Black Liquor Recycling in Agro Based Mills- A Step Towards System Closure and Energy Conservation

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ABSTRACT

Global environmental imbalances coupled with depleting reserves of fossil fuel has forced the paper industry to maximise the use of internal fuel sources. Black liquor when processed in the chemical recovery section serves as the major renewable energy resource. In Agro based mills although chemical recovery system have been installed in few mills, but due to the unfavorable properties of black liquors, the chemical and thermal recovery efficiencies are much lower than those in wood based mills. One of the major constraints while processing the agro based liquors in the chemical recovery section is the low solids concentration of the weak black liquors in comparison to the wood/bamboo liquors. The initial black liquor solids concentration in case of agro based mills falls in the range between 7-10% as against 14-16% in case of wood black liquors. This results in substantial quantities of additional steam requirements during black liquor evaporation in the chemical recovery to remove that extra quantity of water present in the agro based black liquors. Therefore a major challenge before the agro based mills is to improve the initial black liquor solids concentrations without having a bearing on the cost of operation, productivity and pulp quality.

The paper highlights the results the preliminary studies carried out at Central Pulp & Paper Research Institute on liquor recycling when certain portion of the fresh water is replaced with the black liquor during cooking of the agro based raw materials. Although black liquor recycling is commonly being practiced in all integrated wood and most of the agro based mills, but visit to an integrated agro based mill showed that not only due to the wet cleaning system employed, but also due to apprehensions on the quality of pulp and black liquor properties, liquor recycling is not being practiced even at times when there is partial/no wet cleaning of the raw material taking place and also during the shut down of the causticization unit. In these cases the additional water make up is through the fresh water usage.

The benefits of the black liquor recycling on resultant pulp and

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black liquor properties showed an improved pulp yield of around 1.0-2.0% with comparable/slightly better pulp properties. The black liquor properties showed an increase in total solids concentration by 1-1.5%, viscosity reduction to the tune of 100-150 mPaS at firing solids concentration and with improved swelling of the black liquor during combustion. The material and energy balance calculations show a scope of black liquor addition even in mills using a wet raw material cleaning process and energy savings in the range of 0.3-0.7 tonnes steam on per tonne pulp can be achieved depending on the improvements in the black liquor solids attained.

INTRODUCTION

In view of more and more stringent environmental regulations and increasing caustic soda prices, the installation of a technically and economically efficient chemical recovery system for small agro based pulp mills is becoming extremely important. The main problems of agro based liquors are:

- low weak black liquor concentration as against the wood black liquor, which adversely demands higher steam during black liquor evaporation.
- high viscosity of black liquor resulting in low heat transfer rate in evaporators and limiting the maximum attainable black liquor firing concentration.
- Higher amounts of non-process elements such as silica, potassium, calcium and chlorides causing strong scaling/fouling of evaporators and plugging of boiler tubes.
- Slow combustibility of agro based black liquors.

Any modification exercise for improvement of agro based black liquors properties should not affect the pulp & black liquor behaviour adversely. An attempt has been made at CPPRI to show how the unfavourable properties such as low weak black liquor solids concentration of agro based black liquors can be at least partially eliminated by black liquor recycling in order to improve the recovery efficiency. Black liquor recycling is commonly being practiced in wood based mills. But visit to an agro based mill has shown that due to certain apprehensions regarding the black liquor recycling on resultant pulp & black liquor quality, black liquro recycling is not practiced even when it is required.

BLACK LIQUOR EVAPORATION

Evaporation of black liquor is one of the most sensitive operation for agro based black liquor recovery systems due to the low solids concentration of the black liquor. Evaporation of black liquor is an energy consuming operation. Approximate volumes of water to be evaporated at various solids concentrations for wood and agricultural residues are presented in Table-1.

