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Physico - Chemical Properties of Black Liquor Generated from Soda Pulping of Fresh and Stored Bagasse

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Abstract -Black liquor obtained after soda pulping of bagasse is a complex mixture of organic and inorganic components and thus exhibit typical physic- chemical properties. The properties of black liquor depend upon the type of raw material, methods of cleaning, storage methods and storage period. This paper investigates the physico- chemical characterization and comparison of the black liquor generated from fresh and stored bagasse soda pulping process. The chemical characterization of black liquor obtained after 15%,16% and 17% . soda pulping was done by using important parameter like total solid, residual active alkali, elemental composition, organic to inorganic salts and various other non process elements(NPE) like chloride, potassium, sulphur and silica. Present paper shows the effect of storage on the pulp yield and quality of black liquor. Results are discussed at adequate length in the paper.

Key words: Black liquor, soda pulping, Bagasse

INTRODUCTION

Pulp and Paper play an important role in the cultural and social development of a civilized society. As present worldwide there is a demand to banned single use plastic here in India a big opportunity for Pulp and paper technologist to capture 25% market share of single use plastic by 2025. In Comparison to plastic, paper is a eco-friendly green product and biodegradable in nature. Paper making processes involves treating a lingo-cellulosic fibrous raw material under alkaline condition. Due to environmental consideration forest deficient countries have directed attention to use non- woody fibrous in paper making.(1,2)In India paper factories are using 46% raw material from recovered paper, 25% from plantation wood and about 29% from agro residue like bagasse, straw etc. It said adding paper promotes literacy and reduce pollution. During delignification, the alkaline cooking chemical react with lignin in the fibrous raw material to from complex mixture of organic and inorganic components known as black liquor. The black liquor contains 10-18% dry solids lignin salts and degraded carbohydrates along with water black liquor obtained after soda pulping exhibit typical physic - chemical properties. The properties of black liquor depend upon the type of raw material, methods of cleaning, storage method and stored periods. The black liquor is a rich source of energy and inorganic cooking chemicals. In large paper industry black liquor is treated in chemical recovery system to regenerate cooking chemicals used for the delignification of raw materials and generating the energy in the form of steam by burning of organic parts. The efficiency of chemical recovery system to a large extent is influenced by the properties of black liquor. Chemical recovery system is very important in terms of economic as well as environmental points of view because black liquor have a very high level of COD and BOD load.

Chemical recovery is the most capitals intensive operations in pulp and paper industry. Due to high capital costs, installing a chemical recovery system for small mills is not viable (3) Therefore present research work is for used knowing the physico chemical properties of black liquor and effect of storage of bagasse on the properties. The physico chemical properties of black liquor help separating of lignin which utilized for the production of value added by products which finds applications in rubber and plywood industry. Present investigation also helps improving economic and environmental status of the pulp and paper industry.

AIM OF STUDY

Chemical recovery is very important in pulp and paper industry for economical as well as environmental point of view. For efficient running of chemical recovery system it is necessary to know the physical and chemical composition of black liquor. In present investigation we can see the impacts of storage of bagasse on pulp yield and physical and chemical composition of black liquor.

REVIEW OF LITERATURE

Pulp and Paper Industry uses large amount of water in Paper making (4). The amount of water used depends in the chemical used in pulping process and the type of raw material (6). Approximately 7 tons of black liquor is generated in the manufacturing of 1 ton of pulp in a soda puling process (7) In soda pulping process. The products resulted from the digester reactions are the cellulose pulp and the waste water (8) which has a significant impact on the environment. Black liquor is the waste liquor from soda pulping process after pulping is completed (10, 5,21) It contains most of the original cooking inorganic elements and the degraded dissolved wood substance. The latter includes acetic acid, formic acid, saccharinic acid numerous other carboxylic acid(all as the sodium salts) dissolved hemicelluloses (especially xylems) methanol and hundred of other components. It is an extremely complex mixture. The characterization of the black liquor and lignin were analysis by different spectroscopic methods (11)The environmental pollution load of black liquor is evaluated by the amount of biological oxygen demand(BOD) chemical oxygen demand(COD). Total dissolved solids(TDS) inorganic and organic material and colour of effluents (12 ,9)

In this work the chemical composition and physical properties of fresh and stored bagasse soda black liquor was determined (13,14). The black liquor was analyzed to correlates the impact of storage bagasse black liquor and pulp yield, chemical composition of soda black liquor from fresh and stored bagasse.

