Effective use and recovery of chemicals in cold soda pulping

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SUMMARY

Reuse and recycling of pulping spent liquor, fiberizing liquor and washing in cold soda pulping of *Eucalyptus tereticornis* were determined with the closed system. Pulping process consisted of impregnation of chips with caustic soda solution. The treated chips were fiberized in 12" Disc Refiner. The fiberizing liquor from the previous cycle was used together with each previous spent liquor in making up the impregnating liquor for next cycle and also used for keeping consistency during refining and dilution before washing of the pulp in counterflow system. Reusing the liquor 10 times in this closed system increased the total solid contents from original of c.6% to 15%. The pulp yield was increased from 86.5 to 91.6% and the brightness or the washed pulp decreased from 26.3 to 21.2%. There was no change in chemical consumption in 10 cycles, which averaged about 7.5% on oven dry wood basis. The recycling helps in utilizing the residual alkali during impregnation. About 30% of the applied NaOH is being reused from recycled spent liquor and fiberizing liquor. The strength characteristics at 100±10 ml. CSF freeness value have a small variation in burst, tensile and tear index values. The pollution loads in the spent liquor, fiberizing liquor and washings in this closed system have a significant effect to meet limitation of the practical commercial operation. Further spent liquor and fiberizing liquors in cold soda pulping mixed with eta reed kraft black liquor were studied for evaporation and burning behaviour of the black liquor.

The closed liquor recycle system is considered to be economically feasible in cold soda pulping which reduces the pollution load. To avoid a chemical losses after 10 cycles, spent liquor can be used either as make up of dilution in sulphate pulping or directly in chemical recovery.

The cold soda process produces high yield pulp suitable for cheaper grade papers from many hardwood species. With the variation of the treatment, it is possible to obtain pulp that can be substituted for softwood mechanical pulp[1]. The extremely high pollution loads which is generated by this CMP process will be one of limiting factor as it involves the environmental problems. In addition to dissolved organic, the CMP spent liquor usually carried 50% of residual caustic[2]. Baird et.al[3] have studied extensively the effect of reuse and recycling of spent liquors in cold soda pulping.

The recycling of spent liquor will provide a solution for effective reuse of residual caustic in spent liquor and reduction in pollution load. Further recycling of spent liquor will help in the build up of organic matters which will be desirable for chemical recovery.

The present investigation has been directed towards effect of counter current system involving reuse recycling of spent liquor in cold soda pulping of *Eucalyptus tereticornis* species, on pulp properties, pollution load and chemical recovery of spent liquor. The number cycles required amount of total solids (10-15%) and organic matter in spent liquor, has been optimized. The effect of addition of cold soda spent liquor to eta reed black liquor on evaporation and burning properties of black liquors mixtures has been studied in detail. The paper also gives pollution load at various points in cold soda pulping.

EXPERIMENTAL

Chemical Treatment of E. tereticornis

Eucalyptus tereticornis chips were impregnated in sodium hydroxide solution keeping chips to liquor

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ratio of 1 : 4 at room temperature for over night. The concentration of NaOH applied was 35 g/l.

After the first chemical treatment, around 1200 ml of spent liquor was collected. This spent liquor was subsequently used for the next treatment. The alkali level of 35 gpl was maintained by supplimenting with additional sodium hydroxide.

The treated chips were refined in the laboratory Sprout Waldron 12" Disc Refiner keeping the plate pattern same throughout the experiments. The refining was carried out in two stages at 10% consistency with plate clearances 0.25 mm and 0.07 mm respectively. The final volume of fiberizing liquor obtained after the two stage refining was 7000 ml. The refined pulp was washed finally with 8 litres of fresh water and the washed liquor was collected. Details are given in Figure (1).

After refining the pulp was collected and screened in laboratory flat screen of 0.25 mm slit width. Yield and brightness of unbleached pulps were determined. The results are recorded in Table (2).

The spent liquors, fiberizing liquors and washings obtained in each cycle were analysed for pollutional parameters and chemical composition as per standard method given in (4).

All the unbleached pulps were evaluated for strength properties at 100±10 ml CSF according to ISO Standard given in (4).