TABLE-1

Approximate volumes of water to be evaporated at different black liquor solids concentrations

Particulars	Wood black liquor	Agro based black liquors
Initial black liquor solids concn., % w/w	14-16	7-10
Quantity of black liquor generated, m^3/tp	8.57-7.5	17.14-12.0
Quantity of water to be evaporated m^3/tonne of pulp At solids concentration of:		
- **45% w/w**	5.9-4.40	14.48-9.34
- **50% w/w**	6.17-5.1	14.74-9.6
- **58% w/w**	6.5-5.43	15.07-9.93

It is clear from the calculations that the volumes of evaporated water is much higher with agricultural residue black liquors when compared with wood black liquors.

One of the common practice followed in wood based mills is the recycling of weak black liquor. Nearly, 4-5 m^3 of weak black liquor per digester containing nearly 20 tons of raw material is recycled during pulping.

An attempt was made at CPPRI to improve the black liquor solids concentration of agro based liquors by black liquor recycling in the subsequent cooking stage by partially replacing the fresh water with the black liquor.

EFFECT OF ADDITION OF BLACK LIQUOR ON FRESH WHITE LIQUOR STRENGTH

Before the recycling experiments were made, a preliminary study was carried out to find the effect of black liquor addition on white liquor strength in terms of active alkali level. Studies carried showed that due to the availability of residual NaOH in the black liquor, no reduction in the active alkali levels of white liquor is observed.

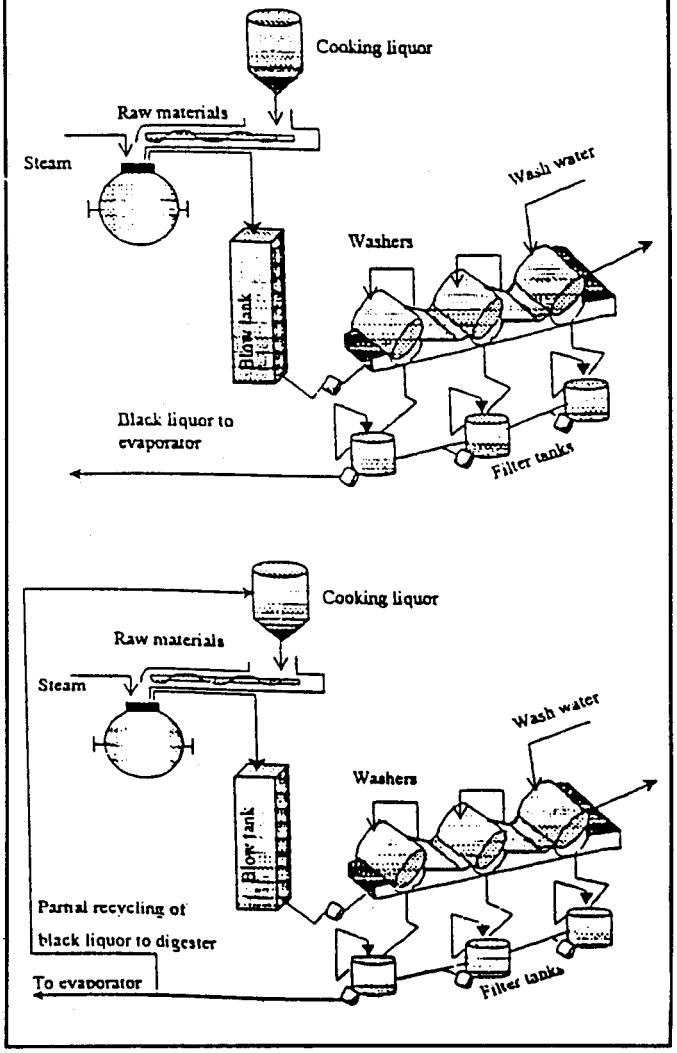
METHODOLOGY OF LIQUOR RECYCLING DURING PULPING OF BAGASSE & WHEAT STRAW

The above two commonly used agro based raw materials were selected for the studies. Initially a reference control sample of pulp & black liquor was generated in the laboratory by maintaining a bath ratio of 1:4.5, Cooking chemical charge of 17% as NaOH on raw material basis and cooking to a temperature of 160°C for 60 minutes.

