Incineration Of Black Liquor Mixed With Waste Biomass-An Option To Achieve Zero Black Liquor Discharge In Small Agro Based Paper Mills

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ABSTRACT

Agro based pulp & paper mills producing unbleached variety of paper normally use less chemical charge comparative to the mills producing bleached variety of paper. Due to lower chemical charge in pulping it ends up with black liquor containing lower Residual Active Alkali (RAA) & pH making it unsuitable to process in the chemical recovery system. Further, scale of operations also does not allow these mills to install the capital intensive chemical recovery system thereby causing concern for environment.

Looking into the above problem being faced by this segment of paper industry below 50 tpd, Central Pulp & Paper Research Institute carried out exhaustive research and development work and could find out a process based on incineration of black liquor after mixing with waste biomass (bagasse pith or any agro forestry waste) as one of the potential option to address the above said problem which could help in achieving zero black liquor discharge.

The present paper highlights the results obtained on bench/pilot scale studies conducted in an identified agro based mill on proposed process of incineration of black liquor mixed with lingo-cellulosic biomass.

Introduction

With the shortage of forest based raw material and to preserve the forest, the paper industry in Asia and other parts of the world is forced to use the non-woody fibrous raw materials. India is also one of the leading countries using substantial proportion of non-wood raw materials such as bamboo, cereal straws, bagasse, etc., which constitute about 50% of the total raw material furnish used for manufacturing virgin fibre based pulp and paper in Indian paper industry.

Non-wood raw materials are characterized by high silica content.(*1*) Silica content in non-wood varies between 1.5 to 16% . This silica passes into black liquor during pulping under high temperature and alkaline conditions.(*2*) Size constraints and economic viability in these mills does not permit to install full fledged chemical recovery system. Presence of silica and other physico chemical properties of black liquor from agro residue based pulp & paper mill further aggravate the problem from view point of installing the chemical recovery & meeting environmental aspect. (*3*)

Black liquor used for the studies was collected from two mills located in western U.P. Both the mills are based on bagasse and wheat straw and are producing low BF unbleached variety of packaging grade paper. Waste biomass (Bagasse pith) was collected from paper mill itself as the mills are employing dry depithing process.

In this background CPPRI initiated R&D work on various options for handling black liquor to achieve zero black liquor discharge. Efforts made in this direction are discussed in the present article.

Results and Discussions

Characterization of Black Liquor

Black liquor collected from the mill was analyzed for Physico-chemical, thermal and Rheological properties to understand its behavior in evaporator and boiler. Characterization of black liquor also gives a lead in accessing the characteristics of ash generated after burning of black liquor along with biomass in boiler.

Characterization of black liquor is shown in table 1.

Table -1
Characterization of black liquor

S/No	Parameters	Value
1.	pH at room temp.	9.9
2.	Total Solids, % w/w.	15.06
3.	Residual Active Alkali, gpl as NaOH.	0.6
4.	Silica as SiO_2, % w/w.	2.9
5.	Total Sodium as Na, % w/w.	12.2
6.	Gross Calorific Value, Cals/gm	3180
7.	Inorganic as NaOH, % w/w.	27.2
8.	Organic, % w/w (by difference)	72.8
9	Suspended solids, gpl	0.24
10.	Chlorides as Cl, %w/w	2.0
11.	Carbon as C, %w/w	37.68
12.	Hydrogen as H, %w/w	4.18
13.	Nitrogen as N, %w/w	0.77
14.	Sulpher as S, %w/w	0.92
15.	Ash, %w/w	34.5

pH of the black liquor was 9.9 which is lower for any chemical recovery point of view Residual Active Alkali content was around 0.6 gpl which is again on lower side. Silica content, in the range of 2.9% which is on the higher side. (*4*) Existing chemical recovery systems could not handle such black liquor with low pH, low RAA and high silica content. Other parameters like calorific value, carbon, organic to inorganic ration are suitable for combustion of this fuel.

Characterization of Bagasse Pith

Bagasse pith as received after dry depithinmg of bagasse in the mill was analysed for desired parameter. Results are shown in table 2.

Table -2
Characterization of Bagasse Pith

S/No	Parameters	Value
1.	Moisture,%w/w	40
2.	Ash, %w/w	8.1
3.	Gross calorific value, cals/gm	4145

The results reveal that pith has high calorific value which shows its suitability for high steam generation during combustion. Burning of pith alone is difficult due to its bulky nature and size of particle. It was decided that this problematic black liquor can be mixed with this problematic waste biomass to produce a better fuel which will not only solve environmental problem of small agro based paper mills but will also generate energy.

