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Delignification of Pakar Wood (*Ficus lacon* Buch) by Organosolv Pulping with Aliphatic Organic Acids

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Abstract. Pakar wood (*Ficus lacon* Buch) of particle size 0.315-1.00 mm was subjected to organosolv delignification with acetic, formic and propionic acids. Optimum delignification was achieved with 95, 80 and 70% of these acids, respectively, with optimum catalyst (HCl) concentration of 0.25, 0.20 and 0.15%, the time being180, 120 and 120 min, respectively.

Keywords: organosolv pulping, pakar wood, delignification, aliphatic acids

Introduction

Lignocellulosic materials (LCM) are renewable resources having great potential for use as alternative raw material in the chemical industry. Efficient fractionation of LCM may allow the separation of their polymeric components (cellulose, hemicellulose and lignin) which could be separately processed to useful and economically competitive end product (Zargarian *et al.,* 1988; Rijkens, 1984; Kouklos and Valkanas, 1982). Pakar wood (*Ficus lacon* Buch), due to its high content of α-cellulose, good pulp yield and fast growth is an important raw material for the pulp industries in the world (Siddiqui *et al.,* 1986). The sulphate process is employed for pulping, but it is inconvenient due to environmental hazard and production of lignin (not recoverable for chemical uses) (Johansson *et al.,* 1987).

Among the alternate processes, pulping with organic acids seems to offer the greatest versatility and potential. Organosolv pulping is an energy-efficient approach to the production of pulp with a wide spectrum of usees. However, no extremely satisfactory organic system has yet been found to delignify all the wood species to produce commercial pulp with low residual lignin content, without seriously degrading the cellulose (Lange, 1981).

Organic acids have advantage over mineral acids in facilitating pulping of softwoods as well. However, none of the tested catalysts had been able to produce pulp of high strength and viscosity at low residual Kappa no. In addition, the pH of the spent liquor remains low and some lignin condensation, cellulose degradation and hemicellulose hydrolysis also occurs (Siddiqui *et al.,* 1986). In the present study, performance of acetic acid, formic acid and propionic acid was evaluated for delignification of Pakar wood, using HCl as catalyst.

Materials and Methods

Pakar wood was dried in oven at 105°C, chipped and disintegrated to a particle size of 0.315-1.00 mm, homogenized and stored in desiccator. It was then extracted with alcohol-benzene mixture (ASTM, 1983). The extracted sample was subjected to analysis of its α-cellulose (Doree, 1950), Klason lignin (ASTM, 1997) and hemicellulose content (Erickson, 1962). All the parameters were determined on the basis of initial dry weight of the raw material utilized in that particular set of experiments.

Delignification of 10 g sample was carried out in 250 ml round bottom flask under reflux conditions, at 101, 118 and 141°C with acetic, formic and propionic acids, (as delignifying media), respectively, and water and HCl (as catalyst) in different proportions (Sarkanen, 1990).

For each acid, 4 sets of experiments were performed for determination of operational conditions relating to percentage of delignifying media (acids), percentage of catalyst (HCl), S/L ratio and time. Percentage of acids varied from 60% through 65, 70, 75, 80, 85 to 95%; percentage of HCl used was 0.15, 0.20 and 0.25 whereas S/L ratio used was 1:10, 1:12.5 and 1:15. The fourth set of experiments was conducted using the established best three parameters for determining the optimum time giving the best result relating to α-cellulose, Klason lignin content and Kappa number (Ericson, 1962).

Detailed kinetic study of the pulping conditions of Pakar wood, was carried out at 15 min. intervals, from 15 to 120 min. The fractionated products obtained from each set of experiment were then evaluated for their yield, α-cellulose,

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Klason lignin content and Kappa no. (Erickson, 1962). The experiments with different delignified products of Pakar wood were repeated twice including three replicates of each treatment. Determination of fibre dimensions viz. length and diameter of unbleached pulp of Pakar wood was carried out using macroscopic methods (Casey, 1981). Adequate data was collected for statistical analysis of frequency of different sizes of fibres.

