Studies on Treatment of Black Liquor from Small Paper Industries

Sharma D.K., Dastidar M.G. and Chahar Suman

ABSTRACT:- Treatment of black liquor was attempted through various pretreatment techniques followed by anaerobic digestion. Studies were carried out on both paper mill black liquor (PBL) and synthetic black liquor (SBL) through chemical and photochemical treatment techniques. The conditions for the treatment were optimised using a synthetic black liquor. The optimised conditions so obtained were used for the treatment of paper industry black liquor. Chemical treatment precipitated out lignin from the black liquor so that the higher value lignin could be used as a feed stock for obtaining various chemicals. Pretreated black liquor still having high biochemical oxygen demand (BOD) value, was subjected to anaerobic fermentation to obtain biogas (0.035 ml/d/mg solids). Degradation of lignin was attempted through photochemical pretreatment (in presence of TiO_2 as a catalyst) which rendered black liquor (containing oxidised lignin products) more amenable to microbial action in anaerobic system to obtain biogas (0.040 ml/d/mg solids). The results indicated a BOD/COD ratio of 0.27-0.21 after anaerobic treatment vs. 0.57 prior to treatment.

INTRODUCTION:

Due to excessive deforestation, the trend has started on the use of agrowastes as raw material for paper industries, especially in small and medium paper mills. There is a need for development of techniques for the treatment of effluents for such mills. Recovery of chemicals from effluents may make treatment processes economically viable. The wastes from the wood pulping operations in the paper industry are gererally highly coloured. The pulping of woods produces considerable amounts of waste liquors containing lignin which is derived from the raw material and is not easily biodegradable, lignin derivatives and other materials in dissolved form (1). The continued discharge of black liquor whick contains non-biodegradable lignin and other organics may cause not only severe pollution problem but also result in wastage of potentially valuable and recoverable energy resources and other value added chemicals. Research and development work for treatment of the effluents from agroresidue based small and medium paper mills has started lately. Recovery of energy in form of steam and of other inorganic chemicals from black liquor has been known for a long time but only for larger paper mills (2). The current trend is towards biological treatment to convert the organic pollutants into either CO_2 and H_2O or CH_4 using microorganisms under aerobic and anerobic conditions respectively (3-6). An alternate approach could be pretreatment of black liquor, in which lignin can either be recovered or degraded followed by anaerobic digestion of the treated liquor. In an earlier work, reduction in

Fuels and Biofuels Engineering Laboratory
Centre for Energy Studies
Indian Institute of Technology, Delhi
New Delhi-110016

total disolved solids (TDS) and chemical oxygen demand (COD) has been reported in an attempt to precipitate lignin from paper mill black liquor (PBL) by the application of gypsum in presence of CO_2 (7). In subsequent work lignin recovery and degradation of lignin have been reported in agroresidues based mill effluent using chemical and photochemical treatment respectively (8,9) in order to make the effluent more amenable to bacterial treatment in anaerobic system. However, there is a need to study and optimise the condition for the recovery and degradation of lignin from black liquor having low concentration of lignin. Therefore it was planned in the present studies to prepare synthetic black liquor (SBL) in the laboratory in order to study and optimise the conditions for the pretreatment of black liquor from agroresidue based paper mills. In the present work, treatment of black liquor was attempted on both PBL and SBL through chemical and photochemical treatment followed by anaerobic digestion.

MATERIAL AND METHODS

EFFLUENT: The effluent selected for the present study was obtained from a typical agrobased Kraft paper mill utilizing mainly bagasse, alongwith jute, wheat husk and elephant grass, respectively as raw materials in separate digesters by using alkaline process where the main constituent of cooking chemical was sodium hydroxide. The synthetic black liquor was artificially prepared in the laboratory as per the characteristics of a typical effluent generated in a small paper mill in order to maintain homogeniety in composition of the black liquor throughout the experiments.

Bagasse was cooked in an autoclave under following standard conditions and filtered effluent was diluted to get about 2.2-2.4% solid concentration usually found in a paper mill effluent.

