

LIGNIN RECOVERY FROM ALKALINE PULPING OF BAGASSE

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ABSTRACT

Bagasse was delignified with aqueous alkali liquors by boiling at ambient pressure. The spent liquors were treated with hydrochloric, sulphuric, acetic acid and sulphur-dioxide. The precipitate so obtained was analysed for its lignin content and mineral matter. The lignin was also analysed for its purity by elemental analysis, Methoxyl and fuel value. The method suggests removal of lignin from alkaline spent liquors using simple equipment and common chemicals. This is expected to reduce considerably the organic matter going into the effluent liquor.

A simple process of pulping of bagasse and straws involving treatment with aqueous alkali at boil and ambient pressure has been found to give a wide variety of pulps, depending on cooking conditions, earlier in this laboratory (1-4). The process does not require high pressure equipment and pulps obtained are easily bleached. However, a large fraction of the organic solids, mainly lignin is brought into the alkaline spent liquor and there is no satisfactory and economical method available to treat this and similar liquors, for chemical recovery (5-7). Treatment of kraft and soda liquors for chemical and lignin recovery has been a subject of numerous investigations and the early literature on it is well documented (5-14). Most of the work pertains to either recovery of chemicals from large scale plants or the raw material involved is mostly wood or bamboo. For spent liquors from agri-residues, a treatment involving removal of suspended solids in lagoons and neutralisation before discharge has been suggested(7).

In view of the simplicity of the suggested pulping process of alkali boil of bagasse, it was thought appropriate to study the

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possibility of recovery and use of lignin from the alkaline spent liquors. This paper reports the results obtained on precipitation of lignins from such liquors by acidification with common chemicals such as sulphur dioxide sulphuric, acetic and hydrochloric acid. The lignin residues so obtained have been analysed for their true lignin content.

RESULTS AND DISCUSSION

The bagasse after pre-soaking and alkali boil gives a pulp which contains 7 % of lignin out of 18.6 % present in the original untreated bagasse. The balance 11.6 % must have gone into alkaline solutions as such or after degradation, together with 8.3 % hemicelluloses estimated as pentosans. The alkali boil does not result in a delignification more than 62.4 % and it suggests that 37.6 % of total lignin is present in bagasse in a different form and remains associated with the pulp (See Table 1).

It is quite possible that these mild conditions of digestion have left certain portions of the cellulosic material unaccessible to the alkali and a slight shear of material during treatment might have solubilised some more lignin.

A comparison of various acids (See Table 2) as lignin precipitants for the alkaline liquor has brought out the following facts.

Acetic acid and sulphur dioxide have given the same amount of precipitates (8.8 % of bagasse) at pH 4.7 and 2.5 respectively. However, some more precipitation is observed when more sulphur dioxide is passed to bring down the pH to 2.5. These residues are having an ash content of 2.6 to 3.8 % and show a lignin content of about 66 %, the balance being probably the carbohydrates.

On the other hand if sulphuric acid is used for acidification to pH 1.5, a large amount of precipitate (15.2 %) is obtained. This

precipitate is lower in lignin content (62.3 %) and richer in ash (4.5 %) as compared to other residues. Some portion of lignin might have remained soluble in acid under these conditions.

The hydrochloric acid appears to be a satisfactory precipitating agent for isolating lignins from alkaline liquor. It gives a residue which is low in ash (1.6 %) and rich in lignin (77.5 %). The filtrates from these treatments showed some turbidity on standing. A systematic investigation was therefore done to get additional precipitation from these liquors by prolonging the time upto 30 days, at pH - 1.5 (See Table 3).

The total precipitate obtained by this method was 14 parts from 100 parts of bagasse, about 85 % of which was obtained after the first filtration.

The additional precipitation is either due to aggregation, agglomeration of colloiddally disperse' lignin or due to slow hydrolysis of lignin - carbohydrate complexes. The rate of precipitation of lignin was found unaffected by addition of aluminium chloride in small quantities, indicating that colloidal peptization of dispersed particles is unaffected. The slow hydrolysis of lignin-carbohydrate complexes, leading to additional precipitation is confirmed by the fact that on boiling the solution, the precipitation is faster.

The soluble portion of the lignin was recovered by neutralisation and evaporation of the acidic filtrate (See Table 4). The residue on analysing shoed 3.1 % lignin, 4.8 % pentosans and a large quantity of ash (73.5 %). The organic matter present in this residue showed a high solubility on extraction with ethyl alcohol(27.2 %).

The lignin precipitated by hydrochloric acid was found comparable to pure lignin samples in its elemental analysis and had 15.8 % methoxyl content. Its fuel value was found to be 24.8 MJ/kg which is better than wood and similar fuels.

The work has indicated that a large amount of lignin, otherwise going with the effluents, can be recovered by a simple acidification step with the hydrochloric acid. A method is being devised in which the acid for neutralisation may be made available, in a preceding step of acid treatment of bagasse to reduce its pentosans content. Work is also in progress to study the utilisation of the lignin residue.

