STUDIES ON *HIBISCUS CANNABINUS*, *HIBISCUS SABDARIFFA*, AND *CANNABINUS SATIVA* PULP TO BE A SUBSTITUTE FOR SOFTWOOD PULP- PART 1: AS-AQ DELIGNIFICATION PROCESS

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Hibiscus cannabinus, *Hibiscus sabdariffa*, and *Cannabinus sativa*, which are renewable non-woody fiber resources having characteristics similar to that of softwood (bast fibers), when used together with hardwood (core fibers), gave higher pulp yield with good mechanical strength properties when using an alkaline sulphite-anthraquinone (AS-AQ) pulping process rather than a conventional kraft pulping process and bleached more readily than kraft and soda pulps with a CEHH bleaching sequence. A comparison of properties AS-AQ pulping processes with soda and kraft pulping processes of *H. cannabinus*, *C. sativa*, and *H. sabdariffa* was made. All the properties were found to be better than soda and kraft pulps except tear index. All of the mechanical strength properties of handsheets of AS-AQ pulp improved except tear index. Therefore, the AS-AQ pulping process can be considered as ideal for manufacturing of paper grades like greaseproof, glassine, and high-quality writing and printing paper.

Keywords: H. cannabinus; C. sativa; H. sabdariffa; AS-AQ pulping; CEHH bleaching; Paper properties; Spent liquor

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INTRODUCTION

The search for new alternative sources of fiber has been underway for a long time (Nelson et al. 1966). Many fast growing annual and perennial plants have been identified, cultivated, and studied for their suitability in pulp and paper manufacture (Dutt et al. 2005). Papermaking fibers from timber sources can be successfully substituted by fibers from non-woody species (Moore et al 1976). Non-wood plants offer several advantages, including short growth cycles, moderate irrigation and fertilization requirements, and low lignin content, which help to alleviate energy and chemical requirements during pulping (Hurter and Riccio 1998; Watson 1974-75). Botanically, kenaf (*H. cannabinus*) belongs to the dicotyledonous family. *Malvaceae*, and roselle (*Hibiscus sabdariffa*) are closely related species, and they have been identified by the U.S. Department of Agriculture as a viable substitute for trees in the pulp and paper making process (Nieschlag et al. 1961; Han et al. 1999). Kenaf can provide a renewable source of fibers to partially alleviate the world's fiber deficit (Atchison 1996). Pulps prepared from the bark fraction (kenaf) resemble softwood pulp in their general papermaking characteristics, whereas those from the woody fractions are more like hardwood pulp but drain more slowly and have lower tearing strength (Dutt et al. 2008, 2009). Pulps from kenaf have desirable properties for papermaking and generally possess strength characteristics compatible to commercial coniferous wood pulp (Abrahamson and Wright 2000). Kenaf contains two distinct types of fibers; the softwood-like bast fibers make up 35-40% of the total dry weight, and the hardwood-like core fibers make up the balance (Thomas 1970). The low lignin content is reflected in low chemical and energy consumption during pulping, as well as low bleaching chemical requirements, which make it suitable for mechanical and chemical pulping processes (Chang and Lee 1991). *Cannabis sativa* has both bast and core fibres; the bast fibres measure from 5 to 50mm with an average length of 20mm and diameter moderately wide ranging from 7 to 50 µm with an average of 22 µm (Dutt et al. 1998). Hemp core fibre is comparable with hardwood fibre and has an average fibre length of 1.7mm (De Groot et al. 1994; Upadhyaya and Dutt 1991). Dicotyledons such as hemp do not have a high silica content in their ash, in contrast to monocotyledons such as straw or other grasses (Dutt et al., 2004).

It has been found that bagasse can be cooked to extremely low kappa number, high yield, and high brightness, and excellent pulp strength properties can be achieved by using the alkaline sulphite–antraquinone (AS-AQ) process (Horn et al. 1992). Modified alkaline sulphite/anthraquinone pulping (so-called ASA process) has emerged as a particularly attractive process owing to its high pulping selectivity (Patt et al. 2001). The addition of alcohol in this process has only a marginal effect on the pulping results (Wang et al. 1987). The AS-AQ process gives delignification, yield, viscosity, brightness, and strength properties superior to those of soda and soda-AQ pulps (Wang et al. 1989). The aim of the present work is to evaluate the suitability of *H. cannabinus*, *H. sabdariffa*, and *C. sativa* prepared by the AS-AQ pulping process for manufacturing of writing and printing paper grades.

MATERIALS AND METHODS

Raw Material Collection

H. cannabinus, *C. sativa*, and *H. sabdariffa* were collected from the nearby vicinity of the Institute at Saharanpur located in the foothills of Shivalik range of Western Uttar Pradesh (India). These raw materials were air dried, and the leaves and flowers were removed by stroking on a hard surface. The stalks of all these plants were chipped and screened. The chips that passing through 12.7 mm screen but retained on a 6.35 mm screen were collected. The accepted chips were air dried under atmospheric conditions. The moisture content of fresh (green) chips varied from 55 to 60%, while that of air dry chips varied from 8 to 12%. The chips of *H. cannabinus*, *C. sativa*, and *H. sabdariffa* were kept in air-tight polythene bags until they were used.

Pulping Studies

The accepted chips of *H. cannabinus*, *C. sativa*, and *H. sabdariffa* were cooked in a laboratory Weverk rotary tumbling electrically heated digester (capacity 0.02 m^3) having four bombs of one liter capacity each, furnishing sufficient pulps for evaluation as well as for conducting bleaching experiments. During these studies, technical grade chemicals were used, except that of sodium sulphite, which was of analytical grade. During the course of pulping, the liquor to wood ratio of 4.5:1 was maintained using the following time schedule for heating the digester.

- Time from room temperature to 105^{o}C = 45 min
- Time from 105^{p}C to 170^{o}C = 30 min

The pulping studies were carried out using different ratios of sodium sulphite to sodium hydroxide in order to find the optimum ratio of these cooking chemicals. The cooking was also performed for varying time periods in order to reveal the effect of cooking time during the course of pulping. During cooking the digester pressure was reduced to zero by gas relief at 105^{o}C. At the end of the cooking cycle, the cooked chips and liquor were blown from the digester, and the cooked chips were passed through a Bauer refiner with a plate clearance of 0.1mm. The cooked pulps were washed on a laboratory flat stationary screen having 300 mesh wire bottom, disintegrated, screened through a Weverk vibratory flat screen with slot size of 0.15 mm, and evaluated for kappa number (TAPPI Method T236 cm-85), pulp yield, and spent liquor for sulphur dioxide, and pH (T628 cm-01) (Anonymous 2007). Different doses of anthraquinone (AQ), a carbohydrate stabilizer and an accelerator to delignification, were added at different ratios of sodium sulphite to sodium hydroxide to bring down the kappa number.

