*Pak J Sci Ind Res 1998 41 (5) 235-239*

# DELIGNIFICATION OF KENAF (*HIBISCUS SABDARIFFA*) BY ORGANOSOLV PULPING PROCESS-*PART I*. ACETIC ACID

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(Received 4 December 1996; accepted 3 September 1998)

Kenaf (*Hibiscus sabdariffa)* was subjected to acetosolv pulping catalyzed by hydrochloric acid. The effect of various operational conditions like percent acid, percent catalyst and solid-liquor ratio on the percent yield and the quality of the resultant fractionated product was studied. Extensive delignification was achieved under a variety of operational conditions, leading to solid residues with lignin contents of less than 5%. The kinetics of the delignification process was also studied. The optimum pulping conditions established for this raw material were 95% acid, 0.25% catalyst and solid-liquor ratio of 1:12.5 in time of 120 mins giving a fractionated product having yield and α-cellulose contents of 54.5 and 85.7% respectively. Further, its fiber dimensions were found to be comparable to that of certain woods with mean fiber length and diameter of 1.506 and 0.0295 mm, respectively.

***Key words:*** Kenaf, Acetosolv pulping, Delignification, Pulping conditions, Fiber dimensions.

## Introduction

Paper consumption in wide varieties of fields of common use may be considered as an effective measure of the economic development of a country. The establishment of a paper industry has thus become one of the basic element of industrial programmes of most developing countries. Unfortunately, the wood based fiber resources of these countries are mainly of tropical hardwoods. Moreover, these resources are scarce and not ideally suited as pulping material. So, the main strategy for the development of this industry in developing countries should be the proper exploitation of non-wood fiber resources and certain exotic plant species on an appropriate scale (Nayeemuddin *et al* 1989).

Kenaf (*Hibiscus sabdariffa)* is a fast growing shrub, which attains a height of about 4 m and can be harvested within a minimum period of 90 days after plantation. It is native of Africa and Asia and is now cultivated throughout the tropics. It is well adapted to all types of soils and is able to tolerate a certain degree of acidity or alkalinity in the soil. It requires a moist climate, high temperature and medium rainfall throughout the growth period (Anon 1959). It has been successfully grown in Pakistan as an exotic species. The bast fibers of this plant are soft, silky and lustrous (Hill 1952), with chemical and physical properties similar to those of jute (*Corchoruf olitorius* L.), being widely used in making carpets, ropes and sacks etc. (Sadawarte *et al* 1975). Its flowers contain citric, maleic and ascorbic acids and also appreciable amount of protein. Increased interest in the fiber of this plant is being shown because of its potential use as a raw material for pulp and paper (UNIDO 1979; Shah *et al* 1980). An added advantage is its availability on an annual basis contrary to that of wood forests.

Conventional chemical pulping processes like Kraft, Soda, Neutral sulfite semichemical (NSSC) etc. used now a days, are too expensive and cause environmental problems due to the nature of their effluents to the extent that the Kraft method has been banned in Germany (Zanetli 1990). One possibility of overcoming the existing problems is the use of a variety of organic solvents including alcohols, ketones, amines, glycols, esters, peroxides and acids (Parajo *et al* 1993). Organosolv pulping processes may be preferred over chemical pulping processes due to their low investment cost, lesser environmental contamination problems, recovery of solvent and carbohydrates, lignins and low operating temperature and pressure (Aziz and McDonough 1988; Baeza *et al* 1991). Moreover, unlike conventional chemical processes, organosolv processes, allow the selective separation and recovery of cellulose, hemicellulose and lignin which can be converted by chemical or biotechnological means into a variety of chemicals (Johansson *et al* 1987; Parajo *et al* 1993). In organosolv pulping, among all the solvents studied, main emphasis is now-a-days being laid upon alcohols and aliphatic acids (Ede and Brunow 1988; Goyal *et al* 1992).