ABOUT RAW MATERIAL

High cost and non-availability of forest based raw material, the pulp and paper Industry is looking for alternate raw material i.e agriculture residues. Bagasse is a sugar mills by product is a potential raw material for pulp and paper Industry.

It was almost established by pulp and paper experts of the world that the bagasse after proper depithing was an ideal raw material for the manufacturing of different kind of paper.

DEPITHING METHOD

In a sugarcane plants the" bast" is the external part and the "Pith" is the internal part of the plants. A good paper making fiber from bagasse is mainly derived from bast portion of a sugarcane plants. Therefore for efficient use of bagasse for paper making, removal of pith is a required. The process of removal of pith from bagasse is known as depthing .

Conventially dry depithing, moist depithing and wet depithing processes are used by paper industry for pith removal. In these processes bagasse is mechanically abraded to break the cluster of pith away from the remaining fibrous portion of bagasse. In present investigation wet depithing process is used which reduced the pith level to 18 – 20% from internal pith level of 36 – 38 % in bagasse.

EXPERIMENTATION

Preparation of spent liquor

Bagasse, the raw material for pulping was procured from a nearby sugar mills. Storing of bagasse was done under atmospheric conditions in open area. The cooking conditions employed for pulping of bagasse are as Table- 1

The chemical charge of 15-17% on raw material basis was maintained. Bath ratio was 1:5 due to bulky nature of bagasse. "H" factor determines the rate of delignification per degree rise in temperature (18). At the end of predetermined time for cooking, the digesters were cooled in water and after cooling the spent liquor was extracted from the pulp by squeezing through a nylon cloth. The resultant spent liquor free from suspended matter was stored at 4 ^{o}C throughout the period of analysis to avoid changes taking place due to the biological activity at higher temperature and air.

Table -1 Condition employed during cooking of bagasse

Raw material	Chemical charge active alkali as NaOH % (on o.d raw material)	Bath ratio*	Cooking temp.^{0}C	H** Factor
Fresh whole bagasse	15,16 &17	1:5	160	328
Fresh depithed bagasse	15,16 &17	1:5	160	328
Stored Whole bagasse	15,16 &17	1:5	160	328
Stored depithed bagasse	15,16 &17	1:5	160	328

*Material to liquor ratio
** The factor expressing the time and temperature as a single variable

Determination of total solids(15) (TS)
The total are defined as the solids remaining after removal of water and other non-aqueous volatile matter by drying at 105+2ºC
Procedure : An overnight drying for estimation of TS was followed. 10ml of the spent liquor was weighed in previously weighed china dish and was placed in the oven for overnight drying. After 12 hours the dish was placed in a desicator ,cooled and weighed. The total solids were calculated as follows:
Total solids % (W/W) = Wt. of dry solids X 100/Wt. of spent liquor

Determination of residual active alkali (16)(RAA)
In soda spent liquor, RAA is the measure of sodium hydroxide content and in sulphate spent liquor it includes both sodium hydroxide and sodium sulfide. 20 ml of the spent pulping liquor was pipette into a 500 ml volumetric flask containing 25 ml of 20% W/W $BaCl_2$ solution.
$BaCl_2$ precipitates lignin salts and Na_2CO_3, leaving a clear supernatant containing NaOH. 100 ml the supernatant was pipette into a 250ml beaker and titrated against 0.1 N HCl using combined glass-calomel electrode till pH 7.00 was attained. The RAA was calculated using the following equation:
RAA, g/l as NaOH =ml of HCl consumed x normality of acid x 40/ml of spent liquor taken