Eta Reed Sulphate Pulping

Kraft black liquors were prepared by pulping Eta reed chips *(Ochlandra travencorica)* with 14% active alkali at 170°C keeping H-factor 943. Different diluents during the eta reed pulping were (a) water (b) fiberizing liquor of cold soda pulping, (c) spent liquor and fiberizing liquor from cold soda pulping in 1 : 2 ratio.

Evaporation and Burning Properties of Kraft and Cold Soda Spent liquors

The evaporation and burning properties, of eta reed and cold soda spent liquors were studied as per the procedures given in (4). The results are given in Table (5).

RESULTS AND DISCUSSIONS

The flow diagram for counter current closed system is illustrated in Figure 1. The system involves complete recycling of spent liquor and fiberizing liquors. About 20% volume of the washings were recycled. The effect of recycling on

FLOW DIAGRAM FOR CLOSED COLD SODA PULPING (LAB. SCALE)

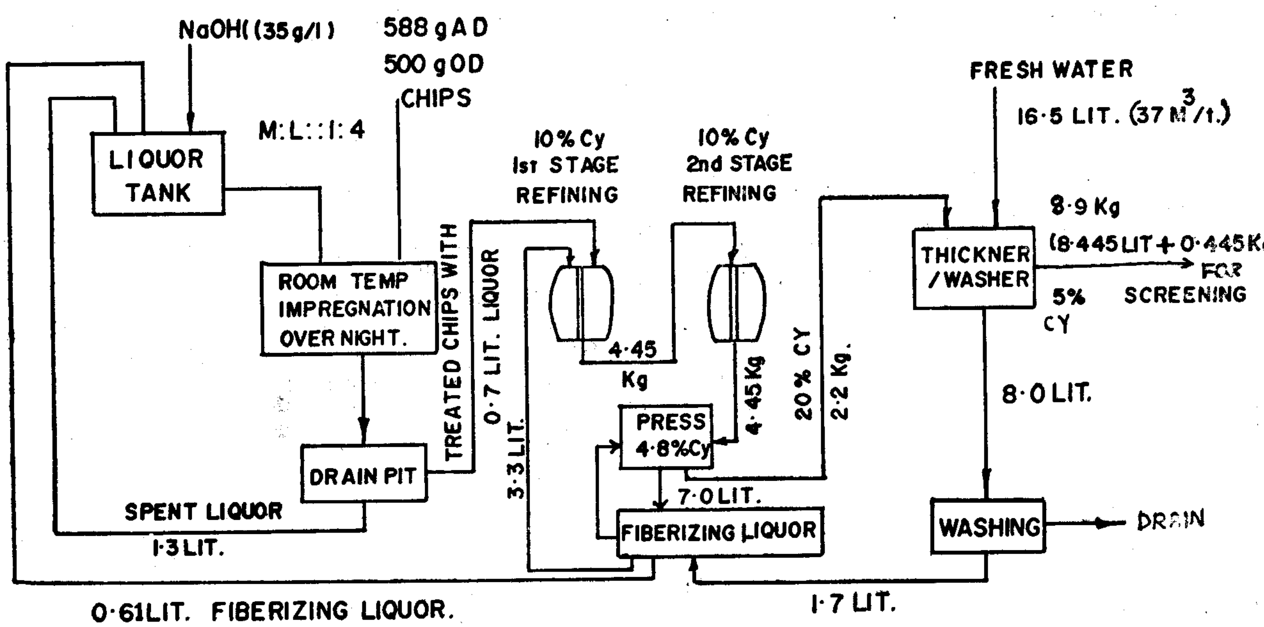

FIG. 1

chemical consumption, pulp properties, and pollution loads is discussed below :

Chemical Consumption

The distribution of residual alkali in different liquor system is given in Table 1. Persual of the results indicate that the concentration of residual alkali has not changed significantly in subsequent cycles. Sodium hydroxide balance in liquor system shows that alkali in the spent liquor is about 60% and 25% is going into fiberizing liquor and about 15% alkali is going to fibers washings. Thus 85% of residual alkali is carried by spent liquor and fiberizing liquor. The recycling helps in utilizing about 85% of residual sodium hydroxide. The results indicate that chemical consumption during impregnation decreases slowly from 1st to 5th cycle and then increases continuously in subsequent cycles. This increased consumption of alkali might be attributed to liberation of more organic acids in subsequent cycles.

