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DELIGNIFICATION OF KENAF *(HIBISCUS SABDARIFFA)* BY ORGANOSOLV PULPING PROCESS. *PART-II.* FORMIC AND PROPIONIC ACIDS

Tamoor Wahab Ahmed, Tanzil H Usmani*, M Tahir Motan and M A Damani

PCSIR Laboratories Complex, Off University Road, Karachi-75280 Pakistan.

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Organosolv delignification of kenaf *(Hibiscus sabdariffa)* mediated by formic and propionic acids, catalyzed by hydrochloric acid, was evaluated. The effect of different variables like concentrations of acid and catalyst and charge ratios on the yield and quality of the delignified products alongwith the kinetics of delignification process was studied. It was, thereafter, established that optimum conditions of delignification of kenaf for these two acids were 80 and 90% concentration (w/w) of acid, 0.2% of catalyst, solid-liquor ratio of 1:12.5 and fractionation time of 120 and 90 minutes for formic and propionic acids, respectively. Furthermore, it was observed that propionic acid gives comparatively a better quality delignified product in good yield and takes lesser time as compared to the other aliphatic organic acids.

Keywords: Organosolv pulping, Kenaf, Delignification, Formic acid, Propionic acid.

Introduction

Due to the higher capital cost and pollution problems of chemical pulping processes such as Kraft and Sulfite, the development of alternative pulping technologies has been pursued for a long time (Lora and Aziz 1985). The pulping method using organic solvents (organosolv), involves the selective extraction of lignin from lignocellulosic raw materials (Baeza *et al* 1991). The processing of lignocellulosic materials by organic solvents provides an interesting alternative to conventional chemical processes. Organosolv based processes allow selective separation and recovery of cellulose, hemicelluloses and lignin. Lignocellulosic materials are a renewable resource with great potential as alternative raw material for the chemical industry.

Solvent pulping options for delignification by solvents can be broadly divided into catalyzed and uncatalyzed processes. Uncatalyzed processes have a very limited application. Organic solvents in the presence of small amounts of mineral acids (which act as catalyst), extensively and selectively delignify the raw materials under mild experimental conditions (Parajo *et al* 1993).

The advantages of organosolv processes include higher pulp yield, ease of bleachability, low capital and production costs and diminished environmental stress (Goyal *et al* 1992). Henceforth, among the upscalable future pulping processes, pulping with organic solvents seems to offer the greatest versatility and potential. In the last decade, solvent pulping made significant progress towards commercialization. As regards formic acid pulping, it is different from other conventional pulping processes in the sense that basically, it is a hydrolytic process, in which valuable chemical by products, like low molecular weight lignin, acetic acid and sugars are obtained. Moreover, formic acid is not consumed chemically in the whole process and may be recovered as such (Bucholtz and Jordan 1982; 1983).

In an earlier study (Ahmed *et al* 1998), kenaf *(Hibiscus sabdariffa)*, a native of Asia and Africa, now cultivated throughout the tropics, was subjected to acetosolv pulping. The present study describes the delignification of kenaf using formic and propionic acids as solvents and hydrochloric acid as a catalyst. Suitable working conditions, like percentage of respective acid, concentration of catalyst, temperature and time have been established in the light of yields and composition of delignified samples.

Materials and Methods

Kenaf stalks were dried in an oven at 105°C, chipped and disintegrated to a particle size of 0.315-1.0 mm and then homogenized and stored in a dessicator. It was then extracted with alcohol-benzene for determining its extractives (ASTM 1983). The extracted sample was subjected to analysis of its α cellulose (Doree 1974), Klason lignin (ASTM 1997) and holocellulose contents (Erickson 1962). All the parameters measured were determined on the basis of initial dry weight of the raw material utilized in that particular set of experiment.

The delignification treatments of the disintegrated samples were carried out in 250ml round bottom flasks under reflux conditions at 101°C and 141°C with formic and propionic acids, respectively. 10g of the original disintegrated and dried sample was used in each set of experiments, containing respective acid, water and hydrochloric acid in varying proportions. Three sets of experiments were carried out sepa-

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* Author for correspondence

rately for each acid for selection of optimum conditions of concentration of acid, catalyst and solid-liquor ratio. The variables of catalyst concentration (% w/w) and solid-liquor ratio for formic and propionic acids were the same viz. 0.15, 0.20, and 0.25% and 1:10, 1:12.5 and 1:15, respectively. However, the variable of acid concentration was 70%, 80% and 90% in formic acid and 85%, 90% and 95% for propionic acid. The fractionation time used in each case was three hours established after a series of experiments.

