Catalyzed Organosolv Delignification of an Indigenous Wood – Partal (*Picea morinda*)

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Summary: Partal (*Picea morinda*) wood in particle size of 0.315 – 1.00 mm was subjected to acid catalyzed organosolv delignification with acetic, formic and propionic acids. The effect of different process variables like concentration of acid, concentration of catalyst and solid-liquor ratio on the yield and quality of delignified products along with the kinetic of the reactions involved was also studied. It was thereafter found that among lower aliphatic organic acids, only acetic and propionic acids could sufficiently delignify this particular species. However, propionic acid had proven to be better of the two, as it gave a good quality product in lesser time (90 minutes) and higher yield (67%). Further, formic acid was not found to be an appropriate medium for delignification of this particular raw material.

Introduction

The worldwide demand of a strong, bleachable papermaking fibre in the last few decades has generally been met by Kraft and Neutral sulfite semi chemical (NSCC) processes. In the light of growing awareness about environmental aspects of chemical effluents generated through these processes and higher capital cost, an extensive search is stimulated for alternate processes. Organosolv delignification processes can potentially overcome these capital cost and environmental constraints [1]. These processes involve the selective extraction/ separation as well as recovery of cellulose, hemicellulose and also lignin from different lignocellulosic raw materials which are a renewable resource with great potential as alternative raw material for the chemical industry [2].

Organosolv delignification processes can be broadly categorized into catalyzed and uncatalyzed processes. Current trends show that uncatalyzed processes have a very limited application, as organic solvent in the presence of small amount of mineral acid as a catalyst, extensively and selectively delignify the lignocellulosic raw material under mild experimental conditions [3].

The wood sources of the world - the main raw material for the pulp and paper industry, are depleting at an alarming rate. However, certain tropical hardwoods, found to be intermixed in the forests, seem to have great potential and may suitably be exploited as raw material for producing pulp and paper. In Pakistan too, where forest covered area is far below the international standards, the use of agro-residues as well as these hardwoods should be properly exploited through extensive R&D efforts, as possible raw materials for the paper industry.

Partal (*Picea morinda*) is a tall and fast growing tree found abundantly all over the country. The tree reaches to a height of 45 – 65 m, and most frequently occurs at an elevation of 1800 – 3300 m in north western hilly regions of the country [4]. The wood of this particular species is not durable and due to its inherent structure, is difficult to treat with preservatives and hence not suitable for furniture making, structural uses etc. In this scenario, in view of its abundant availability and chemical composition, the use of Partal wood as a possible raw material for producing pulp and thereafter paper should be thoroughly investigated. Some workers have already explored the delignification /pulping of Partal (*Picea morinda*) wood by chemical methods [5]. However, no such work is yet known to these authors on the aspect of organosolv delignification of this particular species of wood.

The present study describes the delignification of Partal (*Picea morinda*) - an indigenous tropical wood, using different lower aliphatic organic acids, as solvents and hydrochloric acid as a catalyst. Suitable delignification conditions, like percentage of respective acid used, concentration of catalyst, time and temperature have also been established in the

light of yield, Kappa No., percent residual lignin (PRL) and Klason lignin of the resultant delignified products.

Results and Discussion

The proximate chemical analysis of Partal wood (*Picea morinda*) has been presented in Table 1. It shows that both of the ∝ - Cellulose as well as Klason lignin contents in this particular species are on the higher side, whereas ash is just negligible. All these features closely correspond to a tropical deciduous hard wood [6].

Table 1- Proximate Chemical Composition of Partal (*Picea morinda*) Wood

Constituents Determined	% (W/W)
Ash Content	0.60
Alcohol – benzene extractives	2.90
∝ - Cellulose	53.60
Klason lignin	30.10
Pentosans	13.25

Tables 2,3 and 4 depict the three sets of experiments performed in connection with establishing variables of % acetic acid, % HCl as catalyst and solid-liquor ratio. The optimum conditions in each case were established in the light of % yield, Klason lignin and Kappa No's of the different delignified products, obtained through these sets of experiments.

