Improved Energy Efficiency Through Thermal Treatment of Black Liquor- A Pilot Scale Experience

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ABSTRACT

Firing of black liquor at high dry solids concentration with proper combustion is one of the pre-requisite for generation of high pressure steam and efficient cogeneration. Central Pulp & Paper Research Institute has been actively engaged for last 10 years in research activities related to identification & development of energy efficient process technologies. Modification of black liquor properties & thermal treatment of black liquor have been the priority areas for smooth & effective processing of the black liquor in order to improve the energy efficiency of the chemical recovery systems.

Thermal tratment on non wood/wood black liquor, is a process successfully developed and demonstrated by Central Pulp & Paper Research Institute (CPPRI) both on laboratory and pilot plant scale. Recently the pilot plant trials were conducted at CPPRI jointly with M/s ENMAS Ahlstrom Ltd., a company having licensed agreement for promotion of the technology. The technology has helped in overcoming the problems of higher viscosity. and enables to evaporate the thermally treated black liquor to higher dry solids concentration of 70% and above in pilot plant evaporator by maintaining reasonable viscosity level of 500 mPa.S against 60% achieved normally without thermal treatment. During the pilot scale trials black liquor from a large integrated bagasse & wood based mill having cross chemical recovery system, was used. The results obtained during pilot plant trials were encouraging in respect of viscosity and combustion behaviour. The viscosity was reduced to more than 60% (i.e. to 398 cps as against 1000 cps at a solid concentration of 65% w/w at 98°C temp.) The combustion behaviour of black liquor was also improved as indicated by improved swelling behaviour of black liquor since swelling volume ratio was increased from 8 ml/gm to 17 ml/gm. The results of pilot plant trials has given confidence in up-scaling the technology to commercial scale operation with an option of retrofitting in existing and/or upcoming chemical recovery installaton in non wood based pulp and paper mills. The present paper highlights the efforts made at CPPRI in making the thermal treatment technology - a success, which is a step towards improved energy efficiency in Indian paper industry.

INTRODUCTION

Looking into the high cost component of energy in paper making processes, there is a need to enhance energy generation and the possibility of fuel flexibility in Indian Paper Industry. The Pulp & Paper Industry in developed countries has been able to contain their cost of production by way of increased fuel flexibility and decreased dependence on external fuel sources. The effective utilization of black liquor as a fuel is far from satisfactory in terms of generation of steam and electrical energy through co-generation particularly

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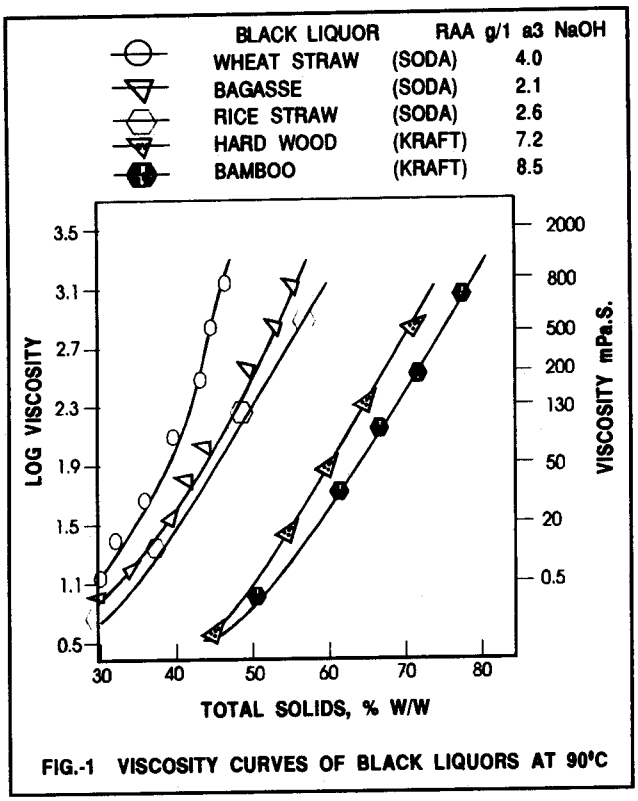