The kinetics of delignification of kenaf were carried out by a series of fractionation treatments for time varying from 15 to 240 minutes and 15 to 180 minutes for formic and propionic acids, respectively. These fractionated/delignified products were then evaluated for their respective yields, Klason lignin and kappa numbers (Vazquez *et al* 1992). The percentage of the residual lignin (PRL), remaining in different fractionated products (Parajo *et al* 1993), was calculated by the formula

$$\text{PRL} = Y \frac{LC}{LCo}$$

where
Y=Pulp yield
LC=Lignin content of treated kenaf
LCo=Lignin content of untreated kenaf

Results and Discussion

The chemical composition of kenaf *(Hibiscus sabdariffa)* has been presented in Table 1. It may be seen that its α cellulose content of 47.6% lies between most of the woods and agrowastes. Moreover, its Klason lignin is also in the lower side. In the light of these observations, it seems to be a potential raw material for pulping.

The three operational variables studied in case of delignification of kenaf by formic and propionic acids were percentages of acid and HCl as catalyst and solid-liquor ratio. The experiment was conducted at low temperature with the advantage of minimum cellulose and hemicellulose degradation and extraction of lignin in its most valuale form (Papatheofanous *et al* 1992). Tables 2, 3 and 4 depict the three sets of experiments performed separately to establish optimum delignification conditions in case of formic acid. The fractionation time used in each case was 180 minutes, established after a series of experiments. It was observed that out of three operational variables studied, variable of formic acid concentration was the most effective, as regards the delignified yields and extracted formic lignin. The increase in formic acid concentration from 70% to 90% drastically reduced the yield from 54% to 38% (Table 2). However, in the light of lower Klason lignin and yield of the delignified product, the concentration of 80% formic acid was selected and applied in further experiments. The Kappa number of the product was 25.8, which according to certain standards is bleachable (Dong *et al* 1991). Moreover, it may

Table 1

Proximate chemical composition of kenaf

Constituents determined	%(w/w)
Alcohol-benzene extractives	1.5
Hot water extractives	7.6
Holocellulose	80.5
α-Cellulose	47.6
Klason lignin	15.3

Table 2

Establishment of formic acid %

Solid-liquor ratio	Formic acid (HCOOH) (%)	Hydrochloric acid (HCl) (%)	Time (min)	Yield (%)	Formic lignin	Klason lignin	Kappa number (%)
1:12.5	70	0.2	180	53.68	8.55	11.55	35.94
1:12.5	80	0.2	180	49.87	12.35	5.69	25.83
1:12.5	90	0.2	180	37.86	15.05	5.36	18.62

Table 3

Establishment of catalyst (HCl) %

Solid-liquor ratio	Formic acid (HCOOH) (%)	Hydrochloric acid (HCl) (%)	Time (min)	Yield (%)	Formic lignin	Klason lignin	Kappa number (%)
1:12.5	80	0.15	180	51.91	9.94	7.16	28.00
1:12.5	80	0.20	180	49.87	12.35	5.69	25.83
1:12.5	80	0.25	180	46.11	13.84	5.11	25.00

Table 4

Establishment of solid-liquor ratio

Solid-liquor ratio	Formic acid (HCOOH) (%)	Hydrochloric acid (HCl) (%)	Time (min)	Yield (%)	Formic lignin	Klason lignin	Kappa number (%)
1:10	80	0.2	180	51.81	10.62	6.11	27.44
1:12.5	80	0.2	180	49.87	12.35	5.69	25.83
1:15	80	0.2	180	49.67	12.42	5.51	25.00

also be observed in Tables 3 & 4, that optimum delignification of kenaf with formic acid as a medium was achieved by catalyst concentration and solid-liquor ratio of 0.2% and 1:12.5, respectively.

The kinetics of delignification of kenaf with formic acid was studied under the established conditions using acid concentration, catalyst concentration and charge ratio of 80%, 0.2% and 1:12.5, respectively. It may be observed in Table 5 that increase of time had a marked effect on the yield of delignified product and eventually on their Klason lignin/kappa number. Moreover, it may also be seen in Fig 1 that percentage of residual lignin (PRL) in fractionated kenaf samples (Table 5), gradually decreased with the increase of time of delignification. However, optimum delignification of kenaf was achieved in 180 minutes.

