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Extraction of cellulose by catalytic reduction of lignin from bagasse with aliphatic acids

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Abstract: Bagasse is an important biomass and source of cellulose synthesis after delignification. Many methods are available for the delignification of bagasse for the synthesis of cellulose for bioethanol production. In this study bagasse is delignified using 93% Vv^{-1} acetic acid and 80% formic acid with HCl as a catalyst. Pulp obtained under these conditions is pulsated pulp having maximum yield, Kappa No. and Klason lignin in the ranges of 52–57%, 27–30% and 7–10% respectively. The presence of water in the experiments with the more diluted formic acid (80%) and 0.2% of HCl as a catalyst and S/L ratio for both acids is 1:12.5, while no delignification was obtained when proponic acid was used.

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INTRODUCTION

Organic solvent or organosolv pulping processes are alternative to soda or kraft pulping to delignified lignocellulosic material for the production of paper and pulp. The several environmental impacts of conventional pulp processes and the increasing demands for pulp and paper increase the search for alternative pulping processes. Many organic solvents have been reported for using organosolv pulping[1].

The main advantage of the organosolv processes over the conventional kraft processes are low environmental impact, highest pulp yields, ease of bleaching and easy solvent recovery. The most technology developed organosolv processes employed alcohol-water mixture[2,3]. Pauly (1917, 1934) was the first to use formic and acetic acid need for delignification of wood and bagasse. The present work deals with the delignification of bagasse, the main wastage product of sugar industries for pulp and paper for future world.

In this study, the acetic acid and formic acid were used for the pulping of bagasse is further explored. A preliminary study of the effect of reaction time and catalyst concentration on the acetic and formic acid pulping of bagasse has been previously reported[4]. Formic acid is a typical organosolv system, has been presently examined under the atmospheric pressure to pulp bagasse fibers.

MATERIALS AND METHODS

Bagasse were dried at 105°C, chipped and disintegrated to particle size not more than 1.0mm. These particles were homogenized and stirred in a desiccator and then extracted. Three sets of experiments were performed for each of the three acids (acetic acid, formic acid and propionic acid) for optimum condition for delignification. The concentration of acid are 93%, 80% and 75% while catalyst concentration were 0.3% and 0.2% respectively and s/l ratio are 1:12.5 for acids.

Alcohol/Extractive

Take a empty thimble and weighted and puts some moisture free sample of bagasse with some extractive pulp in the thimble and weigh again and then placed in soxhlet apparatus in which 33.0ml of alcohol and benzene are present and reflex for 5.0 hours in water bath[5].

Determination of viscosity of pulp from bagasse

Viscosity of the pulp was determined by standard method (ASTM 2007 and 1992). 2.0gm of dry pulp of bagasse was treated with 10.0ml of 72% H_2SO_4 with stirring at 45°C for 7.0 minutes. The reaction was interrupted by adding 25.0 ml of distilled water, the mixture was transferred to the 250.0ml Erlenmeyer flask and made up the volume upto 140.0ml, the flask was autoclave for 30 minutes at 1.05 bars for the complete hydrolysis.

Determination of lignin

Extracted free wood (1.0gm) was mixed with 15.0 ml cold 72% H_2SO_4 (12-15°C) slowly with constant stirring and allow to stand for 02 hours at 18-20°C, wash the material with 360.0 ml distilled water in a 1.0 litre RB flask. Now reflux for 04 hours with boiling and washing with 500.0 ml of hot distilled water (at neutral pH) and placed in an oven for 3-4 hours at 105°C for drying until the weight became constant.

Determination of hollow cellulose content

Sample size are -40+60 and weight 0.5gm of extractive free bagasse in 100ml conical flask at 10ml of NaOH-CH_3COOH solution at pH 3.2 add 1ml of

20% hot aq. $NaClO_2$ at 1 hour interval with frequent stirring (repeat 6 such cycles) at the end of 06 cycles transfer the flask in an ice cold bath for a few minutes and filter with sintered crucible and acid free with distilled water and wash with hot water 1% CH_3COOH at 75°C until free from alkali, it may be 3 or 4 times washing and drying residue in an oven at a constant weight and this hollow cellulose required to calculate alpha cellulose.