There is an extensive literature available on pulping of Kenaf by conventional pulping processes (Bagby and Cunningham, 1974; Huiren *et al* 1991). However, no work is yet known to the authors on organosolv pulping of this particular raw material. This paper describes the pulping of Kenaf, using

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acetic acid as an organic solvent and hydrochloric acid as a catalyst. Main emphasis of this study is to establish proper working conditions like percentage of acid, concentration of catalyst, temperature and time for optimum delignification, which is a primary measure of the suitability of a particular raw material for pulping.

## Materials and Methods

*I: Preparation of Samples.* The dried stalks of Kenaf were collected from the experimental farms of PCSIR Laboratories Complex, Karachi. These were chipped into small pieces and then disintegrated in a Waring blender, screened to a particle size of 0.315-1.0 mm, homogenized, air dried and then stored in airtight bags.

*II: Chemical Composition of the Raw Material.* The sample as in (I), was extracted with alcohol-benzene and extractives determined (ASTM 1983). The extractive free sample was then analyzed chemically for its α-cellulose (Doree 1974), Klason lignin (Casey 1981a) and holocellulose contents (Vazquez *et al* 1992). All the measured parameters were determined on the basis of initial dry weight of the raw material utilized in that particular set of experiment.

*III: Establishing Pulping Conditions.* The fractionation treatments were carried out in 250 ml round bottom flask at 110°C, under constant volume conditions, using liquors containing acetic acid, water and hydrochloric acid in different proportions. Ten gms of the original disintegrated sample was used in each set of experiment.

Three sets of experiments were carried out utilizing 75, 85 and 95% acetic acid solutions as delignification media. The concentration of hydrochloric acid utilized by weight as a catalyst in the delignifying liquors were 0.15, 0.20 and 0.25% using liquor-solid ratios of 10, 12.5 and 15 grammes per gramme, to establish the optimum delignification conditions. The pulping time used in each case was 2 h which was established after a series of experiments.

*IV: Kinetic Studies.* The detailed kinetic studies of the pulping conditions of Kenaf as established in (III), were carried out at different intervals of time varying from 15 to 180 min.

*V: Evaluation of the Fractionated Products.* The fractionated products obtained from each set of experiment were then evaluated for their yield, α-cellulose and Klason lignin contents and Kappa numbers (Erickson 1962). The products obtained in each set of experiment were evaluated by standard methods. The experiments with different delignified products of Kenaf were repeated twice including three replicates of each treatment. Replicates were reproducible and standard deviation was calculated wherever applicable.

*VI. Studies on fiber dimensions.* The determination of fiber dimensions viz. length and diameter of unbleached pulp of Kenaf was carried out using a microscopic count method (Casey 1981b). Adequate data was collected for statistical analysis of frequency of different sizes of fibers.

## Results and Discussion

The proximate chemical analysis of Kenaf used in the present study, has been listed in Table 1. In the light of its chemical composition, it appears to be favourable for pulping due to its higher α-cellulose, lower Klason lignin and extractives (Parajo *et al* 1993).

**Table 1**

Proximate chemical composition of kenaf

| Constituents determined | % |
|---|---|
| Alcohol-benzene extractives | 1.5 |
| Hot water extractives | 7.6 |
| Holocellulose | 80.5 |
| α-Cellulose | 47.6 |
| Klason lignin | 15.3 |

The three operational variables of acetic acid concentration and % catalyst [HCl] and solid-liquor ratio were used in this study within a limit of 75-95%, 0.15-0.25% and 1:10-1:15, respectively to select the appropriate pulping conditions for this raw material. A set of three variables, namely %yield, %Klason lignin and kappa number were used to study the delignification process.