Table 5

Kinetic studies of established delignificaton conditions with formic acid

S. No.	Time (min)	Yield (%)	Formic* lignin (%)	Klason** lignin (%)	Residual lignin (%)	Kappa number
1	15	71.07	7.22	13.52	62.80	38.92
2	30	62.58	7.29	12.09	49.45	37.30
3	45	56.31	7.84	10.81	39.78	36.05
4	60	53.57	9.59	9.50	33.26	33.05
5	90	51.56	10.80	7.26	24.46	29.49
6	120	50.12	11.68	6.94	22.73	28.20
7	150	49.91	12.02	6.26	20.42	27.34
8	180	49.87	12.35	5.69	18.54	25.83
9	210	49.68	12.50	5.61	18.21	24.90
10	240	49.50	12.72	5.50	17.79	24.20

(i) Formic acid=80% (ii)Catalyst (HCl)=0.2%

(iii) Solid-liquor ratis=1:1:5

* Lignin extracted after formic acid treatment

** Lignin remaining in the delignified product

Table 6

Establishment of propionic acid

Solid-liquor ratio	Propionic acide C_2H_5 COOH) (%)	Hydro-chloric acid (HCl) (%)	Time (min)	Yield (%)	Propionic lignin (%)	Klason lignin (%)	Kappa number
1:12.5	85	0.2	180	56.14	10.37	7.06	28.10
1:12.5	90	0.2	180	51.28	13.58	3.60	21.27
1:12.5	92	0.2	180	47.10	13.75	3.10	19.70

One notable observation during formic acid pulping was that, delignified material was quite soft in the wet stage, but if it was allowed to dry then it returned to its original state and was unsuitable for beating. It distinguishes formic acid pulping from other conventional processes (Bucholtz and Jordan 1983).

Table 5,6,7,8 depict the experiments performed for establishing the conditions for optimum delignification of kenaf using propionic acid. It may be seen here, that the variable of propionic acid concentration is more effective as compared

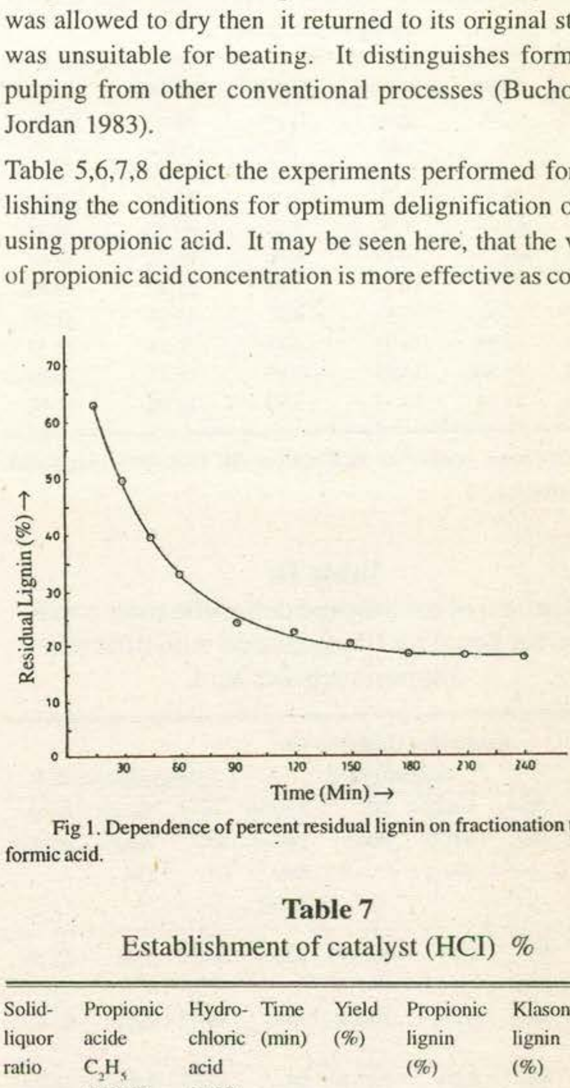

Fig 1. Dependence of percent residual lignin on fractionation time with formic acid.

Table 7

Establishment of catalyst (HCl) %

Solid-liquor ratio	Propionic acide C_2H_5 COOH) (%)	Hydro-chloric acid (HCl) (%)	Time (min)	Yield (%)	Propionic lignin (%)	Klason lignin (%)	Kappa number
1:12.5	90	0.15	180	52.40	11.74	4.25	22.15
1:12.5	90	0.20	180	51.28	13.58	3.60	21.27
1:12.5	90	0.25	180	47.90	15.74	3.11	19.65

Table 8

Establishment of solid-liquor ratio

Solid-liquor ratio	Propionic acide C_2H_5 COOH) (%)	Hydro-chloric acid (HCl) (%)	Time (min)	Yield (%)	Propionic lignin (%)	Klason lignin (%)	Kappa number
1:10.5	90	0.2	180	53.04	12.84	4.50	26.50
1:12.5	90	0.2	180	51.28	13.58	3.60	21.27
1:15.0	90	0.2	180	50.78	13.68	3.50	20.27