FIG.-1 VISCOSITY CURVES OF BLACK LIQUORS AT 90°C

in developing countries mainly due to the nature of black liquor generated from wood & Non wood based fibrous raw material. This calls for review of the existing practices & technology gaps in effective utilization of black liquor as a fuel. Indian Pulp & Paper Industry produces nearly 2.0 million tonnes of virgin pulp while generating similar quantities of black liquor solids per year. Nearly 1.0 million tonnes of black liquor produced in small & medium size agro based mills in not utilized and only 1.0 million tonne is being utilized fuel in large integrated paper mills through chemical recovery system. In most of the mills, black liquor is evaporated to a concentration level of around 58-63% w/w followed by its combustion in chemical recovery furnace as against 75-80% in developed countries.

The chemical recovery which is a complex operation has number of dependent & independent variables. Among these, the black liquor concentration & the combustion air are two important variables having influence on the thermal efficiency of the chemical recovery boiler and also the opportunities for co-generation. Generation of high-pressure steam is one of the prerequisites for co-generation. However one of the present limitation in having high pressure/ temperature steam in Indian paper mills has been, the firing of the black liquor at lower solids concentration, mainly due to higher viscosities of the black liquor resulting from non wood based mills. Thus, for effective steam generation and also for improved co-generation, there is a need for adopting high solids black liquor combustion.

Thermal treatment of black liquor is a process successfully developed and demonstrated on pilot scale at CPPRI mainly for non wood based black liquors which could help in drastic reduction of black liquor viscosity thus, enabling to fire the black liquor at high dry solids concentration.

The present paper highlights results of the pilot plant trials recently conducted at the Institute on thermal treatment of black liquor procured from a large, integrated pulp and paper mill employing bagasse and Eucalyptus as major fibrous raw materials.

BLACK LIQUOR VISCOSITY

The black liquor viscosity characteristics, specifically from non wood based pulp & paper mills is such that even at normal operating temperature of

TABLE-1

EFFECT OF LIGNIN CARBOHYDRATE COMPLEXES (LCC'S) ON VISCOSITY OF BAGASSE BLACK LIQUORS (3)

Particulars	Black liquor, Original	Black liquor after separation of LCC'S
Total Solids, % w/w	Viscosity, mPa.S at 90°C	
55	252	21
60	478	50
65	1000	320
68	Could not be measured	410

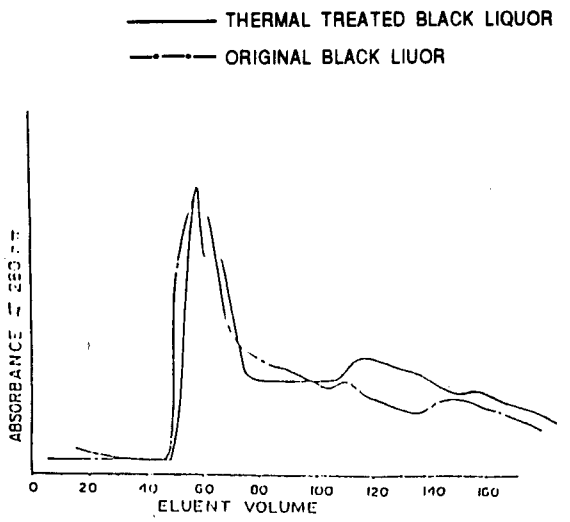

FIG.-2 GEL CHROMATOGRAM SHOWING INFLUENCE OF THERMAL TREATMENT ON SODA BAGASSE BLACK LIQUOR, (SEPHADEX G.25)

100-115°C, the viscosity at 55% w/w total dissolved solids concentration exceeds 500 CPS (1). Fig-1 shows the comparative viscosity results of various wood and non wood based black liquor which shows the non wood black liquor including bagasse & bamboo having very high viscosities as compared to soft wood & hard wood black liquors. These higher viscosities in case of non-wood based black liquors make it impractical to handle such thick black liquors. Thus, the higher viscosity problems lead to firing of black liquor at low solids concentration and thereby lower steam generation.