Raw material	= Bagasse
Chemical (NaOH)	= 16% by weight
Bath ratio	= 1:5
Maximum Temp.	= 160^0 C
Time at maximum temperature	= 90 min.

Both the black liquors were characterised for various parameters (Table 1).

Table-1.

Characterization of effluent

Parameters	Synthetic black Liquor (SBL)	Local paper mill Black Liquor (PBL)
pH	9-9.7	9-9.5
COD*	2460 mgo_2/l	2400 mgo_2/l
BOD_5*	1400 mgo_2/l	1390 mgo_2/l
BOD/COD	0.56	0.57
TDS*	2400 mg/l	2200 mg/l
Organics	1500 mg/l	1400 mg/l
Inorganics	900 mg/l	800 mg/l
Lignin	360 mg/l	350 mg/l
Colour	5000 CPU*	5000 CPU*

*CPU = Cobalt Platinum Unit
*COD = Chemical Oxygen Demand
*BOD = Bio-chemical Oxygen Demand
*TDS = Total Dissolved Solids

CHEMICALS

Reagents used in the present work were as per standard specifications (10). CO_2 gas cylinder was used for getting CO_2 for experiments.

CHEMICAL PRECIPITATION:

The experiments for recovery of lignin by precipitating it from synthetic black liquor (SBL) as well as from paper mill black liquor (PBL) were conducted in a batch reactor system. In a typical experiment a measured quantity of black liquor was taken in a reaction vessel fitted with a thermometer, a reflux condenser, and having an inlet for CO_2 gas introduction. The precipitation was studied under different reaction conditions to optimise the reaction parameters such as temperature and time. Experiments were conducted with CO_2 and gypsum as precipitating agent and simultaneous extraction of precipitated lignin in the solvent phase. The precipitated lignin was recovered through steam distillation and simultaneously solvent was also recovered. During precipitation the liquid samples were withdrawn at different intervals of time from the reaction vessel. The samples were filtered and finally analysed mainly for lignin concentration, colour, TDS, and COD.

PHOTOCHEMICAL TREATMENT:

Experiments on degradation of lignin were conducted through photochemical treatment by irradiating the SBL as well as PBL separately with 125 W mercury high pressure UV lamp, by taking the black liquor (300 ml) in the pyrex glass photochemical reactor. Lamp was placed in the quartz probe in between probe and black liquor water condenser was used continuously. An experiments were conducted under different conditions i.e. using activated TiO_2 and without TiO_2. The samples were filtered and finally analysed for lignin concentration and colour.

PREPARATION OF PHOTOCATALYST

TiO_2 was treated with 1 M perchloric acid, filtered and washed with distilled water and finally dried in oven at 105° C. This was done in order to activate the photocatalyst (TiO_2) (11).

ANAEROBIC DIGESTION

The treated black liquors from chemical and photochemical pretreatment techniques were subjected to anaerobic fermentation at 37°C for 40 days using cow dung as inoculum in a batch fermenter. The pH was maintained at 7.

The following different liquor samples were used for anaerobic fermentation.

1. PBL without any pretreatment.
2. SBL without any pretreatment.
3. Chemically pretreated PBL.
4. Chemically pretreated SBL.
5. Photochemically pretreated PBL.
6. Photochemically pretreated SBL.

Biogas was collected in a gas collection system by water displacement method and samples were collected after 40 days.

Analytical Methods:

Biogas was analysed by using Gas chromatograph (Model No. 5700 nucon) using hydrogen as a carrier gas with thermal conductivity detector.

The SBL as well as PBL were analysed for COD, BOD_5 TDS, and colour using the standard techniques (10). Both the liquors were also analysed after various pretreatments. Colour was measured at 465 nm in the visible region which is the selective wave length for colour generating groups. Visible and UV spectral analyses were performed on Hitachi UV-200 spectrophotometer. Lignin concentration in each liquor was measured at 280 nm (12).