Determination of alpha cellulose

Samples of 1gm of hollow cellulose (with known humidity) were transferred to 110ml beaker and put in a water bath at 20°C then add 11.8 ml of 17.5% NaOH solution with gentle stirring 5 ml NaOH after 1 minutes, 3.4ml after 2.5 minutes 3.4ml after 5 minutes, 3.4ml after 7.5 minutes. The sample were covered and left for 30 minutes at 20°C. The sample was filtered in crucible of porosity No. 2 wash with 8 ml of 8.3% NaOH and wash with 400ml of water. The samples were filtered to remove the CH_3COOH wash with 03 litres of distilled water at room temperature and dry overnight.

RESULTS AND DISCUSSION

The proximate chemical analysis of Bagasse has been presented in table 1. Experiments were performed in order to determine the minimum reaction time for the removal of the maximum amount of lignin and minimum loss of α–cellulose. Lignin extraction during pulping was accompanied by an external hemicellular loss during the reaction as shown in table 1[6].

Table 1: Proximate chemical analysis of bagasse.

α–cellulose	60.0 %
Klason Lignin	29.8 %
Alcohol – Benzene	4.05 %
Ash	4.30 %

This above study shows that removal of cellulose increased and the reaction time increases from 45 min to 120 minutes. the pulps obtained under the different reaction time were cellulose enriched and showed similar Kappa No, cellulose, lignin and hemicellulose content[4].

Effect of concentration of acetic and formic acid

Experiments were carried out under four experiments of acetic acid are 95%, 93%, 90%, 85% and for formic acid are 85, 80, 75, 65% and catalyst concentration are 0.3–0.20 and formic acid are 0.25–0.10. Table 2 shows the establishment of condition of % acetic acid, formic acid and propionic acid are is 93%, 0.3, 1:12.5, 240 minutes, 80%, 0.2%, 1:12.5, 120 minutes and 75%,0.2%, 1:12.5 and 120 minutes respectively.

As you see the table 3 of acetic acid and table 7 for formic acid shows the time 240 min. for acetic acid and 120 min for formic acid would gave klason lignin and Kappa No. Vaz Q 4 and 2 1992 are under the limit to manufacture pulp for making paper. 80% formic acid with different of catalysts at this 30°C which is resulted to removed the rejected and wastage material like PRL (Percent Residual Lignin). The best pulp yield is around 49-58%, a Kappa No. is (23-29%) and Klason Lignin are (5-10%). These results suggest that water may play a significant role in cellulose protection and or in lignin. A possible role of water is may be associated with the decrease in the partial formylation of the primary secondary and phenolic hydroxyl groups of lignin.

It was observed that out of three operational variables studies renewable of formic acid concentration was the most effective as regards the delignified product yield. The concentration of 80% formic acid was selected in further experiments. The Kappa no. of the product was 28.19 which according to certain standard is bleachable of bagasse in Table 2 observed that optimum delignification of Bagasse with formic acid as a medium was achieved by catalyst concentration and S/L ratio of 0.2% and 1:12.5.

It may be observed in Table -3 with formic acid that increase of time had a mark effect on the yield of delignified product and eventually on their Klason and Kappa No. Figure 1 shows that % PRL in fractions of Bagasse samples gradually decrease with the increase of time of delignification. However optimum delignification of Bagasse was achieved in 120 minutes. The behavior of Klason Lignin and Kappa No shows the values in decreasing order in figure 2, increasing kappa no. in the decreasing of klason lignin shows better pulp yield.

The other aliphatic acid is propionic acid would not gave better results of pulping of baggase at ideal condition. The establishment of condition of acid, catalyst % and S/L ratio are for propionic 75% 0.2 and 12.5 ratio. The kappa no. and klason lignin are in the range of better pulping with formic acid. If you look at the kinetic study of acid in 13 shows the gradually decreasing yield and klason lignin with the passing out of time.

At maximum time 120 minutes formic acid gave better condition for pulping but the yield is too low for further processing of raw material not process. In case of propionic acid at maximum time is 120 minutes would not show the kappa No.

Table 2: Establishing of conditions for pulping of bagasse with aliphatic acid.

