

Pulping of Sugar Cane Bagasse with Acetic Acid under Atmospheric Pressure

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ABSTRACT

Pulping of bagasse with acetic acid under atmospheric pressure was studied and the effect of some parameters on pulp properties was investigated. The best delignification was achieved by using 0.1% HCl or 0.2% HBr with acetic acid for 4 hours. However, there was a better selectivity for delignification with HCl than with HBr. With HCl, the increase of acetic acid concentration from 80-92.5% improved the delignification process, whereas with HBr not less than 90% acetic acid had to be used. Impregnating bagasse in acetic acid before pulping led to deterioration of pulp properties. An alkaline extraction step "E" with NaOH before bleaching with H₂O₂ reduced hydrolysis of the carbohydrates, consumption of H₂O₂ during bleaching and increased the brightness of the pulps. The effectiveness of this step was more pronounced when in pulping the concentration of acetic acid decreased and HBr was the catalyst. However, the impregnation step had negative effects on the action of NaOH in the E step. Unbleached and bleached pulps had 3.2 km and 3.8 km breaking length, 13.4 and 16.7 burst factor, 22.5 and 31.5 tear factor respectively.

INTRODUCTION

World wide R&D of organosolv pulping process based on acetic acid, substantially increased during the last two decades (1). The acetosolv pulping process (2) in 1984 is based on the treatment of wood chips with 93-95% aqueous acetic acid containing 0.05-0.5% hydrogen chloride at 110°C and atmospheric pressure for 3-6 hours. The kappa number of the acetosolv pulp was lower than that of kraft and pulp tensile strengths were comparable to kraft but tear strengths were lower. The idea behind acetosolv procedure is that lignin dissolves in acetic acid much more better than in water, while acetic acid is a poor solvent for the polysaccharides. Due to its very complicated structure native lignin has first to be degraded by acidolysis to become soluble in acetic acid. Therefore, a catalytic quality of hydrogen chloride is needed. The cooking temperature is lower than with other pulping procedure. Therefore, refluxing at atmospheric pressure is used. The advantages of this process are : Ease of recovery of the chemicals by evaporation, and ease of separating lignin from hemicelluloses in the spent liquor by dilution with water. It is reported (3) about many useful products

that can be derived from these components. The same authors further developed the acetosolv process by conducting hydrogen peroxide in the late stages of the cook to reduce the kappa number, followed by bleaching with peracetic acid and ozone. Other reseacher (4) also added chloroethanol to acetic acid, but this process was not so attractive as the acetosolv process itself. Other studies to optimize the pulping conditions, such as acetic acid concentration, catalyst concentration, temperature and cooking time, were carried out on different woods and straws (5, 6).

Others (7, 8) studied the behaviour of HCl during delignification by the acetosolv process. Too little HCl led to incomplete rupture of the covalent bonds in the lignin, while too much HCl led to increased recombination of the lignin fragments. The effects of temperature, catalyst concentration and reaction time, have been studied (9) on the acetosolv delignification of eucalyptus from Spain. They optimized the process by employing an incomplete 3x3x3 factorial design and measuring the influence of these factors on pulp yield, lignin and glucose contents. The effects of reactions time (0-180 min) and catalyst concentration (0.15-0.45%) by acetosolv pulping of pine wood on pulp yield, residual lignin, polysaccharide degradation

and hemicellulosic sugar generation have also been studied (10).

A pretreatment step before acetosolv pulping of sugar cane bagasse was conducted where 20-60% acetic acid at 80°C for 30-180 min for the pretreatment step was used. This step was followed by defiberation. Bagasse was then cooked in polyethylene bags in a water bath at 90°C, liquor ratio 3.5:1, acid concentration 20-60% with 0.05% HCl. Chemimechanical pulp was produced. The generation of furfural during the acetosolv pulping of eucalyptus has also been studied (12). Studies are going on atmospheric acetic acid pulping of rice and wheat straws. Their study is the characterization and utilization of acetic acid lignins as well as on pulping conditions and properties of pulp (13-17).