Table-2.

Results of the Pretreatment Techniques

Experimental Conditions	Time (h)	Redn.in lignin conc. (%)	Redn.in colour (%)	TDS redn (%)	COD redn (%)
PBL + CO_2 at 40°C	2	15	10	10	20
	4	20	12	49	25
	6	24	15	52	30
PBL+CO_2– Gypsum at 40°C	2	25	22	20	27
	4	42	47	52	40
	6	59	62	60	54
PBL+CO_2+ Solvent+ Gypsum at 40°C	2	80	60	70	65
	4	82	62	72	68
	6	85	65	76	70
SBL+CO_2 at 40°C	2	20	13	14	30
	4	24	18	49	43
	6	30	21	54	57
SBL+CO_2+ Gypsum at 40°C	2	31	50	40	68
	4	48	52	45	72
	6	62	59	52	74
SBL+CO_2+ Gypsum+solvent at 40°C	2	82	72	80	70
	4	85	72	84	76
	6	87	73	86	77
SBL+Photochemical treatment (without catalyst)	2	10	7	--	--
	4	15	10	--	--
	6	20	12	--	--
SBL+Photochemical treatment with catalyst (TiO_2)	2	45	30	--	--
	4	47	32	--	--
	6	50	38	--	--
PBL+Photochemical treatment (without catalyst)	2	8	5	--	--
	4	12	8	--	--
	6	18	12	--	--
SBL+Photochemical treatment+TiO_2	2	40	28	--	--
	4	44	30	--	--
	6	48	35	--	--

Redn. = Reduction

RESULTS AND DISCUSSION

Analysis of Black Liquor

Table 1 shows that SBL and PBL had almost similar composition excepting that the PBL contained larger amounts of inorganics. Both SBL and PBL were found to be rich in organics contents with high COD values. About 60-63% of the total dissolved solids (TDS) were found to be organic showing that these liquors have a great potential for recovery of energy and chemicals. About 28-30% of the total organics were observed to be lignin. The remaining non-lignin fraction was sodium salt of carboxylic acids and may have great potential for biogas production.

Chemical Treatment

Table-2 shows the characteristics of both SBL and PBL remaining after precipitating out lignin with various precipitation agents under different reaction conditions. Percent reduction in lignin content was found to be maximum (82%) in the pretreated SBL when CO_2, gypsum and solvent (amyl alcohol) were simultaneously used for reaction for 2 h. The increase in reaction time 6 h, enhanced the reduction of lignin up to 87%. An increase in temperature did not make an appreciable enhancement in the lignin reduction. The same trend was observed in case of PBL (table 2). According to UV spectrophotometric analysis 14 to 16% of lignin were recovered after distillation of solvent (to the extent of 220 mg/L). Recovery of amyl alcohol through steam distillation was found to be 85%.

Photodegradation of Black Liquor

Degradation of high molecular weight chlorophenols to low molecular weight compounds has been reported earlier (13). Reduction in lignin and colour were also observed. Photodegradation of PBL and SBL in the present work resulted in the significant colour removal along with reduction of lignin concentration as shown in table 2. Especially, when the liquors were phototreated in the presence of TiO_2,. maximum reduction in lignin concentration and colour was observed.

About 45% reduction in lignin concentration was observed within 2 h when SBL was photo- oxidised in the presence of TiO_2, which increased to 50% after 6 h of treatment. Further, absence of CO_2 in the product gas as collected from the reactor outlet as analysed by gas chromatograph (GC) indicated that photo-oxidative degradation of lignin did not take place completely to CO_2. Reduction in lignin concentration could be assumed to be due to the partial degradation of lignin to low molecular weight compounds which could be expected to be aromatic alcohols and acids.

Anaerobic Treatment

Table 3 shows the analyses of the broth of both SBL and PBL obtained after anaerobic digestion. The rate of biogas production from the use of

Table-3.