Results and Discussion

The proximate chemical analysis of Pakar wood (Table 1) revealed that the percentage of α-cellulose and lignin are high and that of ash is low, which indicates that the wood is hard (Grant, 1959).

Results of the experiments conducted for acetic acid, formic acid and propionic acid are given in Tables 2-5, 6-9 and 10-13, respectively.

The pulping conditions correspond to the concentration of acid (Vazqeze *et al.,* 1992). In the first set of experiments with acetic acid, Kappa no. 22.8 was achieved with 95 % acid and 0.2% of catalyst, whereas the lignin content was reduced to 9.95%, (Table 2). Therefore, acid concentration of 95% was used in the next experiments for the selection of catalyst and S/L ratio.

It was observed that lignin content decreased with the increase of catalyst concentration (Tables 3); the Klason lignin with 0.2% catalyst was 9.95 and with 0.25% catalyst was 8.91%. The catalyst conc. of 0.25% yielded the best Kappa no. (Table 4). By selecting concentrations of acid and catalyst, pulp of S/L ratio 1:12.5, with lower Klason lignin and Kappa no. was obtained (Table 5). Lower Kappa no. yields bleachable wood pulp (Kim, *et al.,* 1991). The established conditions for the pulping of Pakar wood with acetic acid, at this stage were 95% acid, 0.25% catalyst and S/L ratio 1:12.

Details of kinetic studies are given in Table 5. Duration of 180 minutes was found to be quite sufficient for achieving optimum delignification (from 29 to 8.91%) of Pakar wood. The Klason lignin decreased with increase in Percent Residual Lignin (PRL), according to the time factor (Lora and Aziz, 1985). Further increase in time up to 210 min. did not produce any pronounced effect on the process; the ultimate yield was very low, and residual Klason lignin was negligible (lesser by 0.05%). At 180 min. the product had optimum Klason lignin and Kappa no. (Fig. 1) which afterwards gradually increased. For making pulp, Kappa no. should not be more than 27. The pulping conditions established for Pakar wood with acetic acid was 95% acid, 0.25% catalyst (HCl) and S/L ratio of 1:12.5 and duration of 180 min.

Table 1. Proximate chemical composition of Pakar wood

α-cellulose	48.74%
Klason lignin	28.52%
Alcohol/benzene	5.01%
Pentosan	15.65%
Ash	1.40%

Table 2. Establishment of acetic acid percentage for Pakar wood delignification

Acetic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
95	0.2	1:12.5	180	55.35	09.95	22.8
90	0.2	1:12.5	180	59.36	10.91	30.29
85	0.2	1:12.5	180	67.26	10.11	33.12

Table 3. Establishing HCl percentage for Pakar wood

Acetic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
95	0.25	1:12.5	180	51.35	08.91	22.12
95	0.20	1:12.5	180	55.35	9.95	22.80
95	0.15	1:12.5	180	63.66	20.24	37.15

Table 4. Establishing S/L ratio for Pakar wood delignification

Acetic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
95	0.25	1:12.5	180	51.35	8.91	22.12
95	0.25	1:15	180	67.11	10.11	30.29
95	0.25	1:10	180	65.12	13.12	38.06

The experiments with formic acid and propionic acid were conducted at low temperatures with the advantage of minimum cellulose and hemicellulose degradation and extraction of lignin in its most valuable form (Papatheofanous *et al.,* 1992). Out of the three operational variables studied, increase in formic acid percentage from 80 to 90% drastically reduced the pulp yield from 57 to 51% (Table 6). However, in the light of less Klason lignin and yield of the delignified product, 80% acid concentration was selected and applied in the next experiments which yielded best percentage of the catalyst as 0.25%, S/L ratio 1:12.5 and Kappa no. of the product, 24.11, which according to the standard is bleachable (Kim *et al.,* 1991) (Tables 7 and 8).