Tables 2, 3 and 4 present the three sets of experiments, performed in each case for establishing appropriate pulping conditions of %acetic acid, % catalyst and solid-liquor ratio, respectively, keeping the duration of treatment for 2 h as constant in each case. It is clear that as far the former two are concerned, optimum delignification is achieved by treating the raw material with a liquor containing, 95% acetic acid and 0.25% hydrochloric acid as a catalyst. These pulping conditions correspond as regards concentration of acid with the observations of Vazquez *et al* (1992) when pulping eucalyptus wood with acetic acid, but for only 2 h. The results in Table 3 shows that solid-liquor ratio of 1:12.5 was suitable for pulping of Kenaf. Parajo *et al* 1993, have earlier established somewhat lower solid-liquor ratio of 1:10 for Eucalyptus wood. Higher solid-liquor ratio has proved superior in respect to delignification of Kenaf, probably due to the bulky nature of this raw material. The pulping conditions for Kenaf have therefore, been established as 95% acetic acid, 0.25% catalyst

**Table 2**
Establishment of acetic acid percent (%)

| Solid-liquor ratio | Acetic acid % | Hydrochloric acid % | Time h | Yield % | Klason lignin | Kappa number |
|---|---|---|---|---|---|---|
| 1:12.5 | 75 | 0.2 | 2 | 74.1 | 15.2 | 42.4 |
| 1:12.5 | 85 | 0.2 | 2 | 69.5 | 12.2 | 28.9 |
| 1:12.5 | 95 | 0.2 | 2 | 54.0 | 9.3 | 24.8 |

**Table 3**
Establishment of solid-liquor ratio

| Solid-liquor ratio | Acetic acid % | Hydrochloric acid % | Time h | Yield % | Klason lignin | Kappa number |
|---|---|---|---|---|---|---|
| 1:10.0 | 95 | 0.2 | 2 | 64.8 | 13.4 | 45.2 |
| 1:12.5 | 95 | 0.2 | 2 | 54.0 | 9.3 | 24.8 |
| 1:15.0 | 95 | 0.2 | 2 | 46.9 | 9.1 | 23.7 |

**Table 4**
Establishment of catalyst (HCl) percent (%)

| Solid-liquor ratio | Acetic acid % | Hydrochloric acid % | Time h | Yield % | Klason lignin | Kappa number |
|---|---|---|---|---|---|---|
| 1:12.5 | 95 | 0.15 | 2 | 68.7 | 13.3 | 44.1 |
| 1:12.5 | 95 | 0.20 | 2 | 54.0 | 9.3 | 24.8 |
| 1:12.5 | 95 | 0.25 | 2 | 54.5 | 4.6 | 20.1 |

[HCl], 1:12.5 solid-liquor ratio and time of 120 min . These conditions have been selected in the light of lower Klason lignin and Kappa numbers of the resultant fractionated products.

The kinetics of the delignification process under the established pulping conditions was studied in detail by varying the time from 15 to 180 min and the relevant data has been presented in Table 5. It shows that the bulk delignification of Kenaf occurs in fractionation time of 120 min. This behaviour has been further highlighted in Fig 1 in which percentage of residual lignin (PRL) of the fractionated products has been plotted against time of digestion. A sharp slope was observed upon fractionation upto the same delignification time, after which it attains a constant value. The relationships between Klason lignin and % yield of the finished products are shown in Fig 2 which show a fast decrease in the yield from 83 to 54%, with a proportional decrease of Klason lignin from 13.7 to

**Table 5**
Kinetic studies of the established operational conditions

| Time min. | Yield % | Klason Lignin % | Residual lignin % |
|---|---|---|---|
| 15 | 82.8 | 13.7 | 74.1 |
| 30 | 69.3 | 12.3 | 53.0 |
| 45 | 65.9 | 11.1 | 47.8 |
| 60 | 58.5 | 10.5 | 40.1 |
| 90 | 56.0 | 10.0 | 36.6 |
| 120 | 54.5 | 4.6 | 16.4 |
| 150 | 53.9 | 4.1 | 14.1 |
| 180 | 53.8 | 4.5 | 15.8 |

Acetic acid 95%, catalyst (HCl) 0.25%, solid-liquor ratio 1:12.5.

