STUDIES ON *HIBISCUS CANNABINUS*, *HIBISCUS SABDARIFFA*, AND *CANNABINUS SATIVA* PULP TO BE A SUBSTITUTE FOR SOFTWOOD PULP- PART 2: SAS-AQ AND NSSC-AQ DELIGNIFICATION PROCESSES

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Hibiscus cannabinus, *Cannabis sativa*, and *Hibiscus sabdariffa*, fast growing productive annual plants, could provide fiber necessary to partially alleviate the world's fiber deficit. The present study aimed at producing high yield pulp and the best mechanical strength properties with minimum impact on environment by SAS-AQ, and NSSC-AQ pulping processes. A total alkali of 13% (as Na_2O), an alkali ratio of 0.80, and a Na_2SO_3 charge 11.70% (as Na_2O) were found optimum to reduce maximum kappa number. A lower kappa number and good strength properties were achieved by increasing total alkali and Na_2SO_3 charge. SAS-AQ pulps showed good response towards CEHH bleaching. The NSSC-AQ pulping was conducted at a total alkali charge of 8% (as Na_2O) by varying the ratio of sulphite-to-carbonate (100:0-0:100), and cooking time (60-120 min) at 160^0C. A ratio of sulphite-to-carbonate 60:40 was suitable for corrugating medium (cooking time 60 min), while a ratio of sulphite-to-carbonate 70:30 showed better strength properties (longer cooking time).

Keywords: H. cannabinus-kenaf; C. sativa-true hemp; H. sabdariffa-roselle; ASA-AQ pulping; NSSC-AQ pulping; CEHH bleaching; Pulp properties; Waste liquor

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INTRODUCTION

The paper industry worldwide is facing scarcity of cellulosic fibres, and this limitation is an issue not only for fibre deficient nations. North America as well as Europe have started taking into account non-wood fibre utilization (Paavilainen 1998). Therefore, non-wood pulping has picked up momentum during the last 40 years, and the share of non-wood pulp has increased from 7% to 12% (Ates et al. 2008). This large increase in non-wood pulp production motivates research activities worldwide, and various research groups have initiated research to improve non-wood pulping processes that are technically and economically viable with minimum impact on the environment. Non-wood plants offer several advantages including short growth cycle, moderate irrigation and fertilization requirements, as well as low lignin content, which alleviate energy and chemical requirements during pulping (Hurter and Riccio 1998; Watson 1974-75). Such research covers a wide range from conventional soda pulping of bagasse and cereal straw to reeds, bamboo, date palm tree branches, and rachis (Khristova et al. 2005). Kenaf (*H. cannabinus*) and roselle (*Hibiscus sabdariffa*) have been identified by the U.S. Department of Agriculture as viable substitutes for trees as a source of pulp for the papermaking process (Nieschlag et al., 1961; Han et al. 1999). Kenaf and roselle 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 pulps in their general papermaking, whereas those from the woody fractions are more like hardwood pulps but drain more slowly and have lower tearing strength (Dutt et al. 2008; Dutt et al. 2009). Morphological characteristics of core fibers of *H. cannabinus* and *H. sabdariffa* closely resemble to that of softwood except for fiber length, which can be compensated by long bast fibers (Dutt et al. 2009). *C. sativa* (true hemp) has traditionally been regarded as material for cordage and textiles. The long bast fibres resemble those of softwood fibres (Dutt et al. 1998); hemp core fibres are comparable with hardwood fibre (De Groot et al. 1994; Upadhyaya and Dutt 1991).