Table 5. Kinetic study of established operational conditions for Pakar wood delignification with acetic acid

Acetic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Acetic lignin (%)	Kappa no.
95	0.25	1: 12.5	15	73.06	24.02	62.54	37.11
95	0.25	1: 12.5	30	71.01	22.11	55.06	36.17
95	0.25	1: 12.5	45	69.01	20.91	51.42	31.21
95	0.25	1: 12.5	60	65.18	19.12	44.41	36.35
95	0.25	1: 12.5	90	66.19	18.61	43.89	33.34
95	0.25	1: 12.5	120	67.12	15.61	39.73	29.29
95	0.25	1: 12.5	150	63.12	12.91	29.04	25.16
95	0.25	1: 12.5	180	51.35	8.91	18.08	22.12
95	0.25	1: 12.5	210	36.59	8.99	19.18	No response

Table 6. Establishing the concentration of formic acid

Formic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
80	0.2	1:12.5	120	57.31	9.473	25.6
85	0.2	1:12.5	120	66.91	10.00	29.12
90	0.2	1:12.5	120	53.06	10.16	30.12

Table 7. Establishing the concentration of catalyst with formic acid

Formic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
80	0.25	1:12.5	120	51.06	6.5	24.11
80	0.20	1:12.5	120	57.31	9.47	29.10
80	0.15	1:12.5	120	59.81	8.5	29.13

Table 8. Establishing S/L ratio with formic acid and catalyst

Formic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
80	0.25	1:12.5	120	51.06	6.5	24.11
80	0.25	1:15	120	56.16	5.9	29.98
80	0.25	1:10	120	59.13	7.98	31.16

The kinetic study of delignification of Pakar wood by formic acid was carried out by a series of treatments for the duration of 15 to 150 min. These fractionated/delignified products were then evaluated for their respective yield, Klason lignin, Kappa no. (Vazequez *et al.,* 1992) and PRL remaining in different fractionated products (Parajo *et al.,* 1993). The PRL in fractionated Pakar wood samples gradually decreased with the increase in time of delignification with formic acid (Fig. 1), the best duration being 120 min. Formic acid is, therefore, suitable for pulping of Pakar wood; however at higher temperature it destroys the fibre of this wood.

As the carbon chain of acids lengthens, the conc. of the catalyst decreases. Propionic acid contains three carbon atoms and acetic acid has one carbon atom and also the established conc. of these acids was found to decrease from 95-70%; the catalyst concentration decreased on the same pattern from 0.25-0.15%, and simultaneously the Kalson lignin and Kappa no. were also found to decrease. This type of behaviour is mostly found in tropical type of hard wood, which are cheaper in cost (Usmani *et al.,* 2002).

The series of experiments conducted with propionic acid as delignifying medium established optimum operational conditions for pulping of Pakar wood which are 70% acid, 0.15% catalyst and S/L ratio of 1:12.5. (Tables 10, 11 and 12), whereas, the lignin content was reduced to 5.12. Under these conditions, yield was 49.16%, Kappa no. was 22.16. Table 13 depicts the kinetic study of pulping of Pakar wood with propionic acid which reveals that the pulping yield of 67.16% and Kappa no. of 31 is achieved in 90 min. On increasing the duration from 180 to 210 min., the Kappa no. does not respond and the yield is too low. The time factor is therefore, very important in pulp making, since at higher reaction rate, the fibre may be damaged, (Usmani *et al.,* 2001).

Fig. 1 shows that by gradually increasing the time from 15 to 210 min, the residual (acetic) lignin decreases; at 180 min. pulp with lower conc. (18.08%) of acetic acid is obtained. Both, concentration of acid and catalyst, would give better

Table 9. Kinetic study of Pakar wood delignification with formic acid

Formic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.	Formic lignin
80	0.25	1: 12..5	15	70.69	13.71	36.09	34.53
80	0.25	1: 12..5	30	63.59	12.09	33.69	27.39
80	0.25	1: 12..5	45	60.31	10.17	28.20	21.85
80	0.25	1: 12..5	60	58.51	10.67	27.34	20.18
80	0.25	1: 12..5	90	56.96	8.63	25.83	17.51
80	0.25	1: 12..5	120	51.06	6.5	24.11	11.82
80	0.25	1: 12..5	150	43.09	6.01	No response	9.22