Determination of Total alkali (20)
Total alkali is the measure of NaOH, Na_2CO_3,, organically bound sodium in soda spent liquor was taken in a 250 ml beaker and 90 ml of distilled water was added to it. 0.1 N HCl was added through a micro burette in increments of 0.5 to 1.0 ml with uniform stirring employing slow speed magnetic stirrer. Addition of acid was continued till pH 4.0 was achieved. Total alkali was calculated using the following equation:
Total alkali/l as Na_2O=ml of acid used up x normality of x 31/ ml of spent liquor taken

Determination of sulphated ash (20)
Sulphated ash represents the the total inorganics present in spent liquor.5ml of spent liquor was taken in previously weighed platinum crucible and kept in muffle furnance at 600-650 degree C, so as to form the ash. The crucible was then placed in furnance at 850 ºC. After 5-10 minutes the crucible was taken out ,kept in desiccators, cooled and weighed. The sulphated ash was calculated as follows:
Inorganic % as NaOH = A x 0.563x 100/ Total solids in 5 ml spent liquor
Where,
A is the weight of ash

Estimation of organically bound sodium (20)
It is generally associated as sodium salts of organic acids. In soda spent liquors the results are obtained by subtracting Na_2CO_3 and NaOH from the total alkali as follows:
Organically bound Sodium (g/l) = T.A. - (R.A.A + Na_2CO_3)as NaOH

ELEMENTAL ANALYSIS

Carbon, Hydrogen and Nitrogen (C,H,N) Determination
For C,H,N analysis the spent liquor samples were dried at 40-50 degree C in vacuum oven and converted into fine powder. Carbon, Hydrogen, Nitrogen were determined using Heraeus rapid C,H,N analyser. The CHN analysis was carried in Heaeus rapid CHN analyser. The rapid quantitative combustion of the substance takes place in pure oxygen and in presence of helium at a furnance temperature upto 1050 degree C. In the reduction tube at nearly 600 degree C, the nitrogen oxides arising from the combustion are reduced to elemental nitrogen on copper. The mixture of carrier gas helium, carbon dioxide, water vapour and nitrogen on leaving the furnance is led to the separation and measuring chamber. Quantitative separation of the individual gas component takes place by temperature-controlled absorption and description processes in water and carbon dioxide trapping column, so that water and the carbon dioxide can be separated quantitatively, while the nitrogen as first component, is led unaffected to the thermal conductivity detector and measured.

Procedure
100 mg. of sample was weighed to analyse carbon, hydrogen and nitrogen in a disposable tin boat and was put in the sample magazine. The sample was

thoroughly flushed with helium of 99.9 % purity and dropped in the combustion tube. The gases were quantitatively separated and detected. The results were expressed on moisture free sample percentage basis.

Sodium , Calcium, Potassium

Na, Ca, K were determined by flame photometry using Mediflame-127 flame photometer. Spent liquors were diluted in such a way so as to get readings within the range of scale reading of flame photometer. Flame photometer is based on the principle that for an atom to emit light, it has to be excited above its ground state by supplying enough energy to move one electron to higher energy level orbit. The wavelength for sodium, potassium and calcium are 589nm, 767nm and 622nm respectively and filters corresponding to these wavelengths were employed for determination of individual elements. Standards of Na, Ca, K in the range varying from 1 -10 ppm were employed for calibration.