Bleaching Studies

The selected AS-AQ pulps were bleached with a CEHH sequence at 8% total chlorine charge. 62.5% of the total charge was charged in C-stage and the remaining 37.5% in two distinct hypochlorite stages 'H' (25% in H_1 and 12.5% in H_2). The chlorination stage (C) was done in capped plastic bottles at pH 1.92±0.02, pulp consistency 3%, and reaction time 45 min at 25±2 ^{o}C. Chlorinated pulp was extracted with NaOH (E-stage) at NaOH charge 1.5%, temperature 60±2 ^{o}C, pH 11.30, consistency 9%, and time 60 min. The hypochlorite, 1st and 2nd stages, were carried out in polyethylene bags at pH 11, reaction time 90 min, pulp consistency 9%, and temperature 45±2 ºC.

Preparation of Laboratory Handsheets and Testing

Unbleached and bleached *H. cannabinus*, *C. sativa*, and *H. sabdariffa* pulps were beaten in a PFI mill (T200 sp-96) at different beating levels. Laboratory handsheets of 60 g/m^2 were prepared (T221 cm-99) on a British sheet former, pressed, air-dried under atmospheric conditions, conditioned at 27±2^{o}C and 65±2% relative humidity, and tested for various physical strength properties including tear index (T414 om-98), tensile index (T494 om-01), burst index (T403 om-97), double folds (T403 om-97) (Anonymous, 2007), apparent density (GSM, T410 om-02) divided by thickness (T411 om-05), and Bendsten smoothness (IS:9894-1981) as per the Bureau of Indian Standards.

RESULTS AND DISCUSSION

The amount of sodium sulphite charged had a considerable influence on the rate of cooking. The OH^- differs greatly from SO_3^{2-} and HSO_3^{2-} both in its chemical nature and in its effects on the course of reaction with lignin and carbohydrates. The pH values (cold) were recorded during pulping at cooking conditions, and it was found that the pH in alkaline sulphite pulping dropped rapidly in the early stages of a cook, and at the end of pulping the pH ranged from 11.6 to 9.3 for pulping temperatures from 90 to 170 °C. Tables 1, 2, and 3 demonstrate that the alkali ratio had a strong impact on the extent and selectivity of delignification, and in particular influence on pulp yield and kappa number. When the total alkali ratio was fixed at 11% (as Na_2O), and the alkali ratio was varied (both expressed as Na_2O) from 0.0 to 0.80 at 170 °C for 120 min, and AQ dose of 0.075%, both pulp yield and kappa number decreased from 63.0 to 61.2% and 55.2 to 43.0 units for *H. cannabinus*. Similar trends were observed in the cases of *C. sativa* and *H. sabdariffa,* (Table 3, Sl. No. 1-5). An increase in alkali ratio from 0.5 to 0.70 accelerated delignification, but beyond that the delignification rate became very slow (Fig. 1). Statistical correlation of alkali ratio with pulp yield and alkali ratio with kappa number are shown in Fig. 2. Tables 1 through 3 reveal that when the alkali ratio was increased from 0.70 to 0.80, there was an increase in kappa number, but pulp yield remained almost constant (Tables 1 through 3 and Sl. No. 5). With increasing sodium sulphite percentage on the alkali ratio, the kappa number decreased sharply, but the total yield remained almost constant, which can be attributed to the decreasing alkalinity of the corresponding pulping liquors. Under these conditions carbohydrates were better preserved. Alkaline sulphite pulping offers the option to change the alkalinity of the cook by variation of the Na_2SO_3: NaOH ratio. Less NaOH in the cooking liquor reduces the alkaline attack on carbohydrates. When less alkali is added at the beginning of the cook, the extent of cellulose degrading reactions is restricted.

Table 1. Pulping Conditions and Characteristics of *H. Cannabinus* during Alkaline Sulphite-AQ Pulping Process

Sl. No.	Total alkali, as Na_2O	Alkali ratio	Na_2SO_3, as Na_2O	NaOH, as Na_2O	Time at max temp, min	AQ dose, %	pH of liquor				Pulp yield, %	Kappa number	Spent liquor	
							Initial liquor	At 105 °C	At max pulping temp	At the end of cook			SO_2, g/l	pH
1	11.0	0.00	0.00	11.00	120	0.075	13.6	13.0	12.7	11.6	63.0±2.9	55.2±0.8	0.0	11.5
2	11.0	0.50	5.50	5.50	120	0.075	13.2	11.0	10.3	9.9	62.5±2.7	47.4±0.7	5.6	9.8
3	11.0	0.60	6.60	4.40	120	0.075	13.2	10.8	10.2	9.7	61.8±2.5	43.8±0.6	6.2	9.7
4	11.0	0.70	7.70	3.30	120	0.075	13.1	10.5	10.0	9.6	61.5±2.3	40.0±0.5	6.8	9.6
5	11.0	0.80	8.80	2.20	120	0.075	13.1	10.4	9.8	9.3	61.2±2.1	43.0±0.4	7.2	9.4
6	11.0	0.70	7.70	3.30	150	0.075	13.1	—	—	—	61.0±2.0	37.5±0.3	6.6	9.5
7	11.0	0.70	7.70	3.30	90	0.075	13.1	—	—	—	61.7±2.2	43.5±0.2	6.7	9.4
8	11.0	0.70	7.70	3.30	120	0.050	13.1	—	—	—	61.4±2.4	43.0±0.1	6.8	9.5
9	11.0	0.70	7.70	3.30	120	0.100	13.1	—	—	—	61.3±2.1	39.1±0.3	6.7	9.5
10	12.5	0.00	0.00	12.50	120	0.075	13.7	13.2	12.8	11.7	59.6±1.9	50.8±0.2	0.0	11.6
11	12.5	0.50	6.25	6.25	120	0.075	13.3	11.0	10.6	10.2	59.3±1.8	42.2±0.4	5.8	10.2
12	12.5	0.60	7.50	5.00	120	0.075	13.2	10.8	10.3	9.8	59.1±1.7	38.8±0.3	6.4	9.7
13	12.5	0.70	8.75	3.75	120	0.075	13.2	10.7	10.2	9.7	58.7±1.6	35.0±0.1	7.0	9.7
14	12.5	0.80	10.00	2.50	120	0.075	13.1	10.5	10.0	9.4	58.3±1.5	38.0±0.4	7.5	9.5
15	12.5	0.70	8.75	3.75	150	0.075	13.1	—	—	—	57.8±1.6	33.2±0.3	6.9	9.6
16	12.5	0.70	8.75	3.75	90	0.075	13.1	—	—	—	58.5±1.7	37.6±0.4	7.1	9.5
17	12.5	0.70	8.75	3.75	120	0.100	13.1	—	—	—	58.2±1.4	34.2±0.5	7.0	9.5
18	12.5	0.70	8.75	3.75	120	0.050	13.1	—	—	—	58.3±1.3	36.8±0.4	7.0	9.6