In the next subsequent cooking, 25% of the fresh water required for maintaining the material to liquor ratio was replaced with the black liquor.

Fig. 1 shows the schematic of pulping and washing before and after black liquor recycling.

FIG.- 1 SCHEMATIC OF CONVENTIONAL & PROPOSED PULPING SYSTEM IN AGRO BASED MILLS



COLLECTION OF BLACK LIQUOR

In order to simulate the black liquor collection under the mill conditions, 250 ml. of hot water maintained at a temperature of 60-70°C was used. This

TABLE-2

Pulp Properties of Wheat Straw and Bagasse Before and After Liquor Recycling

Particulars	Bagasse pulp		Wheat Straw Pulp	
	Reference	With Black Liquor Recycling	Reference	With Black Liquor Recycling
Pulp Yield :				
Unscreened, % w/w	50.4	52.2	48.53	50.1
Screened, % w/w	47.0	49.2	45.6	47.2
Kappa Number	19.86	19.30	20.1	20.5

TABLE-3

Physical Strength Evaluation of Pulps Before & After Black Liquor Recycling

Particulars:	PFI	Freeness, CSF, ml	Apparent Density, g/c.c.	Burst Index, kPam²/g	Tensile Index, Nm/g	Tear Index, mNm²/g
Bagasse unbleached pulps:						
Bagasse pulp (virgin)	0 500	530 300	0.74 0.82	2.2 3.10	45.5 65.5	4.2 4.0
Bagasse (Black Liquor)	0 500	570 315	0.75 0.83	2.2 3.2	45.5 66.5	4.5 4.2
Wheat Straw unbleached pulps:						
Wheat Straw pulp (Virgin)	0 500	460 260	0.69 0.78	3.8 5.8	61.0 68.0	5.7 5.3
Wheat Straw pulp (Black Liquor)	0 500	465 255	0.70 0.80	4.05 5.9	63 72	5.6 5.4

resulted in total black liquor quantity of around 11m³/ tonne of pulp similar to the mill conditions.

EFFECT OF BLACK LIQUOR RECYCLING ON RESULTANT PULP & BLACK LIQUOR PROPERTIES

The wood based mills are recharging the black liquor in the next subsequent cooking stages. To improve the washing efficiency and to simultaneously improve the black liquor solids concentration in the subsequent cooking cycles, around 20-25% of black liquor generated was recycled during the pulping of wheat straw and bagasse. Table-2 show the pulp properties respectively in case of bagasse and wheat straw before and after liquor recycling.

The results show that there is a consistent

FIG. 2 GEL CHROMATOGRAM OF BAGASSE BLACK LIQUORS

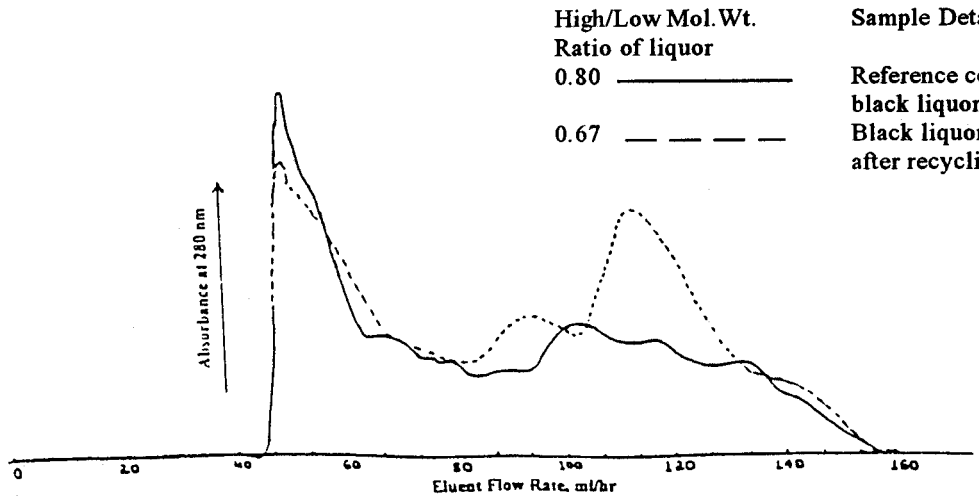


TABLE-4

Black Liquor Properties of Wheat Straw and Bagasse Before and After Liquor Recycling.