With increased understanding & in-depth studies carried out at CPPRI on basic aspects of black liquor, it could be inferred that high molecular weight organic residues like polysaccharides linked with lignin molecules, i.e. Lignin - Carbohydrate Complexes (LCC's and the high molar mass lignin are mainly responsible for abnormally high viscosities of black liquors (2). This is supported from the determination of the viscosities of the black liquor after removal of the LCC'S from the untreated and treated black liquors. The results are shown in Table-1. From the results it is clearly seen that the separation of LCC'S from the black liquors helps in drastic reduction of viscosity,

THERMAL TREATMENT OF BLACK LIQUORS

Increased understanding of the basic black liquor properties of wood and non-wood raw materials based on the research work carried out the CPPRI during last 20 years has led to the development of process for thermal treatment of black liquor. The process basically incorporates heat treatment of semi-concentrated black liquor at temperatures between 180-190°C in presence of certain amount of residual active alkali for specified time period, which results in depolymerization of high molecular weight lignin carbohydrate complexes in to lower mass components. The findings are supported from gel chromatographic studies as shown in Fig.-2. From the chromatogram, it is clear that the thermal treatment of the black liquor resulted in cleavage of Lignin-Carbohydrate Complexes which caused decrease in molar mass of the lignin entity which appears in the form of a new peak of relatively lower molar mass fraction, eluting out at elution volumes of 60 & 68 ml. as compared to the original, where only a single peak at an elution volume of 60 ml is observed.

As a result of thermal treatment of black liqor there was remarkable reduction in black liquor viscosity making it possible to achieve higher dry solids (more than 70% w/w) in remaining bodies of the multiple effect evaporator (M.E.E.) itself and eliminates the need of direct contact evaporator. Reduction in viscosity after thermal treatment could help in handling the black liquor by keeping it is a less viscous form even