Evaporation Studies of Black Liquor

Black liquor is a colloidal system and the viscosity depends largely upon the colloidal stability of the lignin macromolecules present. Viscosity of black liquor is an important aspect in its processing in evaporators. Evaporation studies conducted in CPPRI have shown that this black liquor can be easily evaporated to 40% concentration without precipitation and viscosity problem. This concentration is suitable for its proper mixing with bagasse pith and achieving desired dryness for autogenous combustion. Evaporation was also carried out in pilot scale multiple effect evaporator in the facility existing in a supplier's complex.

Studies on optimization of Mixed fuel Preparation (Black liquor and Pith)

Concentrated black liquor with 40% concentration was mixed with pith in different ratios to check its mixing characteristics and burning properties. Optimizing the ratio of pith and black liquor for smooth operation was the objective for mixing and ashing the same in laboratory. Mixing was done in following ratios of black liquor and pith.

Table 3
Mixing of Pith and Black Liquor

Black liquor, % w/w (Dryness 40%)	Pith, % w/w (Dryness 60%)
50 (20 gms)	50 (30 gms)
60 (24 gms)	40 (24 gms)
70 (28 gms)	30 (18 gms)

This mixed fuel of pith and black liquor were analysed for moisture, ash and calorific value. Both NCV and GCV were determined. This mix fuels were subjected to burning in laboratory furnace for observing their burning characteristics and generation of ash for characterization. Results are shown in table 4. Mixed fuel will be dried prior to burning.

Table 4
Analysis of Mixed fuels (Black Liquor and Pith)

S/No	Parameters	Mixed Fuel Sample		
		50:50 (BL:Pith)	60:40 (BL:Pith)	70:30 (BL:Pith)
1.	Dryness, % w/w.	64.2	61.4	58.7
2.	Ash, % w/w.	13.4	16.3	18.4
3.	Net Calorific Value cals/gm	3150	3110	3060
4.	Gross Calorific Value, Cals /gm	4280	4204	4142

The studies show that mixing of biomass with black liquor in any ratio between 30: 70 to 50:50 is good enough for burning of black liquor.

Studies on combustion of Mixed Fuel (Black liquor + Pith)

Burning behaviour of mixed fuel was carried out in laboratory. Three combinations of biomass and black liquor were subjected to burning in laboratory furnace. It was found that this is a good burning fuel with no combustion related problem. Autogenous combustion could be attained without any auxillary fuel. Nearly 7-8 tons of ash will be generated in a 50 tpd pulp mill. Ash generated was analyzed for various parameters. Results are shown in table 5.

Table 5;- Analysis of Ash

S.No	Parameters	Mixed Fuel Sample		
		50:50 (BL:Pith)	60:40 (BL:Pith)	70:30 (BL:Pith)
1.	Ash, %w/w	13.4	16.3	18.4
2.	Silica as SiO_2, %w/w.	0.5	0.6	0.7
3.	Na as Na_2CO_3, %w/w.	66.1	62.2	61.4
4.	Chlorides as NaCl, %w/w	0.7	0.9	0.95

The Ash thus generated which is rich in sodium carbonate and having more than 65% of active sodium compounds may find applications in various industries like soap/detergent and glass/ceramic.

Requirement and generation of steam in the Process

A. Requirement of steam in the process

Nearly 22 tons of black liquor dry solids will be recovered per day in a 50 TPD mill. Volume of the black liquor will be around 157 M^3 at a concentration of 13.4% achieved through two stage screw press. For mixing of this black liquor with biomass this is to be concentrated in four/five stage multiple effect evaporator up to 40%. Fresh LP steam will be used in evaporators for concentrating the black liquor. Steam demand for evaporators will be 25 tons/day. Flow diagram of process