Pulping conditions: Time from 30 to 105 °C =45 min, time from 105 to 170°C = 45 min, max pulping temp = 170 °C, liquor to wood ratio = 4.5:1, alkali ratio = Na_2SO_3/total alkali (as Na_2O)

Table 2. Pulping Conditions and Characteristics of *C. sativa* during Alkaline Sulphite-AQ Pulping Process

Sl. No.	Total alkali,as Na_2O	Alkali ratio	Na_2SO_3, as Na_2O	NaOH, as Na_2O	Time at max temp, min	AQ dose, %	pH of liquor: Initial liquor	pH of liquor: At 105 ^oC	pH of liquor: At max pulping temp	pH of liquor: At the end of cook	Pulp yield, %	Kappa number	Spent liquor: SO_2, g/l	Spent liquor: pH
1	11.0	0.00	0.00	11.00	120	0.075	13.6	12.9	12.6	11.5	63.4±3.1	56.0±0.8	0.0	11.5
2	11.0	0.50	5.50	5.50	120	0.075	13.2	11.1	10.2	9.9	62.4±2.9	47.5±0.6	5.5	9.8
3	11.0	0.60	6.60	4.40	120	0.075	13.2	10.9	10.0	9.7	62.0±2.7	43.5±0.5	6.1	9.7
4	11.0	0.70	7.70	3.30	120	0.075	13.1	10.3	9.9	9.6	61.8±2.6	40.8±0.3	6.7	9.6
5	11.0	0.80	8.80	2.20	120	0.075	13.0	10.2	9.6	9.3	61.7±2.4	42.8±0.6	7.3	9.5
6	11.0	0.70	7.70	3.30	150	0.075	13.1	—	—	—	61.5±2.1	38.0±0.6	6.7	9.5
7	11.0	0.70	7.70	3.30	90	0.075	13.1	—	—	—	61.8±1.9	42.7±0.5	6.8	9.4
8	11.0	0.70	7.70	3.30	120	0.050	13.2	—	—	—	61.4±1.8	42.5±0.4	6.8	9.5
9	11.0	0.70	7.70	3.30	120	0.100	13.1	—	—	—	61.7±1.7	38.8±0.4	6.7	9.4
10	12.5	0.00	0.00	12.50	120	0.075	13.6	13.2	10.7	11.6	61.7±2.0	51.4±0.7	0.0	11.6
11	12.5	0.50	6.25	6.25	120	0.075	13.3	11.0	10.3	9.7	61.4±1.6	43.8±0.6	5.6	9.6
12	12.5	0.60	7.50	5.00	120	0.075	13.3	10.6	10.2	9.7	60.8±1.5	38.4±0.6	6.3	9.6
13	12.5	0.70	8.75	3.75	120	0.075	13.2	10.5	10.2	9.7	60.7±1.1	35.5±0.5	7.1	9.7
14	12.5	0.80	10.0	2.50	120	0.075	13.2	10.4	10.1	9.7	60.5±1.3	37.0±0.4	7.4	9.6
15	12.5	0.70	8.75	3.75	150	0.075	13.2	—	—	—	60.0±1.2	34.0±0.2	6.9	9.6
16	12.5	0.70	8.75	3.75	90	0.075	13.2	—	—	—	60.6±1.4	37.6±0.4	6.8	9.5
17	12.5	0.70	8.75	3.75	120	0.100	13.2	—	—	—	60.2±1.5	34.2±0.3	7.2	9.5
18	12.5	0.70	8.75	3.75	120	0.050	13.2	—	—	—	60.5±1.3	37.3±0.1	7.0	9.5

Pulping conditions: Time from 30 to 105 ^oC =45 min, time from 105 to 170^oC = 45 min, max pulping temp = 170 ^oC, liquor to wood ratio = 4.5:1, alkali ratio = Na_2SO_3/total alkali (as Na_2O)

Table 3. Pulping Conditions and Characteristics of *H. sabdariffa* during Alkaline Sulphite-AQ Pulping Process

Sl. No.	Total alkali,as Na_2O	Alkali ratio	Na_2SO_3, as Na_2O	NaOH, as Na_2O	Time at max temp, min	AQ dose, %	pH of liquor: Initial liquor	pH of liquor: At 105 ^oC	pH of liquor: At max pulping temp	pH of liquor: At the end of cook	Pulp yield, %	Kappa number	Spent liquor: SO_2, g/l	Spent liquor: pH
1	11.0	0.00	0.00	11.00	120	0.075	13.6	13.0	12.6	11.5	62.4±3.0	54.8±0.6	0.0	11.4
2	11.0	0.50	5.50	5.50	120	0.075	13.3	11.1	10.2	9.8	62.0±2.5	47.9±0.8	5.7	9.7
3	11.0	0.60	6.60	4.40	120	0.075	13.2	10.7	10.2	9.6	61.6±2.3	44.5±0.9	6.2	9.7
4	11.0	0.70	7.70	3.30	120	0.075	13.1	10.4	10.0	9.6	61.4±1.9	40.5±0.5	6.9	9.6
5	11.0	0.80	8.80	2.20	120	0.075	13.0	10.3	9.9	9.5	61.7±2.0	42.3±0.7	7.3	9.5
6	11.0	0.70	7.70	3.30	150	0.075	13.1	—	—	—	61.1±1.5	38.0±0.8	6.5	9.6
7	11.0	0.70	7.70	3.30	90	0.075	13.1	—	—	—	61.5±1.7	42.2±0.3	6.6	9.5
8	11.0	0.70	7.70	3.30	120	0.050	13.1	—	—	—	61.2±1.6	43.2±0.6	6.8	9.5
9	11.0	0.70	7.70	3.30	120	0.100	13.1	—	—	—	61.6±1.5	38.8±0.4	6.7	9.5
10	12.5	0.00	0.00	12.50	120	0.075	13.7	13.1	10.7	11.6	59.8±1.3	50.5±0.6	0.0	11.5
11	12.5	0.50	6.25	6.25	120	0.075	13.3	11.0	10.3	9.8	59.5±1.4	43.2±0.5	5.7	9.7
12	12.5	0.60	7.50	5.00	120	0.075	13.2	10.7	10.2	9.7	59.0±1.2	39.5±0.3	6.4	9.7
13	12.5	0.70	8.75	3.75	120	0.075	13.2	10.6	10.1	9.7	58.5±1.1	35.3±0.2	7.1	9.7
14	12.5	0.80	10.00	2.50	120	0.075	13.1	10.4	10.0	9.6	58.3±1.3	37.0±0.4	7.6	9.6
15	12.5	0.70	8.75	3.75	150	0.075	13.2	—	—	—	58.8±1.4	32.8±0.3	7.0	9.6
16	12.5	0.70	8.75	3.75	90	0.075	13.2	—	—	—	58.0±1.2	38.0±0.2	7.0	9.6
17	12.5	0.70	8.75	3.75	120	0.100	13.2	—	—	—	58.2±1.2	34.0±0.1	7.0	9.5
18	12.5	0.70	8.75	3.75	120	0.050	13.2	—	—	—	58.7±1.1	38.4±0.1	7.1	9.6