Establishment of Conditions (%)	Acid (%)	HCl (%)	Time (min)	S/L Ratio	Yield (%)	Kappa No	Klason Lignin (%)
Acetic Acid	95	0.30	240	1:12.5	46.19	31.16	11.61
	90				59.19	29.14	7.16
	93				56.17	23.89	8.76
	85				67.16	30.69	10.91
Catalyst (HCl)	93	0.30	240	1:12.5	56.17	23.89	7.76
		0.20			57.69	30.16	9.86
		0.15			60.69	29.19	8.56
		0.10			64.16	30.98	9.98
Solid-Liquor Ratio	93	0.3	240	1:12.5	56.17	23.89	8.76
				1:15	59.06	31.11	10.11
				1:10	63.16	31.91	11.12
				1:05	70.19	41.26	13.19
Formic Acid	95	0.2	120	1:12.5	57.17	N.R*	8.19
	90				55.12	29.19	8.31
	85				54.91	30.18	7.61
	80				52.12	24.15	8.98
Catalyst (HCl)	80	0.25	120	1:12.5	40.17	N.R*	N.R*
		0.20			52.12	24.15	8.98
		0.15			48.61	29.00	8.01
		0.10			50.61	28.10	8.98
Solid-Liquor Ratio	80	0.2	120	1:12.5	52.12	24.15	8.98
				1:15	55.98	32.15	8.09
				1:10	57.89	N.R*	7.98
				1:05	51.01	N.R*	7.36
Propionic Acid	85	0.2	120	1:12.5	43.19	N.R*	8.65
	80				51.21	41.21	9.31
	75				56.65	30.15	9.36
	70				59.01	31.61	8.59
Catalyst (HCl)	75	0.30	120	1:12.5	47.65	N.R*	9.15
		0.25			50.99	N.R*	9.26
		0.20			56.65	30.15	9.36
		0.15			67.19	31.67	12.65
Solid-Liquid Ratio	75	0.20	120	1:12.5	56.65	30.15	9.36
				1:15	52.96	N.R*	9.99
				1:10	57.96	N.R*	9.98
				1:05	59.98	30.01	8.86

Table 3: Kinetics studies of selected conditions for pulping of bagasse with aliphatic acid.

Kinetic Studies of Established Operational Conditions	Acid (%)	HCl (%)	Time (min)	S/L Ratio	Yield (%)	Kappa No	Klason Lignin (%)	Residual Lignin (%)
Acetic Acid	93	0.3	15	1:12.5	85.84	44.19	16.75	48.24
			30		81.32	40.16	15.25	41.61
			45		78.58	35.14	14.75	38.80
			60		73.69	28.13	13.08	32.34
			90		69.71	26.12	13.00	30.40
			120		64.81	25.90	12.90	28.05
			150		61.91	24.19	12.70	26.38
			180		58.91	22.99	11.90	30.49
			210		57.65	23.11	10.90	27.19
			240		56.17	19.26	8.76	16.50
			270		47.91	19.31	8.71	14.29
Formic Acid	80	0.20	15	1:12.5	73.95	37.61	15.67	38.88
			30		70.61	33.61	14.12	33.45
			45		69.19	31.21	12.31	28.58
			60		65.31	29.31	10.76	23.58
			90		54.12	28.15	8.18	14.85
			120		52.12	24.15	8.98	15.71
			150		52.13	24.86	9.01	15.76
Propionic Acid	75	0.20	15	1:12.5	79.19	37.36	19.01	50.51
			30		69.19	34.36	16.65	38.65
			45		67.19	33.96	14.37	32.40
			60		59.19	32.19	13.69	27.19
			90		58.19	31.99	12.73	24.85
			120		56.65	30.15	9.36	20.83
			150		50.39	N.R*	9.98	16.87

Effect of catalyst concentration

In table 2, the minimum HCl concentration for the most efficient delignification process was experimentally determined for the pulping of Bagasse with acetic acid and formic acid are 93% to 80% and catalyst concentration is 0.3 and 0.2%. as previously reported[4], chip imperfection at room temp with pulping liquor diminish the PRL of acetic and formic acid pulping. Consequently the treatments with 93% and 80% of acetic and formic acid were performed after socking the chips in liquor for 3 hours at room temperature in order to obtained the lowest PRL in both acids. Nevertheless reaction with 93% and 80% acetic and formic acid pulping catalyst, HCl concentration are 0.3 and 0.2% resulted in a PRL still greater than 30%. Regardless of the formic acid concentration, the best delignification for Bagasse was achieved with 0.3 addition of HCl more than this concentration did not promote any delignification improvement compared with the 0.3% of HCl for 93% acetic acid. 80% of formic would give the lower concentration of Klason lignin in bagasse. We completed studies about delignification of kenaf, sunflower, kallar grass, partal, siris, pakar ,poplar wood, Keekar and bagasse. The higher cooking time of raw material is bagasse is 4.0 hours [7, 8].

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