Table 9

Kinetic studies of established conditions with propionic acid

S. No.	Time (min)	Yield (%)	Propionic lignin (%)	Klason lignin (%)	Residual lignin (%)	Kappa number
1	15	76.83	5.71	11.09	55.69	38.32
2	30	67.37	9.78	9.21	40.55	35.44
3	45	60.23	10.62	6.66	26.21	32.01
4	60	57.33	10.52	5.71	21.39	28.46
5	90	55.62	11.91	4.42	16.07	24.10
6	120	53.55	12.56	4.04	14.14	22.25
7	150	51.86	13.03	3.87	13.12	21.91
8	180	51.28	13.58	3.60	12.06	21.27

(i) Propionic acid=90% (ii)Catalyst (HCI)=0.20% (iii) Solid-liquor ratio=1:12.5

Table 10

Comparison of established delignification conditions for kenaf by fractionation with different aliphatic organic acid

Acids	Established conditions for delignification				Delignified products		
	Acid (%)	Catalyst (HCI) (%)	S/L Ratio	Fractionation time (min)	Yield (%)	Klason lignin (%)	Kappa number
Acetic acid	95	0.25	1:12.5	120	54.50	4.60	22.10
Formic acid	80	0.20	1:12.5	180	49.87	5.69	25.83
Propionic acid	90	0.20	1:12.5	90	55.62	4.42	24.10

to that of catalyst and charge ratio in respect of delignification. Optimum delignification was thereafter obtained by using 90% propionic acid, 0.2% HCI and solid-liquor ratio of 1:12.5. The kinetics of delignification of this study has been described in Table 9, which shows that the rate of delignification is quite drastic in the initial 45 minutes of fractionation time. This pattern of bulk delignification of kenaf with propionic acid in 45 minutes fractionation time may further be observed in Fig 2. However, optimum yield of the delignified product with a lower Klason lignin was obtained in 90 minutes. Further increase of time, from 90 to 180 minutes, reduced the Klason lignin by only 0.82%, in spite of reducing the eventual yield by 4%. Therefore, a review of Tables 6 to 9 shows that the established conditions for delignification of kenaf by propionic acid as a medium are 90% acid, 0.2% catalyst and a charge ratio of 1:12.5 in 90 minutes. Table 10 shows the conditions established for delignification of kenaf by organosolv fractionation with different aliphatic organic acids and various characteristics of the fractionated products. It revealed that comparatively lower concentration (80%) of formic acid was required than that of acetic and propionic acids. As for the quality of the delignified products, propionic acid gave a better end product in higher yield as compared to the lower aliphatic acids; this was also observed by Shimizu *et al* (1992). Moreover, the established fractionation time for propionic acid was also less viz. 90 minutes whereas it was 120 and 180 minutes for acetic and formic acids, respectively. Further, the product obtained by formic acid fractionation had quite a low yield of 50% and its Klason lignin was also on the higher side (5.69%). Its kappa number was quite high as about 50% of the Klason lignin present in the original raw material remained in the end product. The conditions established for acid concentration, catalyst and time for acetic acid were on the higher side (Table 10).

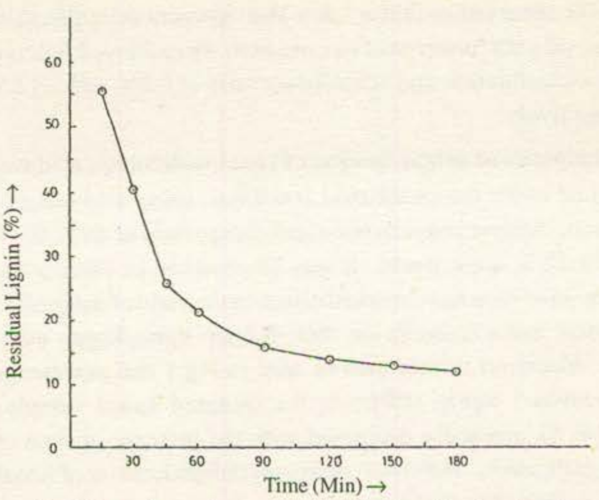

Fig 2. Dependence of percent residual lignin on fractionation time with propionic acid.

It is concluded from these studies that kenaf *(Hibiscus sabdariffa)* may suitably be delignified by fractionation with different aliphatic organic acids. However, propionic acid is better in terms of established conditions, as bulk delignification occurs in initial 45 minutes whereas, in formic acid, this stage is achieved in 90 minutes. Moreover, propionic acid gives a better quality fractionated product with a lower PRL than that of formic acid.

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