A review of these tables shows that, variation of concentration of % acetic acid and hydrochloric acid (catalyst) from 85–90 and 0.10–0.15% respectively, did not significantly affect the process of delignification of this wood up to desired level. However, it is quite apparent therein, that higher concentrations of acid and catalyst (95% and 0.20%), markedly enhance the rate of delignification, as is evident by the lower Klason lignin and Kappa No of the resultant product. The lower Kappa No (20.11) in this case signifies, that it is bleachable [7] and more positively, % yield is also not too much adversely affected by the increase in the concentration of acid and catalyst.

As for S/L ratio, lower ratio of 1:10 was found to be quite ineffective for substantial delignification, whereas too a high S/L ratio (1:15), inspite of excessive consumption of chemicals, could not significantly increase the efficiency of delignification. Henceforth, working conditions of 95% acid, 0.2% catalyst and S/L ratio of 1:12.5 were selected for onward kinetic studies of treatment of Partal wood with acetic acid.

Detailed kinetic studies presented in Table 5 and Fig.1 show that time of 120 minutes has been found to be quite sufficient for achieving optimum delignification (From 30% to 6%) of this particular wood species. Further increase in time upto 180 minutes, did not show any pronounced effect on the process. Henceforth, working conditions established in respect of organosolv delignification of Partal wood with acetic acid, are 95% acid, 0.2% catalyst, 1:12.5 S/L ratio and time of 120 minutes.

Table – 2 Establishment of Acetic Acid Percent

CH_3COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
85 %	0.20	180	1:12.5	52.19	37.12	10.03	17.39
90 %	0.20	180	1:12.5	51.97	35.32	9.19	15.86
95 %	0.20	180	1:12.5	48.10	20.11	5.90	9.43

Table – 3 Establishment of Catalyst (HCl) percent

CH_3COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
95 %	0.10	180	1:12.5	58.19	39.52	12.50	24.16
95 %	0.15	180	1:12.5	52.95	38.32	11.17	19.65
95 %	0.20	180	1:12.5	48.10	20.11	5.90	9.43

Table – 4 Establishment of Solid – Liquor Ratio

CH_3COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
95 %	0.20	180	1:10	64.70	39.02	15.04	32.33
95 %	0.20	180	1:12.5	48.10	20.11	5.90	9.43
95 %	0.20	180	1:15	46.94	21.80	4.70	7.33

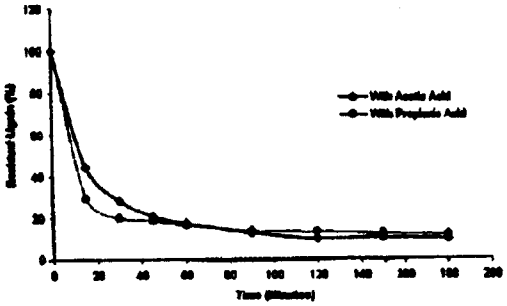

Fig. 1: Dependence of percent residual lignin on delignification time

Tables 6,7 and 8 enlist the three sets of experiments performed in each case, for establishing working conditions of % acid, % catalyst and S/L ratio for propionic acid as a delignification medium.

A review of these three tables clearly depicts, that the variable of % propionic acid has a more pronounced effect on the process of delignification of Partal wood than that of variation of % catalyst in the range of 0.1 – 0.2 %, which seems to have the least influence of the three variables under study. One notable observation in case of propionic acid was that, comparatively lesser concentration of catalyst (0.1%) is required for optimum delignification as compared to that of acetic acid.

The optimum conditions of 90% acid, 0.1 % catalyst and S/L ratio of 1:12.5, as established in the study described earlier (Tables 6-8), were further utilized in the kinetic studies detailed in Table 9.

It shows that rate of delignification is initially quite drastic in propionic acid as compared to acetic acid (Table5), as optimum level of delignification (Kalson lignin≈ 6%) is achieved in 90 minutes time in case of former one, whereas in acetic acid it is rather120 minutes. It may further be observed in Table 9 and also Fig.1, that percent residual lignin

Table – 5 Kinetic Studies of Established Operational Conditions of Delignification with Acetic Acid.