Analysis of liquors after anaerobic digestion

S. No.	Experimental Condition	BOD reduction %	COD reduction %	BOD/ COD	CH_4:CO_2 yield ml/d/mg solids	Biogas in ligin conc.	Reduction
1.	PBL + MB	54.62	50	0.46	80:20	0.031	35
2.	SBL + MB	62	51	0.44	90:10	0.033	40
3.	PBL + Chemical treatment + MB	80	60	0.22	90:10	0.034	92
4.	SBL + Chemical treatment + MB	88	68	0.21	96:4	0.035	94.35
5.	PBL + Photochemical treatment + MB	50	39	0.47	65:35	0.031	30
6.	SBL + Photochemical treatment + MB	55	40	0.42	76:24	0.032	44.87
7.	PBL + Photochemical treatment in presence of TiO_2 + MB	78	68	0.32	80:20	0.033	42
8.	SBL+Photochemical treatment in presence of TiO_2 + MB	88	75	0.27	94:6	0.040	52

PBL= Paper mill black liquor; SBL= Synthetic black liquor
MB= Methanogenic bacteria

untreated PBL and SBL (separately) in the anaerobic fermentation experiments appeared to be very low as indicated by GC analyses from time to time. However the total gas yield from PBL and SBL was estimated to be 0.031 and 0.033 ml/d/mg solid respectively after 40 days of digestion period. This low yield of biogas appeared to be logical as only the nonlignin fractions are expected to get converted into CH_4 in case of untreated liquor leaving behind the lignin fraction which are nonbiodegradable under these conditions. Low yield of biogas 0.036 ml/d/mg solids was also observed from the anaerobic fermentation of black liquor from which lignin fraction had already been precipitated out using CO_2, gypsum and solvent. This indicates conversion of only non-lignin fraction into biogas in both untreated and treated liquors.

Reduction in lignin concentration (40%) in SBL and 35% in PBL without any treatment, could be assumed to be only due to the partial precipitation of lignin during acid forming stage in digester. Lignin concentration reduction enhanced after pretreatments. 51% reduction in COD could be attributed to the fact that both partly to the precipiated lignin and partly to biogas produced from non-lignin fraction. SBL after pretreatment with gypsum and CO_2 followed by anaerobic digestion shows further reduction in BOD values (88%) and lignin concentration (94%).

In case of photo-oxidized (without using any oxidising agent) SBL and PBL, the yield of biogas produced was again low (0.032 ml/d/mg solids). A possible reason could be that photo-oxidation degradation of lignin into intermediary products (i.e. aromatic alcohols, acids, acetates etc.) had not taken place to that extent that the black liquor became amenable to the action of methanogenic bacteria. However, in case of photo-oxidised black liquor (using activated TiO_2), the total gas yield (0.040 ml/d/mg solids) appeared to be higher in 40 days as compared to gas yield observed in case when untreated black liquor was used for anaerobic digestion. This indicated the formation of the intermediary products due to lignin degradation which make the black liquor more amenable to the action of methanogenic bacteria. The rate of biogas production was also found to be faster in case of SBL.

Photo-oxidized SBL and PBL (without using any oxidizing agent) showed less reduction in COD and in lignin concentration while both the liquors photo-oxidized in presence of activated TiO_2 showed a significantly high reduction in both COD values i.e. 60 and 70% respectively and lignin concentration 52 and 42% respectively. Interestingly, biogas also contained 94 and 80% methane respectively in both the cases. This showed that TiO_2 was catalysing the photo-oxidation of black liquor lignin.

CONCLUSIONS:

1. Lignin could be recovered from black liquor and the lignin free black liquor on further treatment in the anaerobic digester would yield biogas.
2. Anaerobic treatability of black liquor is enhanced through various pretreatments. The results are very identical in both SBL and PBL.
3. Photochemical pretreatment requires the presence of photooxidising catalyst (TiO_2). to make the black liquor more amenable to anaerobic digestion.
4. Initially experiments are conducted to simulate the condition with SBL to get more authencity of results, which can be applied to real life application.

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