The volumes of recycled spent liquor and fiberizing liquors during impregnation is about 65% and 30% of the total dilution respectively. During impregnation in subsequent cycles only about 70% of fresh sodium hydroxide is added while 30% sodium hydroxide is being reused from the recycled spent liquor and fiberizing liquor. Thus the recycling will help in saving about 30% of the total chemical required in each cycle.

Pulp Properties

The results of effect of recycling on pulp properties are given in Table-2. The results indicate that the pulp yield increases with number of recycling. About 5% increase in pulp yield was observed at 10th cycle. However, the yield increased after 6th

TABLE—1. DISTRIBUTION OF ALKALI IN VARIOUS LIQUOR SYSTEMS

Cycle Number	Residual NaOH g/l			% of applied NaOH consumed	% NaOH consumed on o.d. wood basis
	Spent liquor	Fiberizing liquor	Washings		
1.	15.20	1.00	0.15	60.7	8.5
2.	14.42	1.30	0.20	58.3	8.2
3.	14.70	1.60	0.46	57.4	7.2
4.	15.84	1.60	0.46	48.0	6.7
5.	20.17	1.85	0.67	35.1	4.9
6.	16.20	1.23	0.61	51.4	7.2
7.	12.60	1.80	0.71	54.3	7.6
8.	16.10	1.41	0.51	54.7	7.7
9.	17.65	2.60	0.51	47.9	6.7
10.	11.22	2.14	0.56	63.8	8.9

TABLE—2. EFFECT OF RECYCLING OF SPENT LIQUOR ON YIELD, BRIGHTNESS AND STRENGTH CHARACTERISTICS OF COLD SODA PULPS

Cycle Number	Total yield	Unbleached pulp brightness %	Strength properties of pulps at 100 ml CSF			
			Apparent density g/cm³	Burst index kPa.m²/g	Tensile index Nm/g	Tear index mN.m²/g
1.	86.5	26.3	0.49	0.30	15.0	1.55
2.	87.5	24.8	0.48	0.30	14.5	1.40
3.	88.1	25.4	0.48	0.15	14.5	1.70
4.	88.5	21.8	0.50	0.15	14.5	1.70
5.	88.0	23.1	0.51	0.15	14.5	1.85
6.	90.8	22.9	0.51	0.15	12.5	1.80
7.	90.9	21.2	0.49	0.25	15.5	1.75
8.	90.4	24.3	0.50	0.20	15.0	1.75
9.	91.1	25.3	0.48	0.20	15.0	1.65
10.	91.6	—	0.46	0.15	14.5	1.40

cycle is not significant. No regular trend was observed in the brightness values of unbleached pulps. The brightness varied between 26 to 21.2%. Inspite of gain in the pulp yield, the strength properties of unbleached pulps were not affected by recycling. The washed pulps with recycling system did not show any substantial alkalinity or carry over of sodium.

Composition of Liquors

Table-3 shows, the variation in composition of spent liquor, fiberizing liquor and washings, with number of cycles. The total solids content of spent liquor was increased from 5.57% to 15% in ten cycles. The solids increase was also substantial in fiberizing liquor. In all the cases the colour load and COD values showed a sharp rise with recycling. Inorganic content of spent liquor showed a decreasing trend indicating. Inorganic content of fiberizing liquor and washings did not show any trend. The suspended solids in spent liquor showed an increasing trend Figure 2 shows variation, in the concentration of total solids, organic and COD in spent liquor with number of cycles. It is clear from the figure that the rise in these properties is sharp between Ist to 6th cycle and rather slow in subsequent cycles. Thus the organics and solids build up had reached a saturation point at 6th cycle.