CONCLUSIONS

1. Acidification of alkaline extracts of bagasse give lignin rich precipitates, by using mineral acids, and are easily filtrable. Sulphur dioxide and acetic acid are not suitable precipitants.
2. Hydrochloric acid gives lignin residue lower in ash than sulphuric acid.
3. Lignin which is not extracted by alkali and the one which is not precipitated by acid is likely to be present in the form of ligno-carbohydrate complexes.
4. Lignins obtained can be used at least for their fuel value.

EXPERIMENTAL

Materials and Methods

Bagasse was obtained from a sugar mill in Maharashtra. The crushed bagasse was pounded and portion passing through 20 mesh and retained over 60 mesh was used after conditioning it over saturated sodium chloride solution. All chemicals used were chemically pure grade. Analysis of pulp and bagasse was done by TAPPI standard methods. Moisture was estimated by oven-drying at 105°C. Results have been reported based on oven dry samples and residues.

Lignin in precipitates was estimated gravimetrically as insolubles in 42 % HCl.

Methoxyl groups in lignin were estimated by the hydroiodic method.(15) Fuel values were determined using the oxygen bomb calorimeter.

Pulping

About 100 g of bagasse exactly weighed was presoaked in water overnight with a solid to water ratio of 1:10. Sodium hydroxide (20 per cent on bagasse) and water were added to get a 0.5 % alkali solution. The contents were boiled in a mild steel kettle with provision for stirring for one hour. The pulp was filtered and the filtrate was kept aside for further experiments. The pulping was also performed on 1 and 2 Kg batches of bagasse.

Precipitation of lignin from alkaline liquor

The filtrates of successive runs were combined and made up to an exact volume. Samples of 1 L were used for all the experiments. Acidification was carried out by slow addition of different acids with stirring at ambient temperature to the desired pH value. Precipitates were allowed to settle overnight before filtration. These were washed with water till free of chloride ions in case of HCl and corresponding acids in case of other precipitants. The residues so obtained were dried at 60°C for 24 hours, weighed and stored over anhydrous calcium chloride. In one set the filtrates from HCl acidification were again adjusted to pH 1.5 and were kept for a prolonged period upto 30 days. The additional precipitate formed was filtered, dried and weighed.

Liquors were also acidified with sulphur dioxide gas obtained from a cylinder.

Strengths of acids used for acidification were 1N acetic acid, 1N hydrochloric and 2.5N sulphuric acid. Filtrate from HCl acidification was neutralised and slowly evaporated to dryness first in a rotating flask with low heat and later in an oven at 60°C, followed by drying over calcium chloride. The analysis is given in Table 4.

Average results of triplicate observations for all the experiments have been reported in the tables.

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TABLE 1

ANALYSIS OF BAGASSE AND PULP
(% on o.d. bagasse)

		Bagasse	Pulp
1	Yield	100	62.0
2	Alcohol benzene extractives	2.2	0.15
3	Lignin	18.6	7.00
4	Pentosans	22.0	13.70
5	Ash	2.9	1.60
6	Alpha cellulose	41.0	40.10

TABLE - 2

PRECIPITATION OF LIGNIN FROM ALKALINE LIQUOR WITH
VARIOUS ACIDS

S.No.		HCl	H ₂ SO ₄	SO ₂	SO ₂	Acetic Acid
1.	Bagasse, g	100	100	100	100	100
2.	Alkaline liquor, L	4.2	5.2	4.2	4.2	4.2
	Final pH after acidification	1.5	1.5	2.5	4.0	4.7
3.	Acid used, g	15.0	23.4	-	-	33.6
4.	Precipitated residue O.d.wt. g	12.0	15.2	8.8	9.2	8.8
5.	% ash in residue	1.6	4.5	2.6	3.3	3.8
6.	% Ash free lignin in residue	77.5	62.3	66.1	63.6	66.5

TABLE - 3

PRECIPITATION OF LIGNIN WITH HYDROCHLORIC ACID

S.No.		
1	Bagasse, g	100
2	Alkaline liquor, L	4.2
3	pH of precipitation	1.5
4	Precipitate after first filtration, g	12.0
5	Additional precipitation, g after (a) 8 days	1.2
	(b) 30 days	1.1
6	Total residue g	14.3
7	% ash in residue	1.64
8	% Ash free lignin in residue	77.0
9	% of total residue in 1st filtration	84.00

TABLE - 4

ANALYSIS OF ACID SOLUBLE PORTION OF ALKALINE LIQUOR
(based on o.d. residue)

Ash	73.5 %
Lignin	3.1 %
Pentosans	4.8 %
Alcohol extraction	27.2 %

TABLE 5

ANALYSIS OF LIGNIN FROM HYDROCHLORIC ACID PRECIPITATION

Carbon, %	61.2
Hydrogen, %	6.4
Oxygen, %	33.4
Methoxyl, %	15.8
Fuel value, Mj/Kg	24.8