Determination of Silica (20)

20 ml of spent liquor was wet oxidsied using 15 ml of concentrated nitric acid and 5ml of perchloric acid in a Kjeldahl flask and contents were evaporated to expel perchloric acid fumes. This was followed by addition of water and 5ml of conc. HCl Contents were boiled and filtered using Whatman No.1 filter paper. The residue was washed with 1:9 HCl followed by hot water washing. The filtered was freed of chlorides. The filter paper was dried and ignited at 600 degree C in a pre-weighed platinum crucible. The ash was weighed, moistened with a drop of distilled water and 2 drops of sulphuric acid to convert any left sodium to stable sodium sulphate (Na_2SO_4). After fuming off the H_2SO_4 acid, 2-3 ml of Hydrofluoric acid (HF) was added to evaporate silica as silicic acid. The crucible was kept in furnance at 800 ºC +_ 25 ºC for 1 hour. After 1 hour crucible was taken out, cooled in desiccators and weighed. The difference in weight was noted as silica content, which was calculated as follows:

SiO_2 in spent liquor % (W/W) = (A – B) x 100/ C

Where,

C is the wt. of total solids in 20ml spent liquor

A is the wt. of crucible + SiO_2 residue

B is the wt. of the crucible after HF treatment

Determination of chlorides

25 ml of the spent liquor was treated with 4N sulphuric acid to precipitated lignin. The precipitate was washed well and the pH of the supernatant was maintained at 8.2 using 1N sodium carbonate. 1 ml of the potassium chromate(5 g of K_2CrO_4 in 80ml of water was saturated with silver nitrate. The solution was filtered to remove red precipitate of silver chloride and made up to 100ml) was added and titrated against standard 0.05N silver nitrate solution. The end point was the appearance of first permanent red colour due to precipitation of silver chromate. A blank was titrated consisting of the same volume of chloride free water.

Calculations

Chloride % (W/W) = (A – B) x 17.75 x 100/ wt. of solids in 25 ml spent liquor

Where,

A is ml of $AgNO_3$ for spent liquor

B is ml of $AgNO_3$ for blank

Proximate Chemical Analysis

Proximate chemical analysis of raw material gives a lead in accessing its suitability in pulp and paper making. Dust for chemical analysis of bagasse was prepared using Wiley mill, after passing through 40 mesh. The results of proximate chemical analysis of all the sample of bagasse i.e. whole bagasse, fresh bagasse and whole bagasse as employed in the present study are shown in table 2.

Table 2 Comparison of proximate chemical Analysis of Various Bagasse Sample

S.N	Parameters	Fresh Bagasse		Stored Bagasse	
		Whole bagasse	Depited bagasse	Whole bagasse	Depited bagasse
01.	Ash content	3.86	2.20	3.92	2.35
02.	Cold water solubilty	4.57	2.59	6.63	6.06
03.	Hot water solubilty	8.02	5.25	9.76	7.32
04.	1/10 N NaOH solubilty	30.31	28.28	32.20	29.84
05.	Pentosan	28.03	26.92	29.63	27.72
06.	Holocellulose	72.80	78.86	69.92	72.92
07.	Alpha Cellulose	37.92	42.13	35.86	39.29
08.	Acid insoluble lignin	22.08	17.98	26.52	24.02

The higher solubility of stored bagasse in hot water and 1/10th normal NaOH indicates that normal atmospheric storage of bagasse leads to considerable deterioration of the raw material.

A characteristics feature of hot water and alkali solubility in all these cases, the whole bagasse has solubility due to pith which indicates that pith has a negative effect on the quality of pulp. Fresh dipithed bagasse indicates thates the sorage of bagasse leads to appreciable degradation of holocellulose.

RESULT AND DISCUSSIONS

The results of pulp properties, spent liquor properties and elemental composition at different alkali concentration i.e 15,16 and 17% alkali as NaOH on raw material are depicted in Tables 3, 4 and 5.