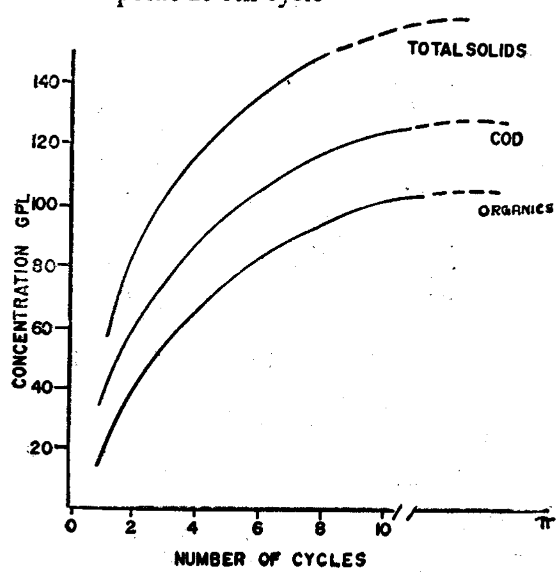

FIG 2

Pollution Loads

The load due to various pollutional parameters in spent liquor, fiberizing liquor and washings were calculated and are given in Table-4. The results indicate that in all the cases the COD and colour loads have increased significantly with recycling. In washings the COD and colour loads have increased by nearly as high as 14 and 9 times respectively from Ist to 10th cycle. The suspended solids load was considerable in spent liquor and fiberizing liquor. The total COD load from spent liquor, fiberizing liquor and washings had increased from 205 Kg/t to 882 kg/t in the 10th cycle. At 10th cycle the COD loads contributed by spent liquor and fiberizing liquors were nearly 42% and 24% respectively. Washings at 6th cycle contribute nearly 15% of the COD load, while at 10th cycle nearly 34%. Thus 6th cycle will be taken as optimum cycle where 85% of COD load was due to spent liquor and fiberizing liquor. In any event as the recycling enhances the build up of pollution load, it is necessary that the spent liquor, fiberizing liquor should not be discharged after repeated recycling.

Properties of Spent Liquors

Spent liquor from Ist cycle will be having low total solids and high amount of inorganic content, which is not desirable for recovery of chemicals. By recycling the solids content and organic contents were raised. The spent liquor from 10th cycle was mixed with eta reed kraft black liquor in varying proportions and the evaporation and burning properties of these mixtures were studied. The results are given in Table 5. The results indicate that with increasing the proportion of cold soda spent liquor the viscosity increases substantially. The swelling volume ratio also falls indicating the poor burning quality of cold soda spent liquor which might be attributed to high inorganic content as compared to eta reed kraft black liquor. Eta reed kraft black liquor prepared by using spent liquor as diluent during cooking also showed higher viscosity and low swelling volume ratio. From extrapolation it was observed that about 10-20% spent liquor when mixed with eta reed kraft black liquor, on dry solids basis will have resonable viscosity level and swelling volume. When fiberizing liquor was used as a diluent during eta reed pulping did not affect the properties of resulting eta reed black liquor. It appears that combined recovery of chemicals from eta reed kraft black liquor and cold soda spent liquor is feasible.

Material Balances

The mass balances for production 30 tonnes of eta reed chemical pulp and 70 tonnes of cold soda pulps is illustrated in Figure 3. Mass balance for cold soda pulping is essentially based on the process followed in laboratory. From the mass balance it is clear that when spent liquor and fiberizing liquor were recycled completely only 33 M^3/tonne of pulp, fresh water is required in washing stage. Without recycling of spent liquor and fiberizing liquor, the