Pulping with acetic acid under atmospheric pressure can be performed with other catalysts such as HBr or KI. Eucalyptus was cooked (18) with 93% acetic acid containing HCl or HBr. They studied the following parameters: liquor ratio, cooking time, chip size and nature and amount of catalyst. The pulps were also characterized by X-ray diffraction and FTIR spectroscopy. Also the delignification of pine wood by acetic acid with HCl or KI has also been studied (19). In his paper results are given on the atmospheric acetic acid pulping of bagasse by using HCl or HBr as catalyst. The effect of some pulping conditions on some pulp properties are studied.

EXPERIMENTAL

Sugar cane bagasse, obtained from Edfu pulp mill, Egypt, had 19.61% Klason lignin, 23.04% pentosan, 1.24% ash and 78.73% holocellulose with 46.72% alpha cellulose.

Pretreatment of the raw material

Bagasse was impregnated in acetic acid at 110°C under atmospheric pressure. The acetic acid used in this step had the same concentration intended to pulp with.

Pulping experiments

Pulping was achieved by refluxing bagasse in a round-bottom flask placed in an oil bath at 110°C with aqueous acetic acid at liquor ratio 10:1 containing a catalytic amount of HCl or HBr. After that the pulp was washed with hot 85% acetic acid under suction, then with hot water. The pulp was then stirred and screened. Pulp yield and rejects were determined gravimetrically.

Alkaline extraction

The pulp was treated with NaOH at 4% consistency in reagent flasks placed in a water bath at 100°C. At the end of the reaction time, the flask was cooled, the content was filtered, washed with water and dried.

Saponifiable fraction

The saponifiable fraction is proportional to the content of acetyl groups in pulp (24). 0.1 g pulp was weighed in a conical flask, then 25 ml 0.1 M NaOH were added. After heating at 100°C for 30 min the solution was cooled and titrated with 0.1 M HCl. The saponifiable fraction was calculated from NaOH which had been consumed by saponification reactions.

Bleaching

Bleaching was performed at 10% consistency, 80°C for 2 hours. The pulp was placed in a plastic bag and the chemicals were added as follows: 2.5% MgSO₄, 0.1% DTPMPA, 2.5% NaOH then 4% H₂O₂. The pulp was hand kneaded, the bag was sealed and immersed in water bath. At the end of the bleaching, the plastic bag was cooled and the liquid was squeezed from the pulp to measure the residual peroxide, iodometrically, according to Vogel (25). The bleached pulp was washed thoroughly with distilled water.

Pulp analyses

Kappa number Tappi Standard T236 -cm 85. Limiting viscosity number modified method based on Zellcheming Merkblatt IV/36/61 and Scan. CM 15:88 Brightness : ISO%, measured in a reflectometer of the type "Carl Zeiss Elrepho Tester". Breaking length: Tappi Standard T 494. Bursting strength: Tappi Standard T 403. Tear resistance: Tappi Standard T414.

RESULTS AND DISCUSSION

The effects of Type and concentration of the catalyst, cooking time, acetic acid concentration and an impregnation step in acetic before pulping, on the pulp properties were studied and discussed.

Effect of type and concentration of the catalyst on pulp properties

Different concentrations of HCl or HBr were used with acetic acid to pulp bagasse, as illustrated in Table 1. In the case of HCl the best results were obtained by using 0.1%. At higher catalyst concentration the kappa number increased while both pulp yield and viscosity decreased. This can be explained (20, 19) as follows: Halogenous acids

Table 1. Effect of catalyst concentration on pulp properties

Catalyst	Catalyst concentration, wt%	Kappa number	Total yield, %	Screened yield, %	[η], ml/g
HCl	0.05	40	55.8	32.6	780
	0.10	20.6	48.3	48.2	850
	0.15	33.8	46.2	46.2	806
	0.20	41.1	45.7	45.7	778
HBr	0.05	Very	Bad	Delignification	
	0.10	33.0	53.3	49.5	944
	0.15	26.8	49.1	48.8	844
	0.20	21.8	46.2	46.2	799
HCl	0.10	20.6	48.3	48.2	850
HCl	0.10	21.0	50.3	50.3	863
HBr	0.20	21.8	46.2	46.2	799
HBr	0.20	25.2	51.3	51.2	793

