscosity data at 50°C for spent liquors from alkali pretreatment of eucalypt chips at 100°C

	o	x	△	□	●	▽	■
N NaOH	0.05	0.05	0.125	0.125	0.25	0.5	0.5
Extraction time, hr	48	24	48	24	48	48	24

rised in Table 5. A control cook was conducted with an active alkali charge of 16% (as Na_2O). The chemical charge for pulping chips extracted with 0.1 and 0.2 N NaOH was 14 and 13% respectively

Pulp yield differences are generally small for the tests with extracted and control chips pulped to nearly equal degree of delignification. The strengths

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TABLE 5

Kraft Pulping of Normal and Extracted Eucalypt Chips

Exp. no.	Extraction		Pulping			
	Temp. °C	N NaOH	Active alkali %	Yield %	Perm. no.	Kappa no.
A. ROTARY DIGESTER						
1	115	0.1	16	41.7	19.0	-
2	-	-	18	43.1	20.6	-
3	-	-	16	46.8	22.5	26.5
4	115	0.1	14	45.7	19.2	-
5	115	0.2	13	46.2	23.5	-
6	-	-	16	47.9	18.1	26.8
7	115	0.1	14	45.7	16.9	25.8
8	115	0.2	13	45.4	16.8	25.7
9	115	0.1	14	45.4	15.1	24.3
10	-	-	16	45.4	15.9	26.1
11	115	0.2	13	45.6	15.0	26.0
12	100	0.1	14	48.6	17.3	-
13	100	0.2	13	47.2	17.4	-
14	-	-	16	45.6	17.7	24.2
B. AUTOCLAVE DIGESTIONS						
15	-	-	16	47.3	-	27.8
16	100	0.05	15	47.5	-	26.4
17	100	0.125	14	46.6	-	26.1
18	115	0.1	14	43.7	-	24.2
19	125	0.1	14	46.2	-	-
20	125	0.2	13	45.3	-	-

Pretreatment time - 4 hours for all runs, 48 hours for (16) and (17)

Liquor:wood ratio; 4:1 for (1), (2); 3:1 for (3)-(5); 3.5:1 for (6)-(14); and 5:1 for (15)-(20).

Perm. no. - Permanganate number

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of the corresponding pulps at 40°SR are given in Table 6. A comparison of the observed mean and standard deviation values shows nearly similar strength for pulps obtained from the control and extracted chips.

Viscosity of Black Liquors

Viscosity data were obtained for black liquors from normal and extracted chips at concentrations upto 61% at 80, 90 and 100°C. Preliminary correlation of viscosity versus black liquor concentration showed the

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TABLE 6

Strength of Kraft Pulps at 40°SR from Normal and Alkali Extracted Chips

Extraction N NaOH	Burst index kPa m^2/g	Tear index mN m^2/g	Tensile index N m/g	Double folds
0	5.9	8.8	92.4	873
0.1	6.2	8.3	87.0	772
0.2	5.4	-	81.1	370
0	6.4	8.3	90.9	750
0.1	6.3	8.6	88.3	693
0.2	6.2	8.9	84.0	554
0.1	5.9	8.6	81.5	380
0	6.2	7.8	87.3	494
0.2	5.6	8.8	79.5	300
0	5.7	7.4	88.1	395
Mean	6.0	8.4	86.0	558
std.dev.	0.3	0.5	4.3	200

expected decreasing trend for alkali extracted chips, with some overlapping at 15-35%. It appears that the residual alkali probably influences viscosity and it would have been desirable to adjust the alkalinity to a constant level for all the samples. Alternatively, the expected viscosity behaviour could be depicted clearly by plotting viscosity versus the concentration of the dissolved organics in the black liquor since the contribution of the inorganic constituents is small. Figure 3 summarises the viscosity data of black liquors

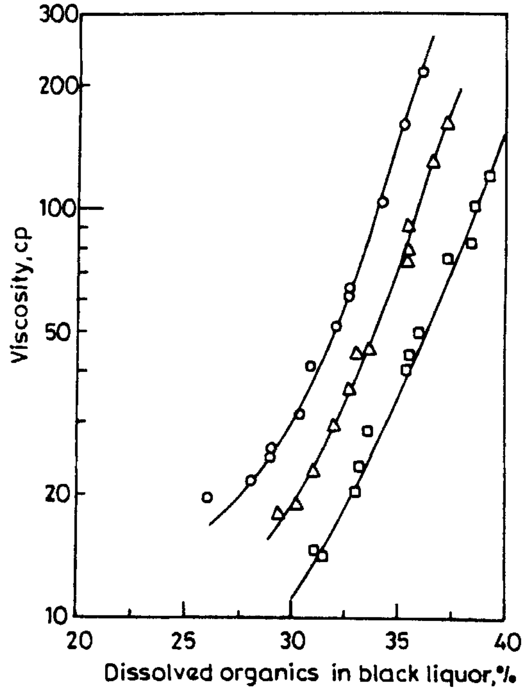

Fig. 3: Viscosity data at 100°C for kraft black liquors from pulping of normal and alkali pretreated eucalypt chips

o Normal chips

Δ 0.1N NaOH treated chips

□ 0.2N NaOH treated chips

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at 100°C. The graphs include data for black liquors from both rotary and autoclave digestions. The results show that the viscosity of black liquor decreases with alkali extraction of the chips.

The problems in the evaporation plant become more serious at total solids concentration levels of 45-55% (27-33% dissolved organics). At these concentration levels the viscosity of black liquors is of the order of 18-70, 13-40 and 7-21 cp at 100°C for the control and for chips extracted with 0.1 and 0.2 N NaOH, respectively. The viscosity of black liquor at 100°C and 30% dissolved organics (about 50% total solids) decreases by one-third and two-third, respectively, for chips extracted with 0.1 and 0.2 N NaOH.

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CONCLUDING REMARKS

Alkali extraction of eucalypt chips can reduce the viscosity of black liquors from kraft pulping. The conditions selected for extraction are 0.1 - 0.2 N NaOH, 115-125°C and 4 hours. Alkali required for pretreatment corresponds to 8-15% of the normal chemical charge for pulping. The possible use of white liquor, weak black liquor or other weak wash liquors would decrease fresh alkali requirement. The effluent from chip extraction step probably has a low potential as a tanning agent and would necessitate suitable disposal methods. Additional digester capacity will be necessary to include the pretreatment step. The yield and Kappa number of unbleached pulps can be maintained at the normal levels with a reduced chemical charge during pulping of extracted chips. The removal of some of the polyphenolic constituents of chips will decrease the calorific value of black liquor solids and possibly modify the swelling characteristics of the spray droplets in the recovery boiler. The above factors need further study to assess the mass and energy balances of the pulp mill and to maintain satisfactory operation of the chemical recovery section.

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