

Studies on changes in chemical components during chemical pulping of bagasse

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ABSTRACT

Bagasse is going to be one of the major fibrous raw material for paper industry in India in coming years. Although the pulping technology for production of chemical grade pulp from bagasse is well established, still there is a scope to conserve basic inputs like chemicals, energy etc. An increased understanding of the changes taking place in various chemical components during pulping stage is essential to choose optimum pulping conditions. In the present studies an effort is made to understand the rate of chemical consumption and extent of delignification at different pulping temperatures from 110° — 165°C. The effect of prehydrolysis on extraction of undesirable carbohydrate fractions on subsequent pulping stage was also studied. The studies clearly indicate that more than 65% of chemical charge was consumed before 110°C and degree of delignification was more than 40% at temperatures below 120°C. Alkaline prehydrolysis was helpful in saving significant amount of cooking chemicals during pulping.

INTRODUCTION :

Although India has achieved self-reliance in the production of writing and printing papers, the future demand and subsequent capacity expansion will have to largely depend upon the agricultural fibres. The additional capacity of about 2.0 million tonnes would have to rely on agricultural residues. India, being a leading sugar cane growing country can provide a base for pulp and paper mills employing bagasse. It is estimated that about 40 million metric tonnes of wet bagasse is produced every year (1, 2). Even if 10% of this bagasse is made available to paper industry it would be possible to have additional paper production as much as 0.7 million tonnes. Thus bagasse is going to be main fibre resource for paper industry. Manufacture of pulp and paper from bagasse has been practiced since decades in many countries. Utilization of bagasse in India is increasing both in small pulp mills as well as integrated paper mills. Although the technology for chemical pulping and bleaching of pulps is well established but the quality of pulps is far from satisfactory and there is a wider scope to improve upon the pulp quality and at the same time reduction of basic inputs

like chemical & energy. Bagasse with its open structure and relatively lower lignin content still require as much as 16-18% chemicals and higher cooking temperatures. There is a need to understand the basic chemistry involved in pulping of bagasse. Not much of information has been published on delignification of bagasse and changes in chemical components. Some efforts have been made to understand the role of lignin-carbohydrate complexes (LCC) & these components appear to have some role on rate of delignification and chemical consumption (3).

EXPERIMENTAL :

Laboratory Pulping & Delignification :

In order to see the rate of chemical consumption & extent of delignification, the bagasse pulping was carried out from 110°C to 165°C 16% w/w cooking chemical was charged and bath ratio of 1 : 5 was maintained. After terminating the cooking at different temperatures, the pulp and spent liquors were analysed.

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Prehydrolysis :

Prehydrolysis was carried out prior to pulping employing alkaline medium and acidic medium at 120°C for half an hour. The prehydrolysed bagasse was subjected to pulping under optimum conditions.

Analysis of Prehydrolysates & Spent Liquors :

Prehydrolysates were subjected to analysis of important components like total solids, pH, lignin, Pentosans according to standard procedures. Spent pulping liquors were analysed according to standard procedures described in CPPRI manual and TAPPI standards described in T-625.

Gel Chromatography :

Gel filtration experiments were carried out using LKB pharmacia gel chromatography unit provided with automatic UV-detector, the chart recorder & the fraction collector. Samples free from suspended matter and equivalent to 35 mgs of total solids were charged to 1.6 cm × 60 cm column of sephadex G-100. This charge was eluted through column by bicarbonate-hydroxide buffer at a flow rate maintained at 29 ml/hr using peristaltic pump.

Determination of Free Phenolic Hydroxyl Contents :

The free phenolic hydroxyl in spent liquor samples were determined by recording the spectra of a pH 12 solution VS pH 6 solution samples on a Perkin. Elmer. UV visible spectrophotometer Model 412, in the region 190-390 nm.

RESULTS & DISCUSSIONS :

Bagasse & Chemical composition :

Bagasse has two major fraction—One the fibre portion and another the pith portion. Although the depithing is part of pulping process, nevertheless some portion of the pith always enter the pulping stream. This pith is characterized by high proportions of hemicelluloses (4). Besides bagasse also contains significant amounts of free sugars. Thus bagasse carries considerable amounts carbohydrate residues in pulping.