Pulping conditions: Time from 30 to 105 ^oC =45 min, time from 105 to 170^oC = 45 min, max pulping temp = 170 ^oC, liquor to wood ratio = 4.5:1, alkali ratio = Na_2SO_3/total alkali (as Na_2O)

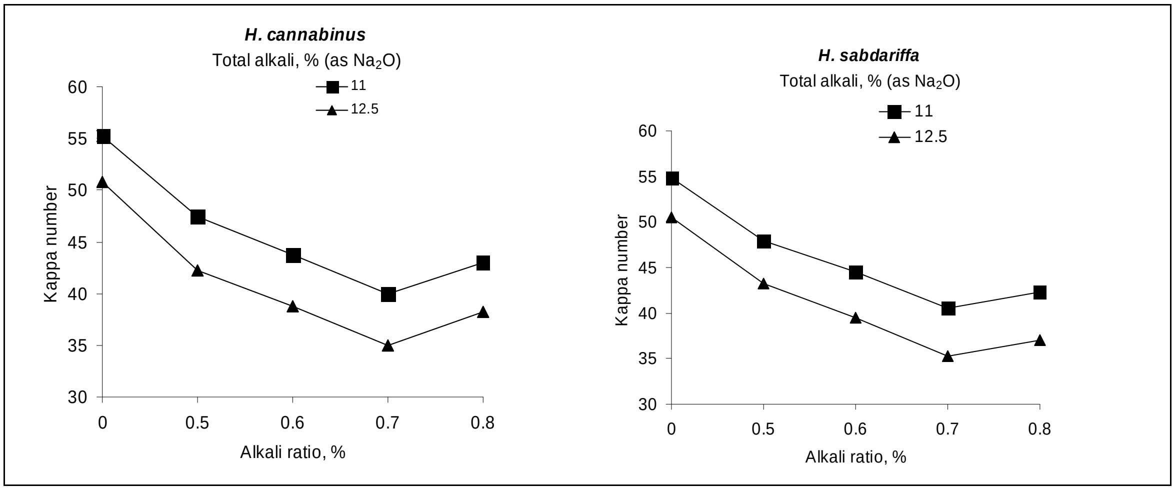

Fig 1. Plots of kappa number *vs.* alkali ratio during alkaline sulphite-AQ pulping

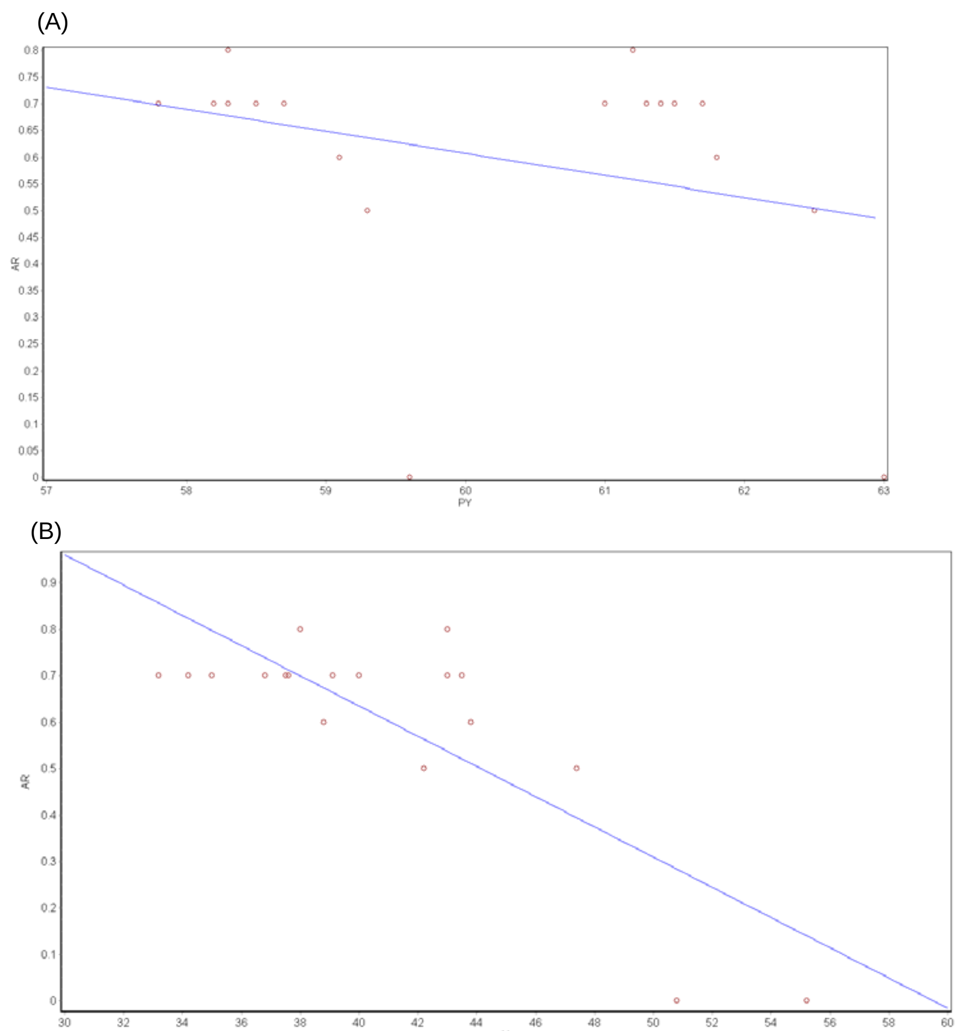

Fig 2. Statistical correlation of (A) alkali ratio (AR) vs pulp yield (PY) (B) alkali ratio (AR) vs. kappa number (K)

Moreover, lignin sulphonation, and thus lignin dissolution, was promoted by NaOH splitting because of the higher percentage of sodium sulphite in the total chemical charge in the initial cooking phase. For a given reaction rate, the cooking time must be controlled to achieve the desired degree of cooking, as measured by the pulp yield or lignin content (kappa number). When maximum cooking time was increased from 120 to 150 min at an alkali ratio of 0.70, while keeping other conditions constant, there was a slight decrease in pulp yield, but kappa numbers were reduced from 4.3 to 5.5 units for *H. cannabinus*, *H. sabdariffa*, and *C. sativa* (Tables 1 through 3, Sl. No. 6). However, on decreasing delignification time from 120 to 90 min under the same conditions, *H. cannabinus*, *C. sativa*, and *H. sabdariffa* produced slightly higher pulp yields, but kappa number decreased from 4.2 to 6.0 units (Table 1-3, Sl. No. 7). The increased time had little influence on the amount of lignin removed, and may possibly even have caused redeposition in cases where the digestions were made with small amounts of sulphite. When AQ doses varied from 0.050 to 0.10% (on oven dry pulp basis) at an alkali ratio of 0.70, while keeping other conditions the same (Tables 1-3, Sl. Nos. 8 and 9), pulp yield remained almost constant, but the kappa number dropped from 3.7 to 4.4 units for *C. sativa*, *H. cannabinus*, and *H. sabdariffa* (Tables 1-3, Sl. No. 8-9).