Table 3 Pulp Properties and chemical composition of spent liquors obtained after 15% soda pulping

Properties	Fresh Bagasse		Storage Bagasse	
	Whole	Depithed	Whole	Depithed
Pulp Properties				
Pulp Yield	52.87	53.66	50.53	51.69
Kappa Number	25.09	22.47	31.87	30.06
Spent liquor properties				
pH at 30 degree C	12.71	11.87	12.10	11.30
Total Solids%(w/w)	9.2	8.5	8.1	7.74
Residual Active Alkali g/l as NaOH	1.04	1.24	0.82	0.94
Total Alkali (g/l as NaOH)	16.01	16.96	12.44	16.26
Organically bound Na (g/l as NaOH)	3.03	3.56	3.41	2.87
Inorganics % (w/w)as NaOH(expressed as sulphated ash)	26.95	24.55	22.60	26.52
Organics% (w/w) by difference	73.05	75.45	77.40	73.48
Silica%(w/w) as SiO2	0.98	0.71	1.9	1.03
Elemental Analysis				
Carbon % (w/W)	33.89	34.36	34.00	33.01
Hydrogen% (w/W)	4.97	3.97	4.00	4.00
Nitrogen % (w/W)	0.83	0.92	0.90	0.97
Sodium % (w/W)	9.20	9.80	7.20	9.30
Calcium % (w/W)	0.16	0.14	0.17	0.13
Potassium % (w/W)	0.29	0.33	0.30	0.42
Chlorides % (w/W)	0.74	0.86	0.92	0.92

Table 4 Pulp Properties and chemical composition of spent liquors obtained after 16 % soda pulping

Properties	Fresh Bagasse		Storage Bagasse	
	Whole	Depithed	Whole	Depithed
Pulp Properties				
Pulp Yield	50.81	51.56	48.83	49.57
Kappa Number	23.47	18.2	27.63	25.94
Spent liquor properties				
pH at 30 degree C	12.34	11.78	11.86	11.45
Total Solids%(w/w)	10.71	9.82	11.60	11.20
Residual Active Alkali g/l as NaOH	4.31	5.23	3.84	4.40
Total Alkali (g/l as NaOH)	30.01	26.58	28.82	27.23
Organically bound Na (g/l as NaOH)	9.38	8.74	11.60	10.60
Inorganics % (w/w)as NaOH(expressed as sulphated ash)	28.95	28.46	31.20	30.71
Organics% (w/w) by difference	71.05	71.54	68.80	69.29
Silica%(w/w) as SiO2	1.34	1.52	1.31	1.49

Elemental Analysis				
Carbon % (w/W)	34.62	34.02	35.62	34.97
Hydrogen% (w/W)	4.32	4.56	3.97	4.06
Nitrogen % (w/W)	0.84	0.83	0.64	0.72
Sodium % (w/W)	17.25	15.21	16.56	15.41
Calcium % (w/W)	0.34	0.67	0.58	0.49
Potassium % (w/W)	0.34	0.29	0.56	0.39
Chlorides % (w/W)	0.75	0.77	0.90	0.85

Table 5 Pulp Properties and chemical composition of spent liquors obtained after 17 % soda pulping

Properties	Fresh Bagasse		Storage Bagasse	
	Whole	Depithed	Whole	Depithed
Pulp Properties				
Pulp Yield	49.03	49.98	47.65	48.93
Kappa Number	21.84	17.23	25.07	22.34
Spent liquor properties				
pH at 30 degree C	11.87	11.03	12.38	12.01
Total Solids%(w/w)	11.03	10.86	11.90	10.97
Residual Active Alkali g/l as NaOH	4.80	5.50	4.83	5.92
Total Alkali (g/l as NaOH)	26.58	30.32	38.48	38.78
Organically bound Na (g/l as NaOH)	8.76	9.39	14.08	14.16
Inorganics % (w/w)as NaOH(expressed as sulphated ash)	30.72	29.88	31.49	29.76
Organics% (w/w) by difference	69.28	70.12	68.51	70.24
Silica%(w/w) as SiO2	1.63	1.52	1.85	1.66
Elemental Analysis				
Carbon % (w/W)	36.02	35.93	34.87	35.94
Hydrogen% (w/W)	4.32	5.06	4.96	3.02
Nitrogen % (w/W)	0.88	0.79	0.94	0.83
Sodium % (w/W)	15.42	17.34	21.85	21.92
Calcium % (w/W)	0.32	0.39	0.33	0.46
Potassium % (w/W)	0.43	0.55	0.62	0.57
Chlorides % (w/W)	0.66	0.71	0.63	0.72