Particulars	Bagasse Black Liquor		Wheat Straw Black Liquor	
	Reference	With Recycling of washings	Reference	With Recycling of washings
pH at 25°C	12.28	12.30	11.83	11.82
Total Solids, % w/w	9.0	10.6	9.47	10.7
Suspended solids, g/l	3.88	4.5	3.69	2.9
Residual Active Alkali, g/l	2.12	2.79	2.27	2.85
Total Alkali, g/l	25.58	30.2	24.87	27.1
Inorganics, % w/w as NaOH	29.2	29.6	27.5	28.0
Organics, % w/w (by difference)	70.8	70.4	72.5	72.0
Silica, % w/w as SiO_2	1.85	1.80	2.9	2.5
Chlorides, % w/w as Cl	0.18	0.20	1.0	1.10
Lignin, g/l	38.97	41.1	26.14	31.52
Gross Calorific Value, Cals/g	3285	3300	3136	3115
Swelling Volume Ratio, ml/g	10	13	8	12
Viscosity, mPa.S at 98°C at Total Solids, % w/w				
40	-	36	40	33
45	-	72	80	75
47	100	82	-	-
50	155	138	174	150
55	407	368	502	447
57	-	-	891	780
58	1000	848		-

improvement in pulp yields of wheat straw and bagasse. Unlike bagasse which shows a marginally lower values of kappa number, there is a slight increase in straw kappa values in case of wheat straw pulp.

EFFECT OF BLACK LIQUOR RECYCLING ON PHYSICAL STRENGTH PROPERTIES OF UNBLEACHED STRAW AND BAGASSE PULPS

Table-3 shows the physical strength properties of the beaten and unbeaten unbleached pulps of bagasse and wheat straw before and after liquor recycling during pulping. The physical strength properties of pulps measured show slight improvements in burst and tensile index values for wheat straw and bagasse pulps. The values of tear index being more or less similar. This confirms the fact that recycling of black liquor plays no adverse effect of pulp properties.

Results in Table-4 show the black liquor properties before and after black liquor recycling. The physico-chemical composition of the black liquor show a marginal increase in inorganic content of the black liquor, although there is a drop in the residual active alkali levels of the black liquors. This is possibly due to the higher pulp yield of the raw materials and stabilisation of the resultant black liquor obtained after recycling. The reason behind the stabilisation of black liquor can be further supported from the gel chromatographic studies and viscosity determination, wherein viscosity of recycled black liquor was reduced

in comparison to the reference control samples.

Fig.-2 shows the gel chromatograms of bagasse black liquors obtained before and after liquor recycling. The gel chromatograms distinctly show lowering of high/low molecular weight distributions of lignin in case of recycled bagasse black liquors. The high/low molecular weight ratio of lignin are 0.8 in reference control sample and 0.62 in case of black liquor obtained after liquor recycling.

ENERGY SAVING IN EVAPORATION

Results in Table-4 clearly show an increase in black liquor solids concentration by partial replacement of fresh water with black liquor during wheat straw and bagasse pulping. Laboratory findings have shown an increase of 1.6% total solids in case of bagasse and 1.23% in case of wheat straw black liquors obtained af ter recycling.

The savings of energy in terms of steam with rise in solids concentration of black liquor is shown in Table-5. Increase of weak black liquor solids concentration will result in reduced steam demand during black liquor evaporation. The data presented in Table also shows the steam savings with 0.5%, 1.0% and 1.5% increase in the weak black liquor solids concentration. It is evident from the results that even 0.5% increase of total solids results in appreciable steam savings. Therefore, even 10-15% replacement of lqiuor during the initial bath ratio maintenance will result in 0.5-0.75% increase in black liquor solids concentration after liquor recycling.