Likewise, when total alkali ratio was fixed at 12.5% (as Na_2O) while varying the alkali ratio from 0.0 to 0.80 at 170 ^oC for 120 min and with an AQ dose of 0.075%, *H. cannabinus*, *H. sabdariffa*, and *C. sativa* followed the same trend (Tables 1-3, Sl., No. 10-14) as in case of (Table 3, Sl. No. 1-5). The drop in pulp yield at a total alkali of 12.5% (as Na_2O), in addition to the peeling reaction, alkaline hydrolysis (depolymerization) of the polysaccharide chains occurred, and the pulp was subjected to further degradation reactions (secondary peeling) (Hinrichs 1967; Lal et al. 2010).

Pulp yields of 57.8% (kappa number 33.2) for *H. cannabinus*, 60.0% (kappa number 34.0) for *C. sativa*, and 58.0% (kappa number 32.8) for *H. sabdariffa* were obtained when total alkali was fixed at 12.5%, and AQ dose 0.075%, varying alkali ratio from 0.80 to 0.70, and maximum cooking time from 120 to 150 min. Under the same conditions, when maximum cooking time decreased from 150 to 90 min, *H. cannabinus*, *H. sabdariffa*, and *C. sativa* followed the same pattern (Table 1-3, Sl. No. 16) as in the case where the total alkali was fixed at 11% (Table 1-3, Sl. No. 7). A high initial rate of delignification was decreased steadily, with an appreciable amount of the lignin being quite resistant. The high initial delignification rate, which is common to a varying degree for nearly all delignification processes, is partly due to a higher initial alkaline concentration in the cooking liquor. It may also correspond to easily assessable, and less condensed lignin moieties, where their high rates of dissolution coincide with that of wood polyoses. The interaction of lignin and hemicelluloses in the wood was probably one of the major factors affecting the rate and selectivity of the delignification during the later stages, whether this involves a primary or secondary valence bond or both. At the same alkali ratio and maximum cooking time 120 min, the decrease in pulp yield was almost negligible, but the kappa number increased from 2.6 to 4.4 units for *H. cannabinus*, *C. sativa*, and *H. sabdariffa*, respectively, when AQ dose was reduced from 0.100 to 0.050%. The addition of AQ apparently did not increase the pulp yield, though the kappa numbers were reduced substantially. The AQ dosage should be between 0.05 and 0.1%, and 0.1% is the upper limit for AQ application regulated by the Food and

Drugs Administration in the USA. An AQ dosage of 0.075 may be taken as being the optimum for AS-AQ pulping of *H. cannabinus*, *C. sativa*, and *H. sabdariffa*. The AQ functions as a redox catalyst that facilitates ß-ether cleavage, producing lower molecular weight lignin fragments, thereby increasing the delignification rate by transferring electrons from carbohydrates to lignin. Thus, the degradation, and solubilization of lignin are accelerated (faster delignification), and by end group oxidation, the carbohydrates are stabilized against attack by alkali (higher yield) (McDonough et al. 1980).

At total alkali dose of 12.5%, Na_2SO_3:NaOH ratio of 8.75:3.75 (as Na_2O), AQ dose of 0.075%, and at a maximum cooking time of 120 min, *C. sativa* produced maximum pulp yield (60.7%), while *H. cannabinus* and *H. sabdariffa* produced almost the same pulp yield. Kappa number in case of all the three raw materials was almost the same.

The *H. cannabinus* and *H. sabdariffa* AS-AQ pulps were easier to bleach, and required lesser chemicals. Due to high initial brightness (about 45%, ISO) the number of bleaching stages could be reduced. The carbohydrate loss during bleaching was less than that of kraft and soda pulps. An unexpected finding was the equalization of the viscosity. CEHH bleached pulp of *H. cannabinus* showed a pulp brightness of 81.2 % (ISO), bleached pulp yield of 49.6%, and pulp viscosity 11.6 cps. Similarly, *C. sativa* showed a brightness of 82.6% (ISO), bleached pulp yield 51.5%, and pulp viscosity 11.9 cps; *H. sabdariffa* showed a pulp brightness of 81.5 %(ISO), bleached pulp yield of 49.3%, and pulp viscosity 11.6 cps (Table 4). Among the three, the brightness of *H. cannabinus*, and *H. sabdariffa* AS-AQ pulps subjected to the same bleaching conditions were almost similar but *C. sativa* produced maximum pulp brightness. Between 0.9 and 1.1% combined SO_2 was a favorable condition for easy-bleaching pulp, while with a higher percentage of combined SO_2; the pulp became harder to bleach unless the cooking time was considerably increased. Since the alkaline sulphite process in its original form is found to be less selective than the kraft process with respect to delignification in the bleachable range, one would expect that the cost of bleaching chemicals would be correspondingly higher; this however, is not the case in actual practice. The *H. cannabinus*, *C. sativa*, and *H. sabdariffa* alkaline sulphite pulps are somewhat easier to bleach, have higher brightness ceiling, and suffer considerably less brightness reversion.

Both unbleached and bleached pulps of *H. cannabinus*, *C. sativa*, and *H. sabdariffa* were beaten to different ^{o}SR levels. The initial beating level of unbeaten pulps was 17-18 ^{o}SR with a drainage time of 3s. These results clearly indicate that the apparent density was almost directly proportional to the slowness of pulps. The unbeaten, bleached pulps had a higher initial apparent sheet density. These results also indicate that both the tear index and porosity were indirectly proportional to the freeness level, i.e. both of these decreased as a result of an increase in beating levels. The apparent density, burst index, tensile index, double folds were in direct proportion with slowness, i.e. all these increased as a result of an increase in slowness. All the strength properties increased up to a certain level of ^{o}SR, after which the strength properties showed a declining trend as a result of over-beating or higher slowness values, except for tear index. Therefore, tearing energy required to pull the fibers from the mesh will be slightly higher.