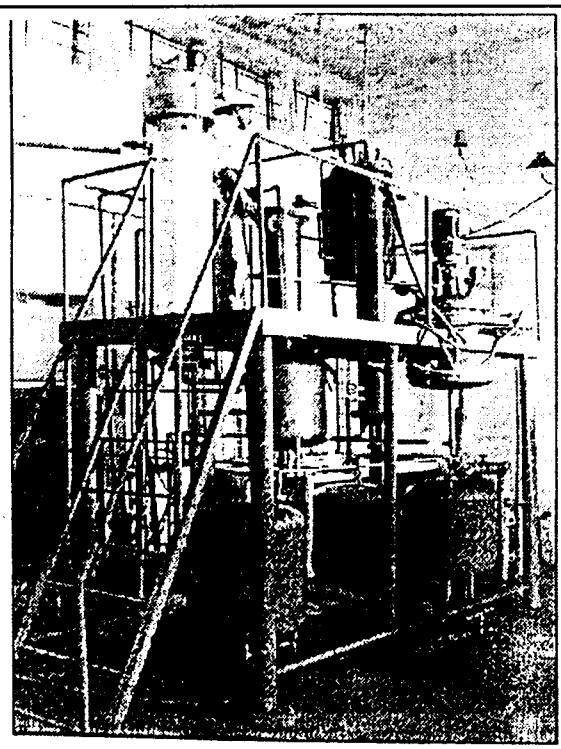

FIG.-3 PHOTOGRAPH OF PILOT PLANT FOR THERMAL TREATMENT OF BLACK LIQUOR

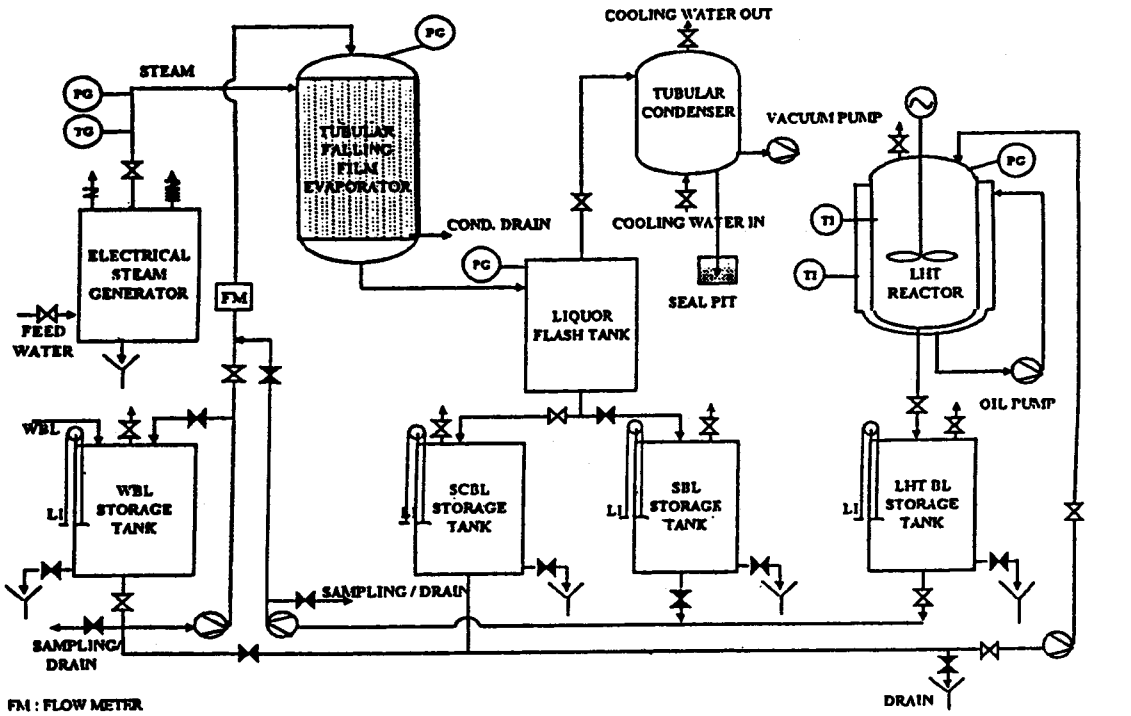

FIG.-4 FLOW SHEET FOR LIQUOR HEAT TREATMENT PILOT PLANT AT CPPRI, SAHARANPUR

TABLE-2

VARIOUS UNITS OF PILOT PLANT FOR THERMAL TREATMENT OF BLACK LIQUOR

Sl. No.	Description of the component	Capacity
1.	Reactor vessel made up of S.S with M.S. heating jacket heating with oil circulation to raise the temperature of the black liquor in the reactor up to 200-220°C, provided with agitator at the top with gear box & motor and appropriate pressure & temperature indicators.	40 Litres
2.	Falling film Evaporator of 2 mts. Height having 10 no. of tubes of 1.0" OD with working steam pressure of 5kgs/Cm^2	Heating Surface area 1.2mt^2
3.	Storage tank made of M.S. 4 Nos.	200, 100, 100 & 80 lts.
4.	Shell & Tube M.S. Condenser for condensing vapour coming out from Calendria	-
5.	S.S. Vapour Separator	50 Kg.
6.	S.S. Recycling gear & Centrifugal pumps for transfer of weak and thick black liquor.	3 No.
7.	Vacuum pump, 5 H.P.	1 No.
8.	Gas holder for Non Condensible gas holder	1 No.

TABLE-3

RESULTS OF COMBUSTIBILITY BEFORE & AFTER THERMAL TREATMENT OF BLACK LIQUOR

Particulars	Black Liquor before thermal treatment	Black liquor after thermal treatment
Calorific value, KJ/kg.	14200	13990
Swelling Volume, ml/gm	8.0	17.0
Temp. of Ignition, °C	765	735

a atmospheric pressure.