Pulping time = 4 hours, acetic acid concentration = 90% (*) or 92.5% (**)

promote hydrolysis of both lignin and carbohydrates. The increase of the catalyst concentration increases the rate of delignification at the expense of pulp yield. The combination of the high temperature and long pulping time at high HCl concentration promotes condensation and precipitation of the lignin until this is the dominant process. Accordingly, high HCl concentrations may be favoured at lower pulping temperature and shorter pulping time.

On the other hand, increasing the concentration of HBr in acetic acid from 0.1 to 0.2% improved the delignification but at the expense of pulp yield and viscosity. Based on the fact that the carbohydrates become less accessible for hydrolysis and dissolution when the concentration of acetic acid increases (21),

92.5% acetic acid was used to delignify bagasse with 0.1% HCl and 0.2% HBr. In both cases an increase in pulp yield was achieved, however, the increase in the kappa number in the case of HBr must be responsible for the increase in pulp yield. In general there is a better selectivity for delignification with acetic acid and HCl (lower kappa number at high pulp yield and viscosity) than with acetic acid and HBr.

Effect of pulping time on pulp properties

Based on the results in Table 2, increasing the pulping time from 2-4 hours in either catalyst improved the delignification and the improvement was more pronounced with HBr. As the time was prolonged to

Table 2. Effect of time on pulp properties

Pulping time (h)	Catalyst	Kappa number	Total yield, %	Screened yield, %	[η], ml/g
2	0.10% HCl	32.0	52.3	51.3	886
3	0.10% HCl	29.0	50.1	49.9	865
4	0.10% HCl	20.6	48.3	48.2	850
6	0.10% HCl	25.7	50.2	50.2	785
2	0.20% HBr	35.4	52.8	50.3	846
3	0.20% HBr	28.0	52.2	52.1	825
4	0.20% HBr	21.8	46.2	46.2	799
6	0.20% HBr	21.9	47.2	47.1	800

Acetic acid concentration = 90%

Table 3. Effect of acetic acid concentration on pulp properties

Catalyst	Acetic acid concentration, wt%	Kappa number	Total yield, %	Rejects, %	Screened yield, %	[η], ml/g
0.10% HCl	80	33.0	49.5	1.0	48.5	896
	82.5	31.6	51.4	0.7	50.7	880
	85	25.5	50.1	-	50.1	863
	87.5	23.	48.3	-	48.3	851
	90	20.6	48.3	-	48.3	851
	92.5	21.0	50.3	-	50.3	863
	95	26.6	48.6	-	48.6	872
0.10% HBr	80-87.5	Very	Bad	Results		
	90	33.0	53.3	3.8	49.5	944
	92.5	33.5	55.0	1.2	53.8	808
	95	36.0	50.9	5.5	45.4	816
	97.5	37.0	52.2	2.1	50.1	863

Pulping time = 4h

be 6 hours the kappa number increased with HCl and was unchanged with HBr, i.e., HCl promotes lignin condensation reactions at earlier time. Accordingly, pulping for 4 hours can be considered optimum pulping time.

Effect of acetic acid concentration on pulp properties

Table 3 shows that 80% acetic acid solution containing 0.1% HCl could achieve lignin hydrolysis and solvation. The improvement of the delignification obtained by increasing acetic acid concentration from 80 -92.5% can be attributed to the increase in the amount of hydronium ions, which caused the acceleration of the acid hydrolysis of lignin (21). However, by using 95% acetic acid solution the kappa number increased which indicates that lignin itself was less accessible than it was in the solutions with lower concentrations. The acetic acid concentration also affects pulp yield and viscosity. The best selectivity for delignification was achieved by 92.5% acetic acid. Moreover, the increase in viscosity by increasing the acid concentration from 87.5-95% indicates enhanced carbohydrate protection.