Table 4. Bleaching Conditions and Results of *H. Cannabinus*, *C. sativa*, and *H. sabdariffa* for Alkaline Sulphite-AQ Pulping Process

Sl. No.	Particulars	*H. Cannabinus*	*C. sativa*	*H. sabdariffa*
1	Unbleached pulp kappa number	35.0	35.5	35.3
2	Chlorination stage			
	Cl_2 applied as available Cl_2 on pulp, %	5.00	5.00	5.00
	Cl_2 consumed as available Cl_2 on pulp, %	4.97	4.98	4.98
	Final pH	1.90	1.94	1.92
3	Extraction stage (E)			
	NaOH applied on pulp, %	1.5	1.5	1.5
	Initial pH	11.30	11.25	11.30
	Final pH	10.10	10.10	10.22
4	Hypochlorite Ist stage (H_1)			
	Hypochlorite applied as available Cl_2 on pulp, %	2.0	2.0	2.0
	Hypochlorite consumed as available Cl_2 on pulp, %	1.95	1.94	1.94
	Final pH		8.25	
5	Hypochlorite IInd stage (H_2)			
	Hypochlorite applied as available Cl_2 on pulp, %	1.0	1.00	1.0
	Hypochlorite consumed as available Cl_2 on pulp, %	0.93	0.92	0.94
	Final pH	8.00	8.10	8.10
6	Total Cl_2 applied on the pulp, %	8.00	8.00	8.00
7	Total Cl_2 consumed on the pulp, %	7.85	7.86	7.86
8	Bleaching losses, %	9.12	9.00	9.24
9	Pulp yield, %	49.6±0.4	51.5±0.5	49.3±0.6
10	Brightness, % (ISO)	81.2±0.7	82.6±0.8	81.5±0.8
11	Viscosity, CED (0.5) cps	11.6±	11.9±	11.6±

Bleaching conditions	C	E	H_1	H_2
Consistency, %	3	9	9	9
Temp, ^oC	25±2	60±2	45±2	40±2
Reaction time, min	45	60	90	90
Final pH	1.90	10.10	8.20	8.30

Further, cutting action, external and internal fibrillations, and brushing action bring the tear index down, whereas all other properties depending upon hydrogen bonding improve with pulp beating. It is obvious from these results that these pulps should not be beaten to a slowness range beyond 42±2 ^{o}SR (Table 5).

Table 5. Mechanical Strength Properties of Alkaline Sulphite-AQ Pulps of *H. cannabis*, C. sativa, and *H. sabdariffa*

Plant species	Beating time, min	Beating level, ^{o}SR	Drainage time, s	*Apparent density, g/cm^3	Burst index, kPam^2/g)	Tensile index, Nm/g	Tear index, mNm^2/g	*Porosity Bendtsen, ml/min)	Double fold, numbers	*Brightness, % (ISO)
Unbleached pulp										
H. cannabinus	0	17	3	0.62	1.1±0.21	17.4±1.12	7.5±0.23	1200	20±2.5	–
	5	30	11	0.65	3.2±0.18	58.2±1.22	9.0±0.24	340	180±5.3	–
	10	41	17	0.70	4.7±0.21	70.6±1.25	8.0±0.27	180	350±2.7	–
	15	50	24	0.73	8.0±0.22	70.8±1.30	7.5±0.12	120	450±6.5	–
	20	62	47	0.75	4.7±0.25	69.9±1.60	6.6±0.23	90	620±7.2	–
C. sativa	0	18	4	0.64	2.8±0.11	35.6±1.32	8.0±0.25	1200	70±3.5	–
	5	27	14	0.69	4.4±0.13	68.0±1.55	9.4±0.23	320	340±1.8	–
	10	34	20	0.74	5.4±0.16	73.9±2.11	8.1±0.27	160	720±5.6	–
	15	41	29	0.79	6.1±0.08	79.0±2.91	7.4±0.25	110	950±4.5	–
	20	57	45	0.81	5.8±0.10	78.5±2.65	6.7±0.17	80	1150±8.5	–
H. sabdariffa	0	16	3	0.61	1.2±0.15	18.0±0.55	7.3±0.20	1300	23±3.2	–
	5	29	12	0.69	3.2±0.23	57.1±1.35	8.8±0.22	330	210±2.6	–
	10	40	18	0.75	4.7±0.13	70.9±1.40	8.0±0.15	180	360±2.8	–
	15	52	25	0.79	4.9±0.19	71.6±1.73	7.4±0.17	110	470±4.6	–
	20	64	48	0.80	4.7±0.17	69.9±1.62	6.6±0.18	80	650±7.8	–
Bleached pulp										
H. cannabinus	0	18	3	0.62	1.0±0.15	16.5±1.12	7.2±0.20	900	5±6.4	81.2
	5	31	11	0.65	3.0±0.17	51.5±1.23	8.2±0.18	260	4±2.7	77.2
	10	41	18	0.69	4.7±0.14	68.5±1.53	7.4±0.22	160	160±2.5	73.5
	15	51	25	0.73	4.8±0.12	69.4±1.74	6.6±0.23	120	250±3.6	72.0
	20	64	48	0.77	4.7±0.10	68.6±1.61	6.1±0.25	90	300±4.3	71.0
C. sativa	0	19	4	0.65	2.6±0.11	35.9±2.23	8.8±0.15	850	40±3.7	82.6
	5	28	15	0.69	4.7±0.08	70.8±3.02	9.2±0.16	230	285±3.8	78.6
	10	34	22	0.76	5.3±0.19	78.6±2.81	8.5±0.20	120	500±4.1	74.8
	15	40	30	0.79	5.6±0.18	79.6±2.09	7.4±0.09	100	605±4.6	73.5
	20	58	46	0.83	5.6±0.24	79.5±2.14	6.8±0.15	80	770±5.6	72.2
H. sabdariffa	0	18	4	0.63	2.6±0.17	17.5±1.17	7.0±0.17	950	4±2.8	81.5
	5	30	13	0.66	4.7±0.18	56.2±1.29	8.3±0.16	260	38±2.9	77.6
	10	41	19	0.70	5.3±0.19	67.8±2.29	7.3±0.28	150	170±3.1	75.4
	15	52	27	0.75	5.6±0.20	68.8±2.05	6.8±0.30	110	260±3.5	71.7
	20	66	50	0.79	5.6±0.23	68.0±2.16	6.2±0.21	90	310±3.6	70.5
Bleached softwood pulp	–	40	–	–	8.6	100.4	10.3	–	–	–
Bleached hardwood pulp	–	40	–	–	3.6	47.8	9.8	–	–	–

Total alkali=12.5% (as Na_2O), alkali ratio= 0.70, AQ dose= 0.075%, max pulping temperature 170 ^{0}C, pulping time 120 min and liquor to raw material ratio= 4.5:1, All experiments were carried out in triplicate and experimental results were represented as the mean ± standard deviation of three identical values. *= average of ten values.

The bleached pulps of *H. cannanbinus*, and *H. sabdariffa* attained a beating level of 40±1 ^{o}SR in 10 min, whereas *C. sativa* required 15 min. Each fiber has primary wall and secondary wall layers with specific alignments of microfibrils. Microfibrils are bundles of cellulose molecules, and their orientation influences the characteristics of a pulp fiber (Smook 2001). The difference in beating time might be attributed to microfibrillar angle, morphological characteristics, and chemical composition of fibers. Compared to bleached hardwood (Indonesian origin) and softwood (Canadian origin) pulps burst, tear and tensile indexes of *H. cannanbinus*, *H. sabdariffa*, and *C. sativa* stood below softwood and above hardwood pulps. Generally, the bast part accounted for about 25-35% of stem mass, and a woody core part comprised the remainder. The mechanical strength properties for *H. cannanbinus*, *H. sabdariffa*, and *C. sativa* might be achieved by increasing the bast fibers portion.