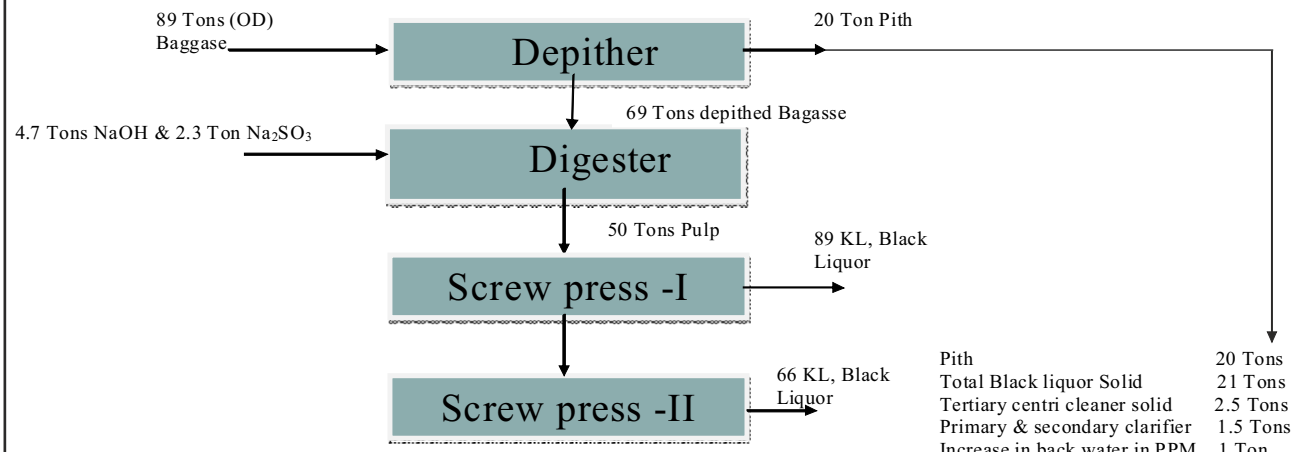
and mass balance are given in figure 1 & 2.

B. Generation of steam in the process

Total mix fuel generated after mixing of black liquor and pith will be 44 ton/day on OD basis. NCV of this Mix fuel is a 3150 cals/gm. Thus steam generated per day with 44 tons biomass at a Thermal efficiency of 70% will be 136 tons.

Thus net Steam Generation from the process will be 111 tons / day (136-25).