CASE STUDY- THE SCOPE OF BLACK LIQUOR RECYCLING FOR MILLS EMPLOYING WET CLEANING OF THE RAW MATERIAL

In order to get rid of undesirable non-process elements like silica, potassium and chlorides, the agro based mills equipped with chemical recovery are going for single or two stage wet cleaning for processing of the raw material. Depending on the capacity of the washing unit, the washing of the raw material is either partial or complete. In one of the mills visited, it was observed that 75% of the wheat straw was going through the wet cleaning system due to limitations with the capacity of the washing system and the rest 25% is being by-passed.

SCOPE OF BLACK LIQUOR RECYCLING

Following calculations show the varying dryness

TABLE-5

Energy Savings with Improved Black Liquor Solids Concentrations.

Particulars		Agro black liquors		
	Reference Control	Increase in black liquor solids after recycling		
Initial black liquor solids concn., % w/w	7-10	7.5-10.5	8-11	8.5-11.5
Quantity of black liquor generated, t/tp	17.14-12.0	16-11.42	15-10.9	14.11-10.44
Quantity of water to be evaporated tons/ton of pulp At solids concentration of:				
- 45 % w/w	14.48-9.34	13.34-8.76	12.34-8.24	11.44-7.78
- 50% w/w	14.74-9.6	13.6-9.02	12.6-8.5	11.71-5.38
- 58 % w/w	15.07-9.35	13.93-9.35	12.93-8.83	12.04-8.37
Steam Savings, tons/tonne pulp	Base	1.14-0.58	2.14-1.1	3.03-1.56
Final Steam Savings, tons per day for 100tpd mill at 58% solids @S.E.=4.2	Base	27.14-13.8	51-26	72-37

ADDITIONAL WATER REQUIREMENTS/DIGESTER

Total Liquor Requirement, m^3 : 32.3

Straw dryness, %	Water with raw material, m^3	Water in the chemical, m^3	Additional water requirements, m^3
40	12.75	12.78	6.77
50	8.5	12.78	11.02
60	5.7	12.78	13.82

CASE STUDY OF MILL PROCESSING 75% OF THE STRAWS TO WET CLEANING SYSTEM

Particulars	75% straw of 40% dryness	25% straw of 80% dryness
Raw material Quantity, O.D., tonnes	**6.375**	**2.125**
Water in raw material, m^3	**9.525**	**0.2996**
Water in the chemicals, m^3	**9.585**	**3.195**
Additional water requirements, m^3	**5.115**	**4.584**

Additional Water Requirements - 9.698 m^3

figures of the raw material and the scope of black liquor addition even in case of mills going for wet cleaning systems.

Initial bath raito maintained, % - 3.8
Raw material charge to the digester (O.D. basis), tonnes - 8.5
Total titrable alkali, g/l as NaOH - 113.0
Chemical charge on raw material, % w/w as NaOH - 17.0
Total fresh water requirements, m^3/digester - 32.3

Therefore we can easily maintain even up to 25-30% of the initial bath ratio requirements with black liquor recycling. This will also be a step towards reduction in fresh water consumption.

CONCLUSIONS

Black liquor recycling improves the pulp yield by 1.0-1.5% without bringing about any significant change in kappa values of the pulps.

The physical strength properties of the unbleached pulps are comparable in case of reference control sample and the pulps obtained after black liquor recycling.

- Recycling of black liquor during pulping results in improved black liquor solids concentrations. The net energy savings per tonne of pulp varies from 13-72 tonnes per day for a 100 tpd mill depending on the rise in solids concentrations.
- The results also show a marginal improvement in black liquor viscosity after liquor recycling.
- The studies have shown that recycling of black liquor during pulping of agro based raw materials does not show any adverse effect on black liquor and pulp properties.
- Black liquor recycling can be practiced in mills using wet cleaning systems, by using improved dewatering devices.

ACKNOWLEDGEMENTS

Authors wish to acknowledge Dr. Y.V. Sood for arranging to carry out the evaluation of strength properties of the pulps.