The alkaline sulphite unbleached and bleached pulps of these plants showed good strength properties, especially burst and tensile. Table 6 shows that the mechanical strength properties of AS-AQ pulp of *H. cannabinus* (except tear), *C. sativa* (except burst index), and *H. sabdariffa* (except tear index) were superior to those of the soda and kraft pulping processes. The mechanical strength properties of *C. sativa* were significantly better than that of *H. cannabinus*, and *H. sabdariffa*.

Table 6. Comparison of Properties of Soda, Kraft, and AS-AQ Pulps of *H. cannabinus*, *C. sativa*, and *H. sabdariffa*

Parameters	*H. cannabinus*			*C. sativa*			*H. sabdariffa*		
	*Soda (Upadhyaya et al. 2008)	*Kraft (Dutt et al. 2009)	AS-AQ	*Soda (Dutt et al. 2010)	*Kraft (Dutt et al. 2008)	AS-AQ	*Soda (Upadhyaya et al. 2008)	*Kraft (Dutt et al. 2009)	AS-AQ
Max cooking temp, ^{0}C	165	160	170	165	165	170	165	160	170
Max cooking time, min	180	120	120	180	120	120	180	120	120
Active alkali, % (as Na_2O)	18	15	–	16	16	–	18	15	–
Sulphidity, %	–	20	–	–	20	–	–	20	–
Total alkali, % (as Na_2O)	–	–	12.5	–	–	12.5	–	–	12.5
Alkali ratio	–	–	0.70	–	–	0.70	–	–	0.70
Pulp yield, % (Unbleached)	–	51.8	58.7	49.5	54.3	60.5	–	51.5	58.5
Kappa number	–	30.2	35.0	33	29	35.5	–	30.0	35.3
Pulp yield, % (Bleached)	–	42.80	49.58	45.0	49.0	51.50	–	41.90	49.26
Brightness, % (ISO)	76.0	78.5	81.2	84	82.0	82.6	–	79.0	81.5
Pulp viscosity, CED (0.5%) cps	9.5	11.2	11.6	9.0	16.2	11.9	9.6	11.3	11.6
Beating level, ^{0}SR	42	41	41	41	40	41	42	40	40
Apparent density, g/cm^3	0.71	0.70	0.70	–	–	0.79	0.73	0.71	0.75
Burst index, kPa.m^2/g	3.39	4.12	4.72	4.65	6.60	6.08	3.53	4.51	4.68
Tensile index, N.m/g	54.0	62. 8	70.6	70.7	79.0	79.0	55.3	62.0	70.9
Tear index, mN.m^2/g	8.1	9.3	8.0	5.5	8.0	7.4	8.3	8.8	8.0
Porosity (Bendtsen), mL/min	260	205	180	–	–	110	250	225	180
Double folds, number	170	200	350	192	290	950	240	250	360

* Pulping results at optimum pulping conditions and paper properties at optimum beating level

The main characteristics of the spent liquor observed from the results (Table 7) were low solids, high proportion of inorganic, low viscosity, and low heating value (HV). The HV of the lignin extracted from hardwood is 25110 kJ/kg and lower than HV (26900 kJ/kg) of the lignin extracted from softwood (Frederick 1997). The HV of black liquor generated from *H. cannanbinus*, *H. sabdariffa*, and *C. sativa* during AS-AQ pulping varies from 11050 to 11160 kJ/kg in contrast to HV of black liquor of pine, which varies from 13400 to 15500 kJ/kg (Frederick 1997). The calorific value is strongly influenced by liquor composition. Organic components contribute to calorific value, whereas inorganic contents act as diluents. Viscosity is a very important property for black liquor handling (pressure drop), heat transfer, and mixing operations. Brookfield viscosity at 30 ^{o}C of black liquor of these raw materials was almost similar. The black liquor viscosity is influenced by its chemical composition, mainly by the concentration of organic compounds, such as lignin and polysaccharides (Frederick 1997). The three fundamental significant characteristics in the field of inorganic chemicals are: (a) volatile mercaptans cannot form from methoxyl groups of lignin and hemicelluloses, (b) H_2S gas cannot be liberated from solutions, and (c) sulphides (oxidation state-2) can be replaced by sulphites (oxidation state+4).

Table 7. Alkaline Sulphite-AQ Spent Liquor Characteristics *H. cannabis*, C. sativa, and *H. sabdariffa* at Optimum Pulping Conditions

Sl. No.	Particulars	*H. cannabinus*	C. sativa	*H. sabdariffa*
1	Black liquor solid, %	22.95	23.18	23.96
2	Inorganic, %	28.80	29.54	29.15
3	Organic, %	71.20	70.46	70.85
4	Calorific value, kJ/kg	11050	10980	11160
5	Brook field viscosity at 30 ^{o}C L_v spindle no 1cp	12.50	12.35	12.70
6	pH of liquor at 30 ^{o}C	9.7	9.7	9.7
7	$^{o}T_w$ at 30 ^{o}C	17.0	18.0	17.5

CONCLUSIONS

The long digestion time required for alkaline sulphite pulping of *H. cannabinus*, *C. sativa*, and *H. sabdariffa* pulps can be reduced by increasing the alkalinity of cooking liquors to a pH level of 10 or above, while still producing pulp superior to kraft. The biggest drawback of AS-AQ pulping is the slow rate of delignification. With increased alkalinity, the rate of delignification also increases and approaches to that of kraft. The selectivity at moderate alkalinity was superior to, and at high alkalinity is the same as kraft. The proportion of sodium hydroxide greatly influenced the rate of delignification during alkaline sulphite pulping of *H. cannabinus*, *C. sativa*, and *H. sabdariffa*.

The AS-AQ pulping process at intermediate alkalinity is characterized by unique maxima of delignification, pulp, and viscosity.

The AS-AQ process produces high pulp yield (6-10% higher) along with light colored pulp having a brightness about 45% (ISO), and kappa number in the vicinity of 34. The AS-AQ pulps are stronger than conventional kraft pulp. The AS-AQ pulp is easier to bleach, and it has great potential for the use of chlorine-free bleaching sequences. The results of this study indicate that AS-AQ pulping and CEHH bleaching is a convincing alternative to produce high-quality pulp from *H. cannabinus*, *C. sativa*, and *H. sabdariffa* for writing and printing paper.