4.6%. It is therefore, inferred that optimum delignification of this raw material has been achieved in 120 min with consequent yield of 54.5%.

Table 6 summarizes the different working parameters for all the experiments performed in connection with the establishment of optimum pulping conditions for *Hibiscus sabdariffa* by organosolv pulping with acetic acid. It also depicts the various characteristics, like % yield, α-cellulose, Klason lignin and Kappa number of the different fractionated products. Experiments 1-7 were performed in connection with establishing the optimum percentage of acid, catalyst and solid-liquor ratio. It would be observed that bleachable grade pulps

**Table 6**

Delignification of kenaf

| Conditions | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (min ) | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 | 120.00 | 15.00 | 30.00 | 45.00 | 60.00 | 90.00 | 150.00 | 180.00 |
| $CH_3COOH$% | 75.00 | 85.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 | 95.00 |
| HCl % | 0.20 | 0.20 | 0.20 | 0.15 | 0.25 | 0.20 | 0.20 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| Solid-liquor ratio | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 | 1:10.0 | 1:15.0 | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 | 1:12.5 |
| *Results* | | | | | | | | | | | | | | |
| Yield % | 74.1 | 69.5 | 54.0 | 68.7 | 54.5 | 64.8 | 46.9 | 82.8 | 69.3 | 65.9 | 58.5 | 56.0 | 53.0 | 53.8 |
| α-Cellulose% | 49.7 | 58.1 | 75.1 | 51.9 | 85.7 | 57.8 | 65.9 | 48.3 | 50.4 | 52.8 | 57.8 | 67.3 | 87.6 | 85.4 |
| Klason lignin% | 15.2 | 12.2 | 9.3 | 13.3 | 4.6 | 13.4 | 9.1 | 13.7 | 12.3 | 11.1 | 10.5 | 10.0 | 4.1 | 4.5 |
| Kappa number | 42.4 | 28.9 | 24.8 | 44.1 | 20.1 | 45.2 | 23.7 | 40.2 | 30.8 | 27.3 | 26.0 | 25.2 | 19.9 | 19.7 |

**Table 7**

Fiber dimensions of kenaf

| Long fiber (L.F.) mm | | Medium Fiber (M.F.) mm | | Short fiber (S.F) mm | | Relation of L.F. to (M.F.+S.F) | Diameter Wide fiber mm | | Diameter Medium fiber mm | | Mean length | Mean diameter mm | Slenderness ratio |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.00 - 3.00 | | 1.00 - 2.00 | | 0.10 - 1.00 | | | 0.025 - 0.040 | | 0.01 - 0.25 | | l | d | l/d |
| %F* | M.L.** | %F | M.L. | %F | M.L. | | %F | M.D.*** | %F | M.D. | | | |
| 27.52 | 2.50 | 44.96 | 1.32 | 27.52 | 0.81 | 1:2.63 | 18.00 | 0.050 | 82.0 | 0.025 | 1.506 | 0.0295 | 51.05 |

* %Frequency, ** Mean length, *** Mean diameter.