TABLE—3. COMPOSITION OF LIQUORS IN CLOSED SYSTEM

Cycle No.	Spent liquor				Fiberizing liquor				Washings			
	T.S.*	TSS**	COD	Inorganics as NaOH	T.S.	TSS	COD	Inorganics as NaOH	T.S.	TSS	COD	Inorganics as NaOH
	%	g/l	g/l	%	%	g/l	g l	%	%	g/l	g/l	%
1.	5.57	1.93	37 3	68.5	0.90	0.55	6.7	32 26	0.22	0.02	0.92	42 23
2.	8.15	7.48	61.8	55.8	1.57	0.63	15.2	39.10	0.32	0.04	1.50	32.96
3.	9 87	9.83	77.4	41.6	[illegible]	0 94	17.4	33.70	0.42	0.06	2.32	42 36
4.	11.10	13.78	88.1	43.8	2.60	1.36	20.4	37.20	0.58	0.08	3 89	42.00
5.	12 00	13.69	94.9	40.0	3.38	1.15	26.1	36 66	0.82	0.10	5 38	39.42
6.	12.13	15.45	104.1	37.7	3.59	1.55	28 1	35.23	0.99	0.69	7.09	38.70
7.	13.15	16.76	110.8	37.5	4.05	1.64	32.3	31.38	1.27	0.17	8 85	38.35
8.	14.00	17.58	112.0	36.1	4.76	2.62	36.7	35.04	1.51	0.34	10.63	38.45
9.	14.25	18.85	119.5	38.9	5.19	2.64	41 2	37.32	1.62	0.06	11.40	40.56
10.	15.00	19.33	127.1	38.0	5.57	0.94	46.0	37.53	1.67	0.16	13.70	37.76

*Total Solids.

* Total Suspended Solids.

TABLE—4. POLLUTION LOADS OF VARIOUS PARAMETERS IN COUNTER CURRENT CLOSED SYSTEMS

Cycle No.	Spent liquor				Fiberizing liquor				Washings			
	Suspended solids	Organics	COD	Colour	Suspended solids	Organics	COD	Colour	Suspended solids	Organics	COD	Colour
1.	5.6	53	110	1180	8.9	100	108	884	0.37	24	17	165
2.	21.9	121	181	1695	10.1	152	243	1629	1.6	39	27	251
3.	28.8	179	228	1871	15.0	243	277	2264	—	44	42	361
4.	40.5	195	259	2795	21.5	261	324	2746	1.8	61	70	559
5.	40.9	229	283	3349	18.3	341	415	2727	1 4	91	98	740
6.	45.2	234	303	3271	21.6	328	390	2852	1.4	106	125	944
7.	49.1	258	324	2981	19.1	330	447	2995	2.5	138	156	1373
8.	52.7	288	335	4080	24.3	294	341	3150	6.0	165	188	1669
9.	56 0	281	354	4129	19.1	243	299	2253	1.1	162	200	1725
10.	56.6	296	372	4231	5.5	211	271	2379	2 8	183	239	1467

Note : Pollutional parameters are expressed in term of kg/tonne of B.D. pulp.