Most of the problems of the kraft process would simply disappear when using the AS-AQ process in the absence of volatile odorous substances. No precautions would be necessary from the digester to liquor combustion unit. The modern sulphite recovery system has made it possible to achieve a closed system of mills employing the AS-AQ process. Thus, AS-AQ can be practiced within acceptable environmental limits. The alkaline sulphite unbleached and bleached pulps show good mechanical strength properties, especially burst and tensile strength.

REFERENCES CITED

Abrahamson, L., and Wright, L. (2000) "The status of short-rotation woody crops in the U.S," In: Jandl, R. et al. (eds.), *Proceedings, XXI World Forestry Congress Volume 2- Abstract of Group Discussions*, Kuala Lumpur, Malaysia, August 5-12, pp. 9.

Atchison, J. E. (1996) "Twenty-five years of global progress in non-wood plant fiber repulping," *Tappi J.* 70(10), 87-95.

Chang, F., and Lee, H. (1991) "The pulp properties of some non-wood plants," *Agricultural Report, Taipei, Taiwan*, 40(2), 119-136.

De Groot, B., Dam van, J. E. G., Zwan van dar, R. P., and Riet van't, K. (1994). "Simplified kinetic modelling of alkaline delignification of hemp woody core," *Holzforschung* 48 (3), 207-214.

Dutt, D., Rao, G. N., Tiwary, K. N., and Upadhyaya, J. S. (1998) "Studies on use of *Cannabis sativa* and *Ipomea carnea* for manufacturing of Razor blade wrapper," *IPPTA J*. 10 (2), 63-68.

Dutt D., Tyagi, C. H., Malik, R. S., and Upadhyaya, J. S., (2003) "Development of specialty paper is an art: Barrier paper from indigenous raw materials Part –VII," *J. Sci. Ind. Res*. 62(7), 694-98.

Dutt, D., Upadhyaya, J. S., Malik, R. S., and Tyagi, C. H. (2004) "Studies on pulp and paper-making characteristics of some Indian non-woody fibrous raw materials: Part-II," *J. Sci. Ind. Res*. 63(2), 58-67.

Dutt, D., Upadhyaya, J. S., Malik, R. S., and Tyagi, C. H. (2005) "Studies on pulp and paper-making characteristics of some Indian non-woody fibrous raw materials: Part-I," *Cellulose Chem. Technol.* 39 (1-2), 115-128.

Dutt, D., Upadhyaya, J. S., Tyagi, C. H., Kumar, A., and Lal, M. (2008) "Studies on *Ipomea carnea* and *Cannabis sativa* as an alternative pulp blend for softwood: An optimization of kraft delignification process," *Ind. Crops Prod*. 28, 128-136.

Dutt, D., Upadhyaya, J. S., Singh, B., and Tyagi, C. H. (2009) "Studies on *Hibiscus cannabinus* and *Hibiscus sabdariffa* as an alternative pulp blend for softwood: An optimization of kraft delignification process," *Ind. Crops Prod*. 29, 16-26.

Dutt, D., and Tyagi, C. H. (2010) "Studies on *Ipomea carnea* and *Cannabis sativa* as an alternative pulp blend for softwood: Optimization of soda pulping process," *J. Sci.*

Ind. Res. 69 (6), 460-467.
Frederick, W. J. (1997). "A description of how new source requirements apply," In: *Kraft Recovery Boilers*, T. N. Adams, T. M. Grace, M. Hupa, K. Lisa, A. K. Jones, and H. Tran (eds.), TAPPI Press, New York, ISBN 0-9625985-9-3, Ch. 3, 381.
Han, J. S., Miyashita, E. S., and Spielvogel, S. J. (1999) "Properties of kenaf from various cultivars, growth and pulping conditions," *5th Chemical Congress of North America*, The American Chemical Society, Cancun, Quintana Roo, Mexico.
Hinrichs, D. D. (1967) "The effect of kraft pulping variables on delignification," *Tappi J*. 50(4), 173-175.
Horn, R. A., Wegner, T. H., and Kugler, D. E. (1992). "Newsprint from blend of kenaf CTMP and deinked recycled newsprint," *Tappi J*. 75(12), 69-72.
Hurter, R. W., and Riccio, F. A. (1998) "Why CEOS don't want to hear about nonwoods—or should they?" In: *TAPPI Proc. Non-wood Fiber Symp.*, Atlanta, 1-11.
Lal, M., Dutt, D., Tyagi, C. H., and Upadhyay, J. S. (2010) "Characterization of *Anthocephalus cadamba* and its delignification by kraft pulping," *Tappi J.* 9(3), 30-37.
McDonough, T. J., and Van Drunen, V. J. (1980) "Pulping to low residual lignin contents in the kraft-anthraquinone and kraft processes," *TAPPI J.* 63(11), 83-87.
Moore, C. A., Trotter, W. K., Corkern, R. S. and Bagby, M. O. (1976) "Economic potential of kenaf production," *Tappi J*. 59(1), 117-120.
Nieschlag, H. J., Nelson, G. H., and Wolff, I. A. (1961) "A search for new fiber crops," *Tappi J*. 44(7), 515-516.
Nelson, G. H., Clark, T. F., Wolff, I. A., and Jones, Q., (1966) "A search for new fibre crops: analytical evaluation," *Tappi J*. 49(1), 40.
Patt, R., Kordsachia, O., and Rose, B. (2001) "New developments in sulphite pulping," In *7th Brazilian Symp. Chem. Lignin Other Wood Components: Oral Presentations Book*, Silva, F. T., and Ferraz, A. (eds.), Belo Horizonte, Brazil, pp. 107-113.
Smook, G.A., (2001) "Characteristics of wood and wood pulp fibers" In: *Handbook for Pulp and Paper Technologists*, Angus Wilde Publications, Vancouver, 10-11.
Thomas, A. R. (1970) "Recycling kenaf paper: A commercial experience," *The American Chemical Society*, 5th Chem. Congress .North Amer., Cancun, Quintana Roo, Mexico.
Upadhyaya, J. S., and Dutt, D. (1991) "Studies on alkaline sulphite pulping of *Sesbania aculeate*," *IPPTA J.* 36 (3), 174-183.
Upadhyaya, J. S., Dutt, D., Singh, B., and Tyagi, C. H. (2008) "Studies on *Hibiscus cannabinus* and *Hibiscus sabdariffa* as an alternative pulp blend for softwood: An optimization of soda pulping process," *Ind. J. Chem. Technol*. 15(3), 77-286.
Wang, D. L. K., Ramirez, F., and Patt, R. (1987) "Alkaline sulphite–anthraquinone pulping of bagasse with or without the addition of ethanol," *Holzforschung* 41(6), 383-388.
Wang, D. L. K., and Patt, R. (1989) "Alkaline sulphite–anthraquinone pulping of bagasse," *Holzforschung*, 43(4), 261-264.
Watson, A. J. (1974-75). "Kenaf as a source of papermaking fiber," *Division of Chemical Technology*, *Research Review CSIRO*, 34-46.

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