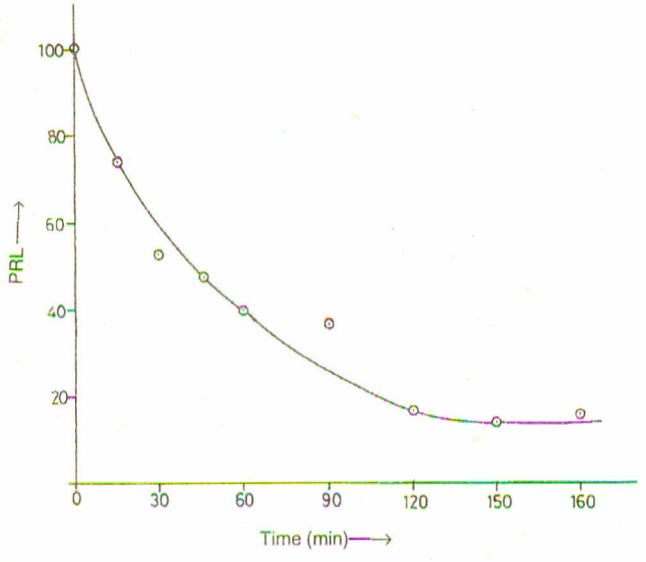


**Fig 1.** Dependence of percent residual lignin on time.

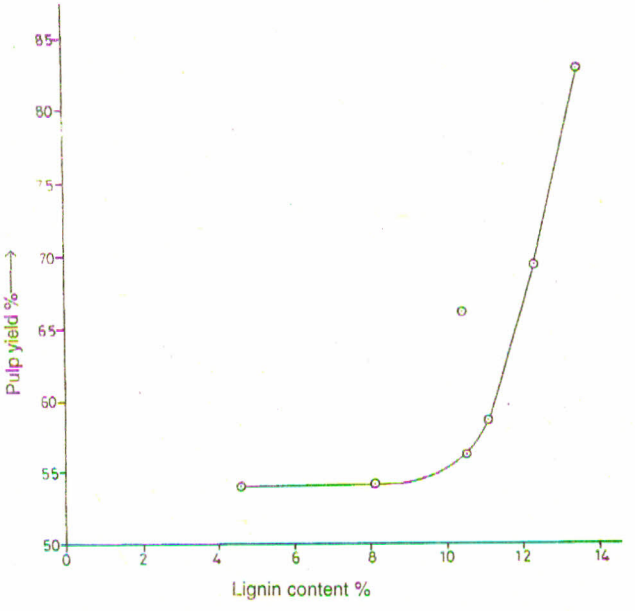


**Fig 2.** Relationship between pulp yield and lignin content.

of kappa number <30 (Dong *et al* 1991), were obtained from experiments 3, 5 and 7. α-cellulose was quite low and Klason lignin was rather on the higher side in assay number 3 and 7. The kinetics of the delignification process for this material in the particle size of 0.315 mm to 1.0 mm show that a solid residue with a suitable composition of 85.7% α-cellulose and 4.6% Klason lignin was obtained with a high yield of 54.5% and Kappa number 20.1 in assay number 5, extracted with 95% acetic acid and 0.25% HCl in cooking time of 120 min

Of the variables studied during the acetosolv cooking, it was observed that all of them showed their significance during the delignification process. However, higher solid-liquor ratio of 1:15 has an adverse effect on the %yield and even on the quality of the fractionated product in terms of lower α-cellulose and higher Klason lignin. Moreover, higher concentration of acid and catalyst [95% $CH_3$ COOH and 0.25% HCl] were selected for further kinetic studies as the solid residues obtained after subsequent treatments [assay number 3 and 5], had comparatively higher percentage of α-cellulose and lower Klason lignin/Kappa number.

The mean fiber length and diameter [mm] of Kenaf were measured (Table 7). An examination of the data concerning its fiber dimensions revealed that the mean fiber length and diameter were of the order of 1.506 and 0.0295 mm, respectively. The slenderness ratio calculated from the length and diameter of this fiber was found to be 51.05 which is close to that of woods (Rydholm 1965). In order to draw a pertinent conclusion, the fiber length data has been further categorized into long, medium and short fibers, according to the classification suggested by Klemm (Casey 1960) and their percent frequencies calculated. A further review of Table 7 clearly indicated that the mean length of long and medium fibers in Kenaf was far higher than that of the short fibers.

It may be inferred from the preceeding discussion that Kenaf (*Hibiscus sabdariffa)* may be efficiently delignified by acetic acid pulping process. As for fiber dimensions, it has a medium length fiber with a slenderness ratio comparable with that of certain woods.

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