Table 10. Establishing percentage of propionic acid for Pakar wood delignification

Propionic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
70	0.15	1:12.5	120	49.15	5.12%	22.16
65	0.15	1:12.5	120	46.83	5.39%	23.19
60	0.15	1:12.5	120	50.16	6.17%	24.61

Table 11. Establishing HCl percentage for Pakar wood delignification with propionic acid

Propionic acid (%)	Catalyst HCl	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
70	0.15	1:12.5	120	49.15	5.12	22.16
70	0.20	1:12.5	120	37.61	4.99	22.06
70	0.25	1:12.5	120	30.11	4.82	No response

Table 12. Establishing the S/L ratio of Pakar wood with propionic acid

Propionic acid (%)	Catalyst HCl	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.
70	0.15	1:12.5	120	49.15	5.12	22.16
70	0.15	1:15	120	43.20	5.91	No response
70	0.15	1:10	120	46.11	5.56	No response

reduction of lignin and Kappa no. Fig. 2 shows that with the increase in percentage of Klason lignin from 8.91 to 24.02, residual (acetic) lignin percentage increases from 18.08 to 62.54.

Conclusion

This study concludes that Pakar wood (*F. lacon*) may be delignified by fractionation with three aliphatic organic acids namely acetic, formic and propionic acids, but acetic acid is more suitable for delignification. Moreover, as compared to

Table 13. Kinetic study of Pakar wood delignification with propionic acid

Propionic acid (%)	Catalyst HCl (%)	S/L ratio	Time (min)	Yield (%)	Klason lignin (%)	Kappa no.	Propionic lignin
70	1	1: 12.5	15	76.6	21.22	34.98	57.59
70	1	1: 12.5	30	79.19	11.12	30.99	53.95
70	1	1: 12.5	45	75.17	17.17	35.12	45.99
70	1	1: 12.5	60	69.12	15.61	35.32	38.45
70	1	1: 12.5	90	67.68	13.68	31.16	32.99
70	1	1: 12.5	120	58.98	11.26	29.06	23.66
70	1	1: 12.5	150	56.15	5.16	27.16	10.32
70	1	1: 12.5	180	49.15	5.2	22.16	68.93
70	1	1: 12.5	210	37.60	5.06	No response	6.7

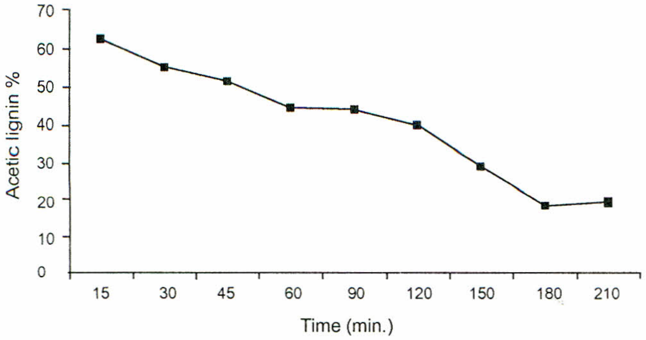

Fig. 1. Relation between acetic lignin and time.

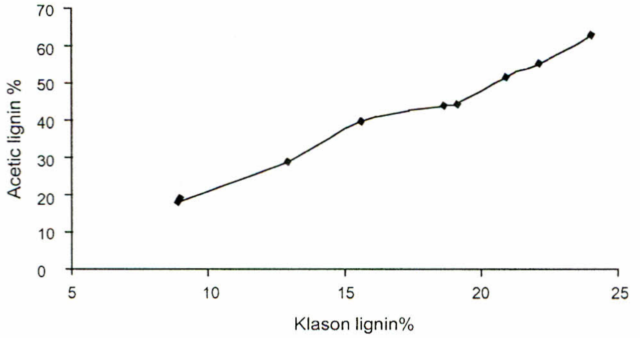

Fig. 2. Relation between acetic lignin and Klason lignin.

formic acid, acetic and propionic acids give better quality fractionated product with lower percentage of residual lignin than that of formic acid.

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