CH_3COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
95	0.20	15	1:12.5	77.69	37.23	17.23	44.47
95	0.20	30	1:12.5	70.48	34.70	12.13	28.40
95	0.20	45	1:12.5	58.26	30.26	10.78	20.86
95	0.20	60	1:12.5	55.62	26.70	9.47	17.49
95	0.20	90	1:12.5	51.93	25.30	7.26	12.52
95	0.20	120	1:12.5	48.25	23.90	6.03	9.67
95	0.20	150	1:12.5	49.15	22.25	6.26	10.22
95	0.20	180	1:12.5	48.10	20.11	5.90	9.41

Table – 6 Establishment of Propionic Acid percent

C_2H_5COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
85	0.10	180	1:12.5	68.20	43.60	9.72	22.02
90	0.10	180	1:12.5	61.90	25.40	5.60	11.52
95	0.10	180	1:12.5	47.10	17.90	4.90	7.66

Table – 7 Establishment of Catalyst (HCl) Percent

C_2H_5COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
90	0.10	180	1:12.5	61.90	25.40	5.60	11.52
90	0.15	180	1:12.5	55.90	24.00	4.75	8.82
90	0.20	180	1:12.5	49.80	23.30	4.52	7.48

Table – 8 Establishment of Solid – liquor Ratio

C_2H_5COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
90	0.10	180	1:10	60.16	31.10	10.40	22.50
90	0.10	180	1:12.5	61.90	25.40	5.60	11.52
90	0.10	180	1:15	58.19	26.00	6.10	11.80

(PRL), decreases in the delignified product with increase of time. Moreover, bulk delignification although occurs in first 30-45 minutes, but optimum yield of the resultant product, having a lower PRL and Klason lignin was obtained in digestion time of 90 minutes. Therefore this study on delignifaction of Partal wood with propionic acid (Tables 6-9); establishes that appropriate conditions in this particular case are 90% acid, 0.1% catalyst, S/L ratio of 1:12.5 in 90 minutes of time. Further the pattern of linear decrease in the yield of delignified product with the decrease in its Kappa No, which is more pronounced initially in propionic acid than that of acetic acid, may better be seen in Fig.2.

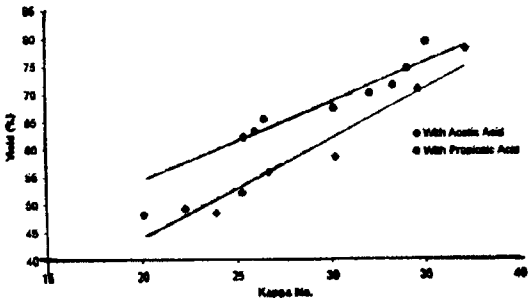

Fig. 2: Correlation of Kappa No. with % yield

Different sets of delignification experiments performed in this continuation with formic acid have been given in Table 10.

In this particular case, % formic acid varied in the range of 70 – 80% [8] and catalyst 0.15 – 0.25%. A review of experimental data obtained in case of delignification of Partal wood by formic acid reveals that, this acid could not sufficiently delignify this species of wood, as is evident by the rather unaffected percentage of Klason lignin (reduced just from 30% to 27-28 %) in the different sets of experiments depicted in Tables 10 and 11. Instead in case of higher percentage of formic acid and catalyst (80% and 0.25% respectively), the resultant product rather charred.

It has therefore been concluded from these studies that among lower aliphatic acids, propionic acid in 90% concentration gave a better delignified product from Partal (*Picea morinda*) wood, in comparatively quite higher yield (67%) and lesser time (90 minutes) as compared to that of acetic acid. However, formic acid was not found to be a suitable medium in this respect. This study closely corresponds to our prior study [9 – 10], on Kenaf (*Hibiscus sabdariffa*)- an exotic species, where also propionic acid had proven to be a better delignifying medium [11] than that of other lower aliphatic acids.