In the case of HBr, only when acetic acid concentration reached 90% it was possible to obtain pulp with comparable properties with that obtained by 80% acetic acid with HCl. The high percentage of rejects indicates inadequate defiberation. Moreover, high acetic acid concentration caused decrease of the swelling and accessibility of lignin.

Effect of an impregnation step in acetic acid prior to pulping

As shown in Fig. 1, the delignification was deteriorated when bagasse was treated with acetic acid for different time intervals before pulping.

By fixing the impregnation time at 3 hours and

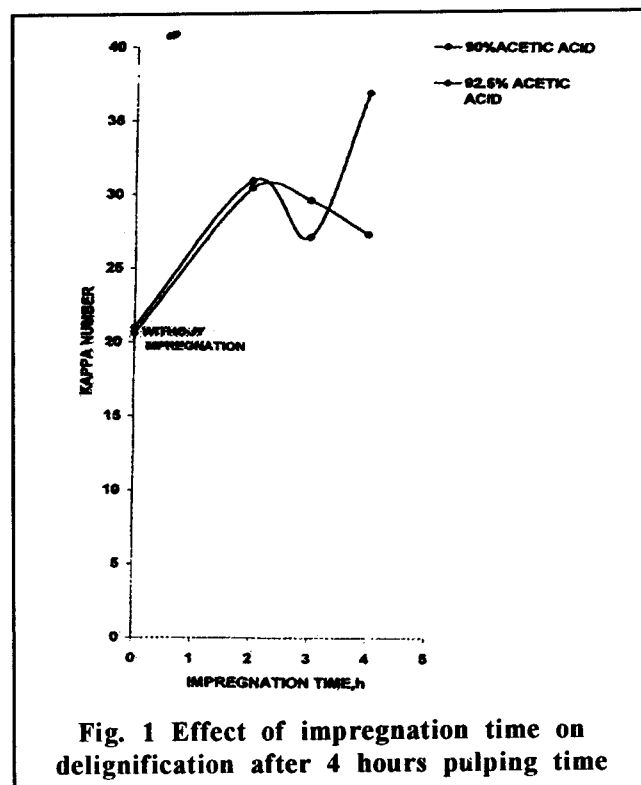


Fig. 1 Effect of impregnation time on delignification after 4 hours pulping time

Table 4. Pulp properties at different cooking time.

Impregnation time, h	Pulping time, h	Acetic acid Concentration, wt%	Kappa number	Total yield, %	Screened yield, %	[η], ml/g
-	2	90	32.0	52.3	51.3	886
3	2	90	30.8	50.6	49.9	852
-	3	90	29.0	50.1	49.9	865
3	3	90	31.0	45.6	45.6	824
-	4	90	20.6	48.3	48.3	851
3	4	90	29.7	46.0	45.6	827
-	4	92.5	21.0	50.3	50.3	863
3	4	92.5	37.0	46.3	45.8	744

Pulping time = 4h, catalyst 0.10% HCl

Table 5. Effect of increasing the time of E and NaOH concentration in E step on the saponifiable fraction and properties of bleached pulp.

NaOH, %	E Time, (min)	Saponifiable fraction	Properties of the bleached pulp		
			Kappa number	Brightness, ISO%	[η], ml/g
1.5	75	4.7	12.7	43.3	763
1.5	90	4.6	14.5	34.8	774
2.0	75	4.0	16.9	29.8	761

varying the pulping time, it was found, as shown in Table 4, that the impregnation step caused not only deterioration of the delignification but also excessive degradation of the carbohydrates. Lower pulp yield and viscosity values were obtained, even when the acetic acid concentration was raised to 92.5%.