As is evident from the Tables (3to 5) the pulp yield in case of fresh bagasse is higher than stored bagasse. The depithed bagasse shows higher yield than whole bagasse. The Kappa number which is a measure of residual lignin content in the pulp, is on the higher side in stored depithed and whole bagasse as compared to the fresh whole and depithed bagasse. The whole bagasse contains pith which is a parenchymatous tissue and consume high cooking chemicals . The residual sugar contents in the presence of moisture play a dominant role in determining the quality of bagasse upon longer storage. Residual sugar undergoes fermentation due to the action of enzymes and Bacteria. As a result of fermentation, the temperature of bagasse increases leading to partial deterioration and darkening. Acid formed during the fermentation lower the pH of the bagasse. A combination of high temperature and acidity results in hydrolysis of cellulose, ultimately resulting in low pulp yields.

From the tables (3 to 5) it can be observed that total solids concentration of spent liquor increase in alkali concentration. The whole bagasse spent liquors have high total solids concentration than depithed bagasse due to the solublization of pith fraction. The total solid concentration in weak spent liquor is an important factor from energy conservation point of view. In case of agricultural residues, spent liquors have low total solid concentrations than wood dye to low chemical charge, higher material to liquor ratio and higher dilution factor maintained during washings.

Residual active alkali is indicative of free alkali and increases with increase of alkali charge. The depithed bagasse spent liquor as higher residual active alkali contents as compared to the whole bagasse spent liquor. This is due to higher amount of organic acids in whole bagasse which depletes RAA. Thus, it is always important to maintain certain minimum level of RAA in spent liquor to keep the organic residue in colloidally stable state.

The organically bound sodium in case of stored bagasse is high which is related to pulp yield and storage time. Organic acids that are produced during storage by the degradation reaction get neutralized by the free alkali associated with sodium (Na) in the form of organically bound sodium (Na).Gupta, 1993 (22) has reported that out of 16% alkali charge, 12% of alkali is consumed by hemicelluloses and celluloses, while only 4% alkali is consumed by lignin and more than 65% of total chemical charge is consumed before 110 ^{o}C. The distribution of alkali or sodium in the spent liquor is in the form of NaOH, Na_2CO_3 and organically bound sodium.

Silica which is undesirable component poses many problems in recovery operation. Bagasse spent liquor contain high amount of silica. In presence of calcium it forms hard making conventional recovery system unsuitable and hence silica removal is desirable.

CONCLUSION

The proximate chemical analysis clearly indicates that storage of bagasse lead to degradation of carbohydrates and hence there is a need for improved storage practice, which can prevent microbial attack on carbohydrate fraction. The study shows if we remove the hemicelluloses attached to lignin, there was remarkable improvement in the quality of the spent liquor which is better to processes in the chemical recovery system.

The pulp yield in case of fresh bagasse is higher than that of whole bagasse. The Kappa number which is a measure of the residual lignin content in the pulp is on higher side in stored depithed and whole bagasse as compared to the fresh whole and depithed bagasse. Total solid concentration of spent liquor increase with increase in alkali concentration, The black liquor generated from whole bagasse have higher total solid concentration than depithed bagasse due to solubilization of pith fraction. Residual active alkali is an indication of free alkali which increases with increase of alkali charge. The depithed bagasse has higher residual active alkali content than the whole bagasse. Higher values of organically bounded sodium in stored bagasse black liquor is an indication of the presence of higher amount of degenerated organic molecules. Higher amount of organic acids in the stored bagasse depletes the residual active alkali (RAA). Therefore, it is always important to maintain certain minimum level of RAA to keep the organic residue in a comparatively stable form.

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