MATERIAL BALANCE FOR CHEMICAL AND CHEMIMECHANICAL PULPINGS

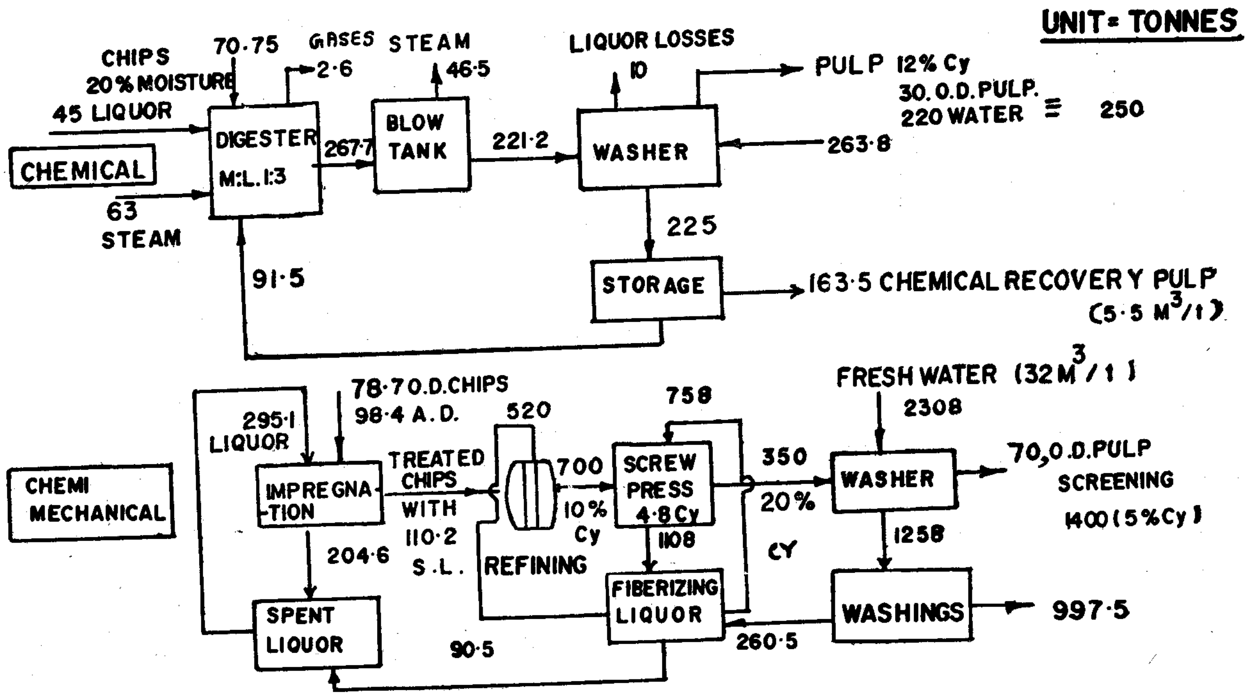

FIG. 3

TABLE—5 PROPERTIES OF SPENT LIQUORS

Sample*	Total solids %	R.A.A. as Na_2O g/1**	Inorganics as NaOH	SVR ml/g	Brook field viscosity cps at 80°C at % solids 35	45	50	55
100% CMP	15.00	10.70	37.97	5	16	58	141	501
70% CMP + 30% Eta reed	15.95	7.62	32.45	5	13	48	118	398
50% CMP + 50% Eta reed	16.60	6.60	32.87	--	9	37	100	372
30% CMP + 70% Eta reed	17.10	6.87	31.57	8	9	30	68	204
100% Eta reed (a)	18.20	5.92	29.91	40	5	14	30	93
100% Eta reed (b)	20.35	4.92	35.36	6	6	19	45	141
100% Eta reed (c)	18 62	5.41	34.26	9	7	18	36	87

* Mixed on dry solid basis.

a) Water as diluent during cooking.
b) Spent liquor and fiberizing liquor as diluent (SL:FL: : 1:2).
c) Fiberizing liquor as diluent.

** At 200 g/l solids.

quantity of fresh water required in the system would be about 56 M^3/kg. Thus by recycling we can restrict the quantity of fresh water, leading to conservation of water of about 41%. From the chemical pulping flow diagram it appears that about 5.5 M^3 black liquor per tonne of pulp will be available for chemical recovery. When the recycling will be terminated at 6th cycle the quantity of eta reed kraft black liquor and cold soda spent liquor going to recovery will be 980 M^3 and 205 M^3 respectively. On dry solid basis the ratio of eta read black liquor and cold soda spent liquor comes to 87:13. When the recycling is terminated at 10th cycle the quantities of eta reed and cold soda spent liquors available will be 1635 M^3 and 205 M^3 respectively. On dry solid basis the ratio comes to about 89:11. However, these figures are subject to alterations depending on the nature of treatment in cold soda process and quantity of weak black liquor available in chemical pulping. In any case the proportion of cold soda spent liquor available will not be more than 20%.

CONCLUSIONS

1. By reuse and recycling of cold soda spent liquor and fiberizing liquor the residual sodium hydroxide can be used effectively, which helps in saving of about 30% of the applied chemical.
2. The recycling will not affect the quality of pulp.
3. Recovery of chemical from recycled cold soda spent liquor alongwith kraft black liquor appears to be feasible. The recovery of chemicals will help in reducing the pollution load.
4. Th[illegible] [illegible]cled for six times to attain sa[illegible] However, the [illegible]erizing liquor cou[illegible] for more number of times.
5. Water consumption can be reduced by about 41% by recycling of spent liquor and fiberizing of spent liquor and fiberizing liquor.
6. From the study it appears that this counter current closed system is economically feasible from the view point of effective use of chemical, conservation of water and prevention of pollution load.

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