Alkaline extraction "E" step of acetic acid pulps

An alkaline extraction step was applied on an acetic acid pulp before bleaching with hydrogen peroxide "P step". As NaOH applied in the E step causes the swelling of the fibres and higher cell wall permeability, facilitating thereby the extraction and removal of lignin in the subsequent steps (22) Table 5 shows that 1.5% NaOH and 75 min reaction time represent optimum condition for the E step (23). Prolongation of the reaction time did not change the saponifiable fraction but decreased the delignifying action and enhanced the darkening reactions of the peroxide during the P step (the pulp had higher kappa number and lower brightness). However, a slight increase in pulp viscosity was observed. It was also found that raising NaOH concentration to 2% led to deterioration of the delignifying and brightening actions of the

peroxide in the P step although the saponifiable fraction decreased.

Effect of pulping conditions on the effectiveness of the E step

By comparing the P experiments with the corresponding EP experiments given in Table 6 it can be concluded that the use of HBr with acetic acid in pulping enhanced the delignifying action and bleaching potential of the peroxide after the E step more than HCl did. Pulps with lower kappa number and higher brightness gain were obtained in the former case. Also the properties of the bleached pulps are affected by the concentration of acetic acid used in pulping. The positive effect of the E step are more pronounced at lower acetic acid concentration. On the other hand an impregnation step prior to pulping reduced the effectiveness of the E step (cf. the EP experiments with the corresponding IEP experiments).

It was also found that the degradation reactions of the carbohydrates occurring during bleaching with hydrogen peroxide are reduced when the E step was applied before bleaching. It was also possible to reduce the consumption of the peroxide by using the

Table 6. Effect of pulping conditions on the effectiveness of the E step.

Pulp characteristics	Pulping condition	Kappa number	Brightness, ISO%	Brightness gain, ISO %	[η], ml/g	Part of H ₂ O ₂ consumed/ unit gain in brightness
P	90% acetic	20.7	17.8		747	10.9
EP	acid+0.2%	12.7	43.3	25.5	763	1.9
IEP	HBr	14.6	22.2	4.4	680	7.3
P	92.5% acetic	19.0	20		697	29.5
EP	acid+0.2%	15.7	28.3	8.3	722	7.1
IEP	HBr	19.9	27.8	7.8	757	7.5
P	90% acetic	15.8	34.8		803	5.4
EP	acid+0.1%	15.4	37.5	2.7	810	4.6
IEP	HCl	13.0	29.2	-	751	8.8
P	92.5% acetic	15.3	25.2		668	6.4
EP	acid+0.1%	15.6	28.5	3.3	663	5.4
IEP	HCl	21	26.8	1.6	689	6.9

E step before P.

Papermaking properties

Optimization for pulp strength was not the main goal of this study. However, acetic acid pulps possessed moderate strength properties like other acidic pulps. Unbleached acetic acid pulps had 3.2 km breaking length, 13.4 burst factor and 22.5 tear factor, whereas after bleaching those values were 3.8 km, 16.7 and 31.5, respectively.

CONCLUSION

This work aims at presenting an environmental friendly pulping method that can participate in satisfying the increase in paper consumption. The initial goal of this study was to determine the effect of some applied conditions on the pulp properties. Pulping bagasse with acetic acid at atmospheric pressure was successful by using 0.1% HCl or 0.2% HBr as catalyst. However, HCl is more advantageous with respect to kappa number, pulp yield and viscosity. Also HCl permits the use of lower concentrations of acetic acid in pulping. However, impregnating bagasse in acetic acid before pulping led to deterioration of the pulp properties. An alkaline extraction step "E" of acetic acid pulps facilitated the removal of lignin in the subsequent bleaching step with hydrogen peroxide "P". The E step reduced hydrolysis of the

carbohydrates during bleaching and contributed to lower consumption of the peroxide at higher pulp brightness. The effectiveness of the E step was influenced by the pulping conditions. The positive effects of this step were more pronounced when HBr was used as catalyst or when lower concentration of acetic acid was used. On the other hand, impregnating bagasse in acetic acid before pulping had negative effects on the action of NaOH in the E step. It was also found that unbleached and bleached acetic acid pulps had moderate papermaking properties like other acidic pulps.

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