Kinetics of delignification :

Kinetics studies are useful in obtaining information on rate of delignification and extent of chemical consumption. The alkaline pulping is a complex process

and involves number of chemical reactions taking place simultaneously and these are influenced by both physical and chemical factors. It has been well established that major portion of alkali is consumed in the initial phase of pulping. This might be attributable to both lignin dissolution and carbohydrate degradation. The kinetic studies would help in analysing the reason for chemical consumption in the initial stages. Degradation reaction starts at around 100°C and are completed at the temperature where the delignification becomes the main reaction. The results of the kinetics of delignification during soda bagasse pulping is shown in Table-1. From the results, it is evidenced that more than 65% of the alkali is consumed at temperature around 110°C which presumably is attributed to dissolution of the carbohydrates and in neutralization of various organic acids both present in the raw material and those formed in the degradation of hemicelluloses. Result shows that in the overall delignification of bagasse, most of the lignin is removed rapidly in the initial stages. From the results of Klason lignin values in the pulp, it is noticed that more than 50% got dissolved before the temperature of 125°C. The subsequent delignification is rather slower and it is primarily due to low concentration of alkali available. The Kappa number of resultant pulp show slow decrease in the later stage of pulping and acceptable kappa number is obtained only when the cooking time was maintained for one hour at 165°C. This slow decrease might be due to slow auto condensation reaction taking place in low alkali concentrations.

Lignin Carbohydrate Complexes :

If we look into the lignin values determined by UV in spent liquor collected at various temperature from 110, there was a wide difference in lignin determined at 280 nm and at 205 nm upto temperatures of 165°C. After giving sufficient time of 60 minute at 165°C lignin values are almost same i.e. 41.0 & 37.0% w/w respectively. This might be due to the interference of hemicelluloses linked with OH groups of lignin molecules in the form of lignin-hemicellulose complexes reflecting at 280 nm, thereby giving higher values. These linkages got broken at higher temperatures i.e. 165°C by giving sufficient time of one hour. Gelchromatography (Fig-1) shows the same. The absorbance at 205 nm is primarily due to aromaticity while the absorbance at 280 nm is both due to aromaticity and

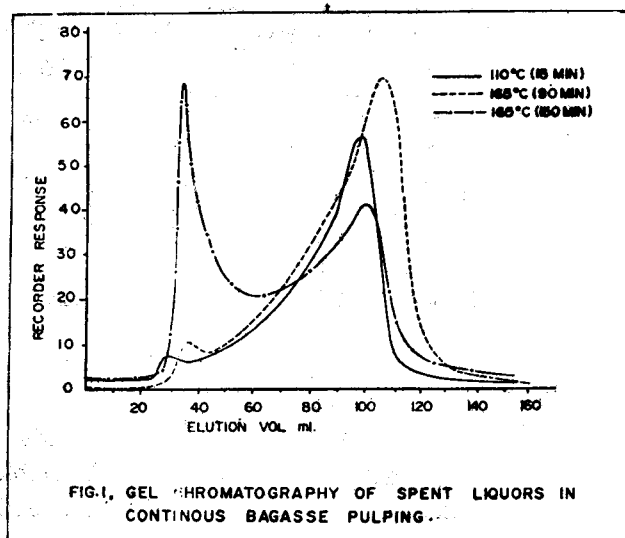
TABLE-1
ANALYSIS OF PULP & BLACK LIQUOR DURING DELIGNIFICATION OF SODA
PULPING OF BAGASSE AT VARIOUS TEMPERATURES.

Parameters	Temp. Time, min.	110°C 15	125°C 38	140°C 60	150°C 75	165°C 90	165°C 150
Pulp yield, % w/w		73.5	67.1	65.3	60.3	56.5	52.4
Kappa no of pulp		82	59	51	39	29	22
Klason Lignin in pulp, %		14.4	13.0	11	9.5	5.5	3.5
Lignin dissolved, %**		40%	45.8	—	60.4	77.0	85.4
BLACK LIQUOR ANALYSIS							
pH		12.21	12.14	12.11	11.96	11.86	11.35
Total Solids, % w/w		8.15	8.92	9.37	8.52*	9.18	8.14*
RAA as NaOH, % w/w***		13.0	10.4	9.56	9.38	6.80	2.0
Alkali consumed, % w/w		66.87	71.00	72.00	75.00	80.50	94.90
Organics, % w/w		64.8	68.0	69.6	69.7	69.0	70.1
Silica as SiO		1.89	2.27	2.28	2.58	1.94	1.73
Lignin in Black Liquor							
at 205 nm, % w/w		32.9	35.3	36.9	36.4	37.1	37.5
at 280 nm, % w/w		59.70	63.2	66.2	64.8	69.1	41.0
Phenolic-Hydroxyl, % w/w (on Lignin basis)		Nil	Nil	Nil	Nil	Nil	0.3246

* Including minimum wash water.

** Expressed on lignin present in original raw material.

*** (Initial 32 g/l)



phenolics. Determination of phenolic hydroxyls by scanning of UV spectra shows the presence of free phenolic in final spent liquor collected at 165°C kept for one hour where as there is no free phenolic hydroxyl group in any of the spent liquor collected from 110°C to 165°C. This supports the condensation of the low molecular weight lignin liberated in the initial stage of pulping.