Experimental

The wood of Partal (*Picea morinda*) was procured through the courtesy of Forest Department. The wood was first cut into small pieces in a saw

Table – 9 Kinetic Studies of Established Operational Conditions of Delignification with Propionic Acid

C_2H_5 COOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
90	0.10	15	1:12.5	79.11	35.15	11.13	29.25
90	0.10	30	1:12.5	74.12	34.11	8.11	19.97
90	0.10	45	1:12.5	71.11	33.37	7.95	18.78
90	0.10	60	1:12.5	69.80	32.12	7.00	16.23
90	0.10	90	1:12.5	67.11	30.20	6.11	13.62
90	0.10	120	1:12.5	65.12	26.50	5.96	12.89
90	0.10	150	1:12.5	63.00	26.00	5.80	12.14
90	0.10	180	1:12.5	61.95	25.40	5.60	11.52

Table – 10 Establishment of Formic Acid Percent

HCOOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
70	0.20	180	1:12.5	72.1	No Response	29.8	-----
75	0.20	180	1:12.5	64.2	No Response	29.8	-----
80	0.20	180	1:12.5	58.8	No Response	27.1	-----

Table – 11 Establishment of Catalyst (HCl) Percent

HCOOH (%)	HCl (%)	Time (Min)	Solid liquor Ratio	Yield (%)	Kappa No	Klason lignin (%)	Residual Lignin (%)
80	0.15	180	1:12.5	60.2	No Response	29.1	------
80	0.20	-----	1:12.5	58.8	No Response	27.1	------
80	0.25	180	1:12.5	Charred	------	----	------

machine and then disintegrated in a pilot plant disintegrator and further in a Warner blender to a particle size of 0.315–1.00 mm. The sized material was then thoroughly washed with a stream of water to get rid off any dirt and foreign material and dried in an oven at 105–110°C to constant weight. The disintegrated, washed and dried wood was then extracted with alcohol-benzene mixture for determining its extractives [12]. The extracted sample was further subjected to analysis of its α Cellulose [13], Klason lignin [14] and ash content.

The delignification treatments of classified, washed and dried wood samples were carried out in 250 ml round bottom Pyrex flask, placed inside a thermostatically controlled heating mantle fitted with a reflux condenser. 10 gm of wood sample was used in each set of experiment, containing respective acid, water and catalyst (hydrochloric acid) in varying proportions, depending upon the working conditions utilized in that particular set of experiment. These delignification treatments with acetic, formic and propionic acids were conducted at 118, 101 and 141°C for acetic, formic and propionic acids respectively [15]. The experiments on treatment of Partal wood with the lower aliphatic organic acids were repeated twice, including three replicates of each treatment. Replicates were reproducible, and standard deviation was calculated wherever applicable. Three sets of experiments were carried out separately for each of the three acids under study, to select appropriate working conditions of percent acid, percent catalyst and solid-liquor ratio for optimum delignification of Partal wood. The time utilized in this part of study for selection of appropriate conditions for delignification was 180 minutes, established after a series of experiments. All the three variables under study of % acid, % catalyst and S/L ratio were the same viz 85,90 & 95%, 0.10, 0.15 & 0.20% and 1:10, 1:12.5 & 1:15 respectively, in case of acetic and propionic acids. However in case of formic acid, the variables of % acid and % catalyst being investigated were, 70, 75 & 80% and 0.15, 0.20 & 0.25%.

The kinetics of the process of delignification of Partal (*Picea morinda*) wood, for the acids under study was carried out, by undertaking a series of fractionation treatments, varying from 15 to 180 minutes. The working conditions as regards % acid, % catalyst and solid-liquor ratio, used in each case were the same as established earlier. The resultant delignified products were then evaluated for their respective yields, Kalson lignin and Kappa number [16]. The percentage of residual lignin (PRL), remaining in these products [3] after acid treatments was calculated by the formula.

$$PRL = Y \frac{Lc}{Lc_o}$$

where

Y = Pulp yield
Lc = Lignin content of treated Partal wood.
Lc_o = Lignin content of untreated Partal wood.

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