PILOT PLANT TRIALS

Based on data generated from laboratories studies at CPPRI, a pilot plant was designed for processing 200 lit./h of black liquor. The photograph & the process flow sheet of the pilot plant is shown in Fig.-3 & 4. The pilot plant was commissioned with involvement of M/s Enmas Ahlstrom Ltd. during August, 1999 after overcoming various difficulties faced during commissioning trials which was basically the leakages of the steam and liquor from the reactor operating at high pressure & temperature. The pilot plant consists of the basic components as shown in Table-2.

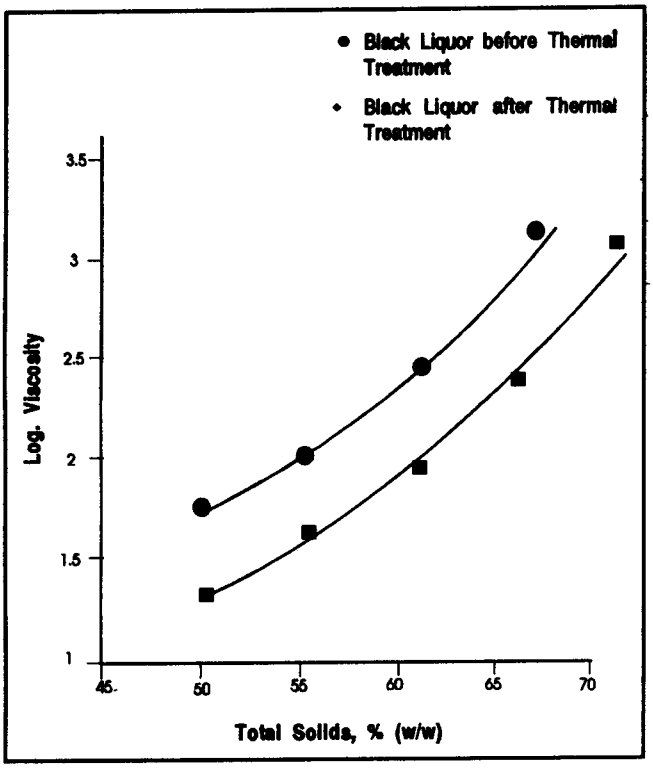

FIG.-5 Viscosity results of Pilot Plant Trial during Thermal Treatment of Mill's Black Liquor (Bagasse 85% + Eucalyptus 15%)

Having completed commissioning trials, pilot plant was run with black liquor procured from a large integrated bagasse/Eucalyptus based mills in order to test the response of thermal treatment on the mill's black liquor to generate data for exploring the possibilities of retrofitting the thermal treatment process in existing chemical recovery system.

RESULTS AND DISCUSSIONS

i. Effect of Thermal Treatment on Viscosity & Combustion of Black Liquors

The results of pilot plant trial for thermal treatment of black liquor in respect of viscosity & combustion characteristics are shown in Fig.-5 & Table-3 respectively. From the results of viscosity, it is evident that there is a drastic reduction in viscosity of the black liquor after thermal treatment which was reduced by more than 50%. Reduction in viscosity could make it possible to evaporate the black liquor in the evaporator to a solids concentration level of more than 70% (w/w) while maintaining the viscosity level of 350 mPa.S. This reduction in viscosity could help in keeping the black liquor in a form, which can now be easily pumped even at higher solids concentration & at atmospheric pressure allowing to store the thick black liquor in atmospheric tanks. Reduction in viscosity further helps in reducing the requirement of electrical energy during pumping of thick black liquor, which is evident from the fact that 30% increase in bagasse black liquor viscosity results in remarkable increase in the requirement of pumping energy to the tune of 200% as compared to the softwood black liquor for which the comparative pumping energy requirement is at 33% whereas it is 63% from Indian hard wood black liquors.