Prehydrolysis :

Prehydrolysis is a step usually employed for removal of undesirable hemicelluloses, before pulping. Alkaline hydrolysis results in formation of acids, water hydrolysis leads to dissolution of low molecular weight carbohydrates and acid hydrolysis usually results in formation of alcohols. In the present studies the step of prehydrolysis was employed to see the influence of removal of part of carbohydrate fraction before pulping on chemical consumption, pulp yield and spent liquor properties. The results of analysis of prehydrolysates,

prehydrolysed bagasse and pulping of prehydrolysed bagasse are given in Tables 2-4. The results in Table-2 show that in acid hydrolysis the pentosan extraction was maximum compared to steam hydrolysis which was less effective. Maximum extraction of organics was observed in case of alkaline hydrolysis when the extracts were tested for UV—absorbance at 280 and 205 nm it was observed that the absorbance at 280 nm was much higher as compared to 205 nm. The higher lignin absorbance at 280 nm is presumably due to strong absorbance of dissolved higher carbohydrate complexes (LCC).

In order to avoid neutralizations in second stage of pulping the acid hydrolysis was not employed. The results in Table—3 show the analysis of alkali prehydrolysed bagasse sample. The alkaline prehydrolysis did help in dissolving about 3% of the total lignin and at the same time the pentosan contents was also reduced substantially.

The results in Table—4 show the pulping of prehydrolysed bagasse samples. In alkaline pulping it was possible to attain much lower kappa number with 12% NaOH as compared to 16% in original sample. The acid hydrolysed sample showed unusually very high kappa number. This might be attributed to formation of condensation products during acid hydrolysis and the condensed products are difficult to dissolve as compared to low molecular weight lignin. One possible reason

TABLE—2
ANALYSIS OF PREHYDROLYSATES

Parameters	Steam Hydrolysis	Alkaline Hydrolysis (2% NaOH)	Acid Hydrolysis (2% H ₂ SO ₄)
pH	6.4	7.6	1.9
Total Solids % W/W	0.89	1.97	1.48
Inorganics % W/W (Sulfated ash)	18.0	32.0	ND
Organics, % W/W	82.0	68.0	ND
Pentosans, % W/W	6.5	5.0	25.0
Lignin, % W/W (UV Method)			
at 280 nm	27.3	29.0	8.9
at 205 nm	16.6	15.2	—

TABLE—3
ANALYSIS OF PREHYDROLYSED BAGASSE

Parameters	Original Bagasse	Alkaline Hydrolysis
Yield loss, % W/W	Nil	8.0
Holocelluloses, % W/W	73.0	75.0
Klason lignin, % W/W	24.0	21.3
Pentosans, % W/W	16.0	13.0
Ash, % W/W	2.53	3.5

TABLE—4
PULPING OF PREHYDROLYSED BAGASSE & ANALYSIS OF BLACK LIQUORS

Chemical Dose% as NaOH	Original Bagasse		Alkaline Hydrolysed		Acidhydrolysed 16%
	14%	16%	12%	14%	
Pulp yield %	60	54	56	54	52
Kappa no.	35	25	22	18	50
pH	10.9	11.3	11.5	12.0	10.9
Total Solids, % w/w	9.67	10.27	9.33	9.85	9.70
RAA % w/w	0.6	0.9	1.2	1.9	0.5
Inorganics, % w/w (By sulfated ash)	25.1	28.9	25.4	26.6	29.6
Organics, % w/w	74.9	71.1	74.6	74.4	70.4
Lignin at 280nm % w/w	29.2	29.7	34.8	34.8	
Silica, % w/w	1.83			1.48	1.48
Precipitation point, solids % w/w	Colloidally stable		Colloidally stable		Unstable above 29
Viscosity, m. Pa. Sec. at 82°C at Solids 49% w/w	130	12			

might be the condensation of furfural liberated during acid hydrolysis with lignin. Thus acid hydrolysed bagasse was not effective in producing acceptable quality of pulps. From the results it is evident that by employing alkaline hydrolysis prior to pulping it would be possible to save more than 15% of the total chemical demand and at the same time it was possible to improve spent liquor properties. The viscosity of spent liquor was drastically reduced after prehydrolysis. The reduction in viscosity is primarily attributed to inhibition of increased condensation of lignin molecules and possible interference of lignin-carbohydrate complexes during delignification.

CONCLUSIONS :

- The preliminary studies on rate of delignification at different temperature clearly indicate that, the delignification commences at much lower temperature—110°C.
- More than 65% of chemical is consumed before 110°C, and major portion of which appear to have been utilized by lignin-carbohydrate complexes.

- Alkaline prehydrolysis prior to pulping show distinctive advantage of reduction of chemical consumption.
- In-depth studies would be required to understand the precise nature of chemical reaction taking place during pulping.

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