Fig. 1
Mass Balance of 50 TPD bagasse Based Pulp Mill

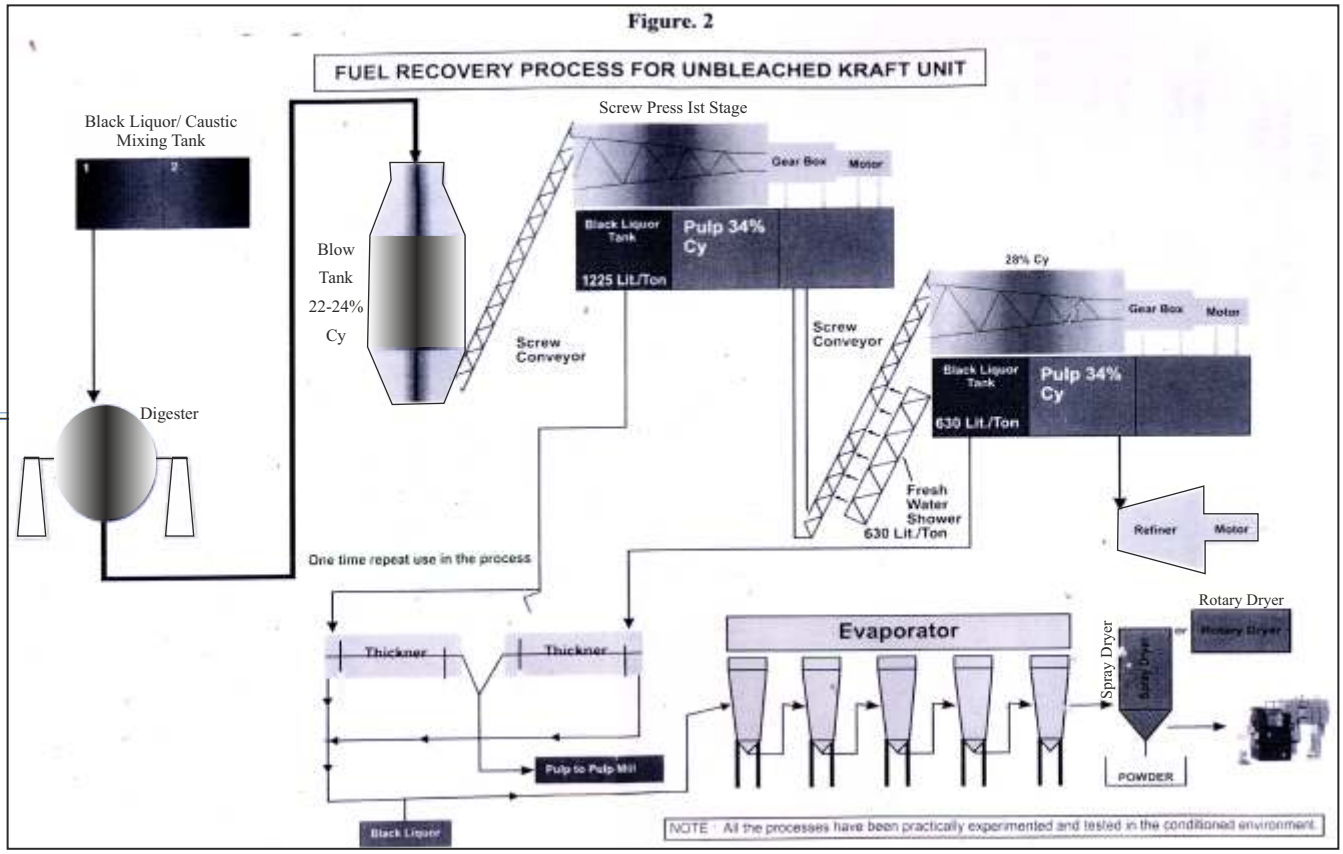


Pith	20 Tons
Total Black liquor Solid	21 Tons
Tertiary centri cleaner solid	2.5 Tons
Primary & secondary clarifier	1.5 Tons
Increase in back water in PPM	1 Ton
Total of above Mass	**46Tons**
Pulp	**50 Tons**
G. Total	**96 Tons**

Total Black liquor = 155 KL

The total Solids in Black Liquor Will be 13.5 % which will come out to be 21 tons

Figure. 2



C. Emission Data

Combustion studies were carried out to compare the emissions generated from the proposed system with the conventional chemical recovery in respect of CO_2, NOX, SOX & H_2S contents and data are shown in the table. 6

Table. 6
Comparison of emissions of the proposed system with conventional chemical recovery

Parameters	Conventional Chemical Recovery	Proposed Black Liquor Incineration process	
CO_2, %w/w	9.0-12	10.0	
O_2, %w/w	9.0	5.0	
NOX, ppm	50-100	35	
SOX, ppm	10-15	4.0	
H_2S, ppm	1.0-2.0	0.2	

As indicated from the results, the sulphur emissions are comparatively much less compared to the conventional chemical recovery system obviously due to the negligible quantity of sulphur in the biomass containing black liquor being used for incineration. NOX emissions are also reduced by almost 50%which is a positive sign in this regard.

Comparison of FBR Recovery System and Proposed Black liquor Incineration System

Fluid Bed Chemical recovery system has been practiced & installed only in agro based pulp & paper mill producing writing and printing or absorbant kraft grade of paper. These mills are using higher doses of cooking chemicals. As a process requirement to produce good quality writing and printing grade paper these mills have to installd raw material washing which may not be economical for small agro based mills producing low grade packaging paper. Small agro based having less capacity and producing packaging grade paper are cooking with less chemical and the black liquor is not suitable for FBR recovery system. A comparison of the two system is given below in table no 7.

Conclusions

1. The proposed process for incineration of black liquor mixed with waste biomass could emerge as one of the potential option to achieve zero black liquor discharge in the small agro based mill.

2. The ash thus generated after incineration containing more than 65% of active sodium compounds (Carbonate & caustic soda) may find its application in the detergent/soap and glass industry.

3. The process should prove to be an ideal candidate for carbon credit as supported by the following facts.

Saving of fossil fuel (12-13 ton in a mill of 50 tpd capacity) by way of utilising waste biomass and black liquor.

Strong possibilities of utilising rice straw as fibrous raw material in packaging grade paper manufacturing which due to its inherent nature could not be utilised in mills having other chemical recovery processes. Rice straw is burned openly in fields in northern India which causes green house gas emission.

No black liquor discharge thereby eliminating green house gas emission liberated by discharged black liquor

4. SOX, H_2S & NOX emissions are reduced by more than 50%.

The stakeholders including paper industry should come forward to set up a demonstration mill scale commercial plant to establish the credibility of the technology and to create confidence among the entrepreneurs.

Table 7
Comparison of FBR Recovery and Proposed Black liquor Incineration System

Parameter	FBR Recovery System	Proposed System
Capital Cost (approx. in Rs.)	High (7-8 crores) for minimum 60 tpd mill	Low (2.5 crores) for 30-50 tpd mill
Pulp mill producing alkaline Sulphite pulp	Not suitable	Suitable
RAA of Black liquor	6-7 gpl	Low RAA is suitable
Raw Material Washing	Absolute Necessary for removal of chloride and potassium	Not required
Water Consumption	High as water is required for washing of Raw Material. This water is again a source of pollution	No water requirement/ pollution free
Production Capacity	Not suitable for mill having less than 60 TPD black liquor solids	Highly flexible suitable even for mill having black liquor solid around 15 TPD

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