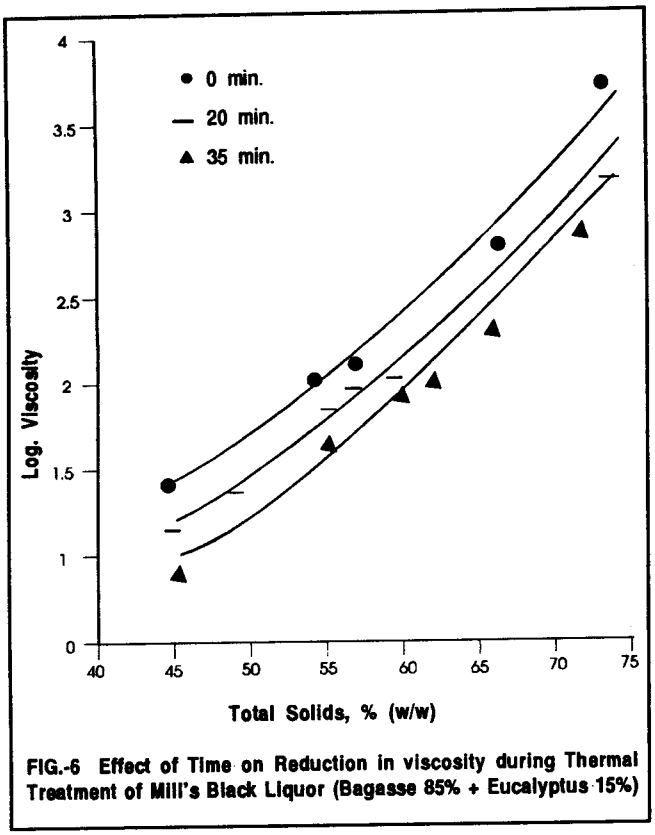

FIG.-6 Effect of Time on Reduction in viscosity during Thermal Treatment of Mill's Black Liquor (Bagasse 85% + Eucalyptus 15%)

ii. Effect of Time on Viscosity Reduction

Time for thermal treatment of black liquor was found to have pronounced effect on extent of reduction in viscosity, as evident from the results shown in Fig.-6. It is clearly seen that increasing the time of thermal treatment of black liquor from 20 minute to 35 minutes, there is improvement in reduction in viscosity however, beyond 35 minutes, the black liquor becomes unstable resulting in phase separation and making it difficult to evaporate further.

iii. Effect of Treatment on Combustibility of Black Liquor

Combustibility of the black liquor is highly influenced by thermo-plasticity of the organic residues in black liquor which is related to molecular size and uniform dispersion of the molecules. This influences the swelling characteristics of the black liquor during combustion. Swelling of the black liquor droplet during firing into the recovery furnace determines how the black liquor will behave during combustion. Higher swelling is an indication of better combustibility. Results in Table-3 show the swelling of the thermally treated black liquor was improved from 8 ml./g to 17 ml./g which is an indication of improved combustibility after thermal treatment of black liquor The differential thermal analysis of the two black liquors also show reduction in Temperature of ignition (Tig.) in case of thermally treated black liquor which was reduced from 765 to 735°C. The results clearly indicated that the combustibility of the black liquor was improved in terms of swelling behaviour and temperature of ignition.

CONCLUSION

1. The Thermal Treatment of black liquor is a promissing technology especially for bagasse based mills where, higher black liquor viscosities has been one of the major problem restricting to fire the black liquor at high dry solids thereby resulting in poor thermal efficiency of recovery boiler.
2. The thermal treatment technology developed & tested onpilot scale at CPPRI with bagasse & Eucalyptus black liquors collected from the mills has resulted in drastic reduction in viscosity & has enabled to evaporate the black liquor to more than 70% solids concentration after thermal treatment as against 60% before thermal treatment.
3. Successful pilot scale trials conducted at the Institute with black liquors collected from the mills gave confidence in up-scaling the process to commercial scale where in retrofitting of thermal treatment system could improve the energy efficiency by more than 10% by generation of additional steam to the tune of 0.35 t/t solids.
4. Besides the benefits of improvement in energy efficiency of chemical recovery system, the process also result in improvement in environmental situation of the mill by way of reduced SO_2 emission of direct cascade evaporator.
5. The process is safe & simple and can be easily retrofitted in existing chemical recovery systems & could be an integral part of upcoming recovery installation in bagasse based mills.

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