Among conventional pulping processes, the neutral sulphite semi-chemical process (NSSC) is surviving, maintaining its relative importance. A new and potentially very important development in sulphite pulping is the moderately alkaline sulphite, semi-alkaline sulphite or neutral sulphite anthraquinone (AQ) process, all terms used to describe the same new process. Even when the NSSC process is generally considered only for the production of hardwood corrugating medium, the current trend is to use it as a partial kraft pulp replacement in linerboard and bag grades (von Koeppen et al. 1986; Phillips et al. 1991; Odom et al. 1991; Farrington et al. 1989). In addition, bleached NSSC pulp is used to produce printing and writing papers, business forms, reply cards, and tissue paper (NLK Consultants 1992). It has also been suggested that NSSC pulping is more flexible than the kraft process. It provides higher yields for similar development of strength characteristics. At the same yield, NSSC pulps are more easily bleached, and they require less energy to be refined (Phillips et al. 1991). Traditionally neutral sulphite pulping has been used for producing coarse pulps in high yield, mainly from hardwoods. There is no other single pulping process that is as versatile as sulphite. It can produce well-defined marketable pulp products over a range of 30 to 90% yield and over a pH range of 1 to 13. Conventional sulphite is characterized, among other things, by its high unbleached brightness and moderate physical strengths. Its high initial brightness and subsequent ease of bleaching are of insignificant economic importance. Perhaps the most promising development in the past few years for the production of kraft-like sulphite pulp has been the discovery of neutral sulphite pulping with AQ addition, producing pulps that are very close to conventional kraft pulps in physical strength, but at significantly higher in yield (Dutt et al. 2010; Ingruber et al. 1982; Hauki and Reilama 1984). Several investigations have been carried out to accelerate pulp delignification and gain higher yields by addition of AQ in *C. sativa* (Dutt et al. 2008), *H. sabdariffa* (Khristova and Tissot 1995; Upadhyaya et al. 2008), and *H. cannabinus* (Fenz and Alén 2002; Yoshito et al. 2001) soda pulping, which resulted in pulps with physical strength properties similar to kraft pulp grades. Part 1 of the present work dealt with alkaline sulphite-antraquinone (AS-AQ) delignification of *Hibiscus cannabinus*, *Cannabis sativa*, and *Hibiscus sabdariffa*, and showed that these raw materials could be cooked to extremely low kappa number, and produced high pulp yield, high brightness, and excellent pulp strength (Dutt et al. 2010).

According to Ingruber et al. (1982), alkaline sulphite (AS) cooking corresponds to a cold cooking at a pH of 10 to 13.5 with the cooking liquor containing mainly Na_2SO_3 and NaOH. Neutral or semi sulphite (NS or SAS) corresponds to a cold cooking pH of <12.5 with the cooking liquor containing mainly Na_2SO_3 and Na_2CO_3 (Ingruber et al. 1982). Such pulps, both bleached and unbleached, have been in commercial use for many years. Normally, these pulps are mixed in furnish for the production of printing papers such as newsprint, magazine paper, and the base paper for coating. The preliminary conclusions of these studies indicated that this process is very interesting from the point of view of both economy and quality, but is still in the developing stage. The most promising initial applications of the process seem to be in production of packaging grades of papers, and news reinforcement. Keeping this in view, the present study aims at compensating the scarcity of wood fibers, pulping of three non-woody fibrous raw materials namely *H. cannabinus* (kenaf), *H. sabdariffa* (roselle), and *C. sativa* (true hemp) by semi-alkaline sulphite anthraquinone (SAS-AQ) and neutral sulphite semi-chemical anthraquinone (NSSC-AQ) delignification processes for producing high yield and strong pulp comparable to kraft.

EXPERIMENTAL PROCEDURES

Raw Material Preparation and Pulping Studies

Kenaf, true hemp, and roselle were collected from the nearby vicinity of the Institute at Saharanpur located in the foothills of the 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 the plants were chipped and screened. The chips passing through a 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 8-12%. The chips of kenaf, true hemp, and roselle were kept in air-tight polythene bags until used. For optimization of pulping conditions, 100 g oven dry chips of kenaf, true hemp, and roselle were digested in a laboratory Weverk rotary tumbling electrically heated digester (0.02 m^3 capacity), having four stainless steel bombs of one liter capacity, furnishing sufficient pulps for evaluation as well as for conducting bleaching experiments. During these studies, the technical grade chemicals were used except for Na_2SO_3, which was of analytical grade. Anthraquinone (0.1%) – a carbohydrate stabilizer and an accelerator of delignification, was added during SAS and NSSC delignification of kenaf, true hemp, and roselle. All dilutions were made with tap water. The cooking was also made at different time to be able to determine the effect of cooking time during the course of pulping. During cooking the digester pressure was reduced to zero by gas relief at 105^oC. At the end of cooking cycle SAS-AQ or NSSC-AQ cooked chips were defibered through a defibrator with a plate clearance of 0.5 mm followed by a second pass at 0.1 mm plate clearance. The pulps were washed and screened through a laboratory vibratory flat Weverk screen with 0.15 mm slots, and the screened pulps were washed, pressed, and crumbled. The pulps were evaluated for kappa number (T236 cm-85), pulp yield, screening rejects, and spent liquor pH (T628 cm-01;

TASPPI, 2007). The cooking of kenaf, true hemp, and roselle chips was carried out under the following conditions:

SAS-AQ cooking

- Total alkali (as Na_2O) = 13–17 %
- AQ dose = 0.1% (oven dry basis)
- Alkali ratio (Na_2SO_3: total alkali) = 0.60-0.95
- Liquor to raw material ratio = 4.5:1
- Time from ambient temperature to 105 ^oC = 45 min
- Time from 105 ^oC to 170 ^oC = 45 min
- Time at 170 ^oC = 120 min

NSSC-AQ cooking

- Total alkali as Na_2O charge = 8% (on oven dry chips basis)
- Na_2CO_3: Na_2SO_3 = 0:100, 80:20, 60:40, 30:70, 20:80 and 0:100
- Weight ratio of Na_2SO_3: Na_2CO_3 = 0.00, 1.78 and 2.77
- AQ dose = 0.1% (oven dry basis)
- Time from 30^{0}C to 105^{0}C = 45 min
- Time from 105 ^{0}C to 160 ^{0}C = 45 min
- Maximum pulping temperature = 160 ^{0}C
- Time at maximum temperature = 60-120 min
- Liquor to raw materials ratio = 4.5:1

Bleaching Studies

Semi-alkaline sulphite pulp of kenaf, true hemp, and roselle was bleached by the CEHH bleaching sequence. The selected AS-AQ pulps were bleached by the CEHH sequence. The chlorination stage (C) was carried out in capped plastic bottles at pH 1.82±0.02, pulp consistency 3%, and reaction time 40 min at 25±2 ^oC. Chlorinated pulp was extracted with NaOH (E-stage) at temperature 60±2 ^oC, consistency 10% and time 60 min. The hypochlorite, 1st and 2nd stages were performed in polyethylene bags at reaction time 90 min, pulp consistency 10% and temperature 45±2 ºC. After each bleaching treatment the pulps were thoroughly washed with deionised water. Unbleached and bleached pulp characteristics and strength properties were determined as per TAPPI Standard Test Methods (TAPPI 2007)

Fiber Classification

The fiber classification studies of kenaf, true hemp, and roselle SAS-AQ pulps were made with help of a Bauer-McNett fiber classifier using screens with mesh numbers 20, 60, 80, and 120.

Preparation of Laboratory Handsheets and Testing

Unbleached and bleached kenaf, true hemp, and roselle 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 in atmospheric conditions, conditioned at $27\pm2^{o}C$ 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) (TAPPI 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 most important factors influencing the result of SAS cooking were found to be the total alkali charge, the alkali ratio (Na_2SO_3:total alkali, both expressed as Na_2O). Especially, when delignification is aimed at producing fully defibred pulp, the impregnation of cooking liquor into the chips is essential. The influence of total alkali ratio during the course of kenaf, true hemp, and roselle pulping indicated that the alkali ratio should be in the vicinity of 0.80 to achieve pulp of low kappa number. An increase in total alkali charge accelerated the delignification. It was also observed that Na_2SO_3 charge had a greater influence on delignification than the total alkali charge. Table 1 reveals that screened pulp yield, screening rejects, and kappa number decreased with increasing Na_2SO_3 or alkali ratio up to an alkali ratio of 0.80 and Na_2SO_3 charge of 11.70% (as Na_2O), and beyond that all these showed an increasing trend. These effects were attributed to the fact that pH of the cooking liquor decreases as the amount of Na_2SO_3 increases in total alkali. Although in SAS pulping Na_2SO_3 is the main delignifying agent, at lower pH level it is comparatively less effective than at higher pH level, i.e. the rate of delignification increases at higher pH level, the more pH of SAS cooking liquor the higher will be the rate of delignification and shorter will be the cooking cycle. The increase in screened pulp yield, screening rejects, and kappa number beyond 0.80 alkali ratios is due to the fact that beyond this alkali ratio the pH of the cooking liquor showed a decreasing trend, thereby reducing the rate of delignification, and the cooking was carried out for a particular time. As a consequence, the cooking time was insufficient to achieve complete delignification. The delignification stoped at a kappa number of around 46.6±0.4 during SAS pulping of kenaf, true hemp, and roselle.

A lower kappa number may be achieved by increasing Na_2SO_3 charge and cooking time. Likewise, the addition of 0.075% AQ to the cooking liquor during SAS delignification of kenaf, true hemp, and roselle contributes to preservation of the polysaccharides. Further, the beneficial effect of AQ addition was reflected in a higher pulp yield, indicating less damage of cellulose at better delignification. This is due to the catalyzed delignification and the stabilization of the end-groups of the carbohydrates through oxidation to aldonic acids, which are stable to end-wise degradation (Irvine and Nelson 1986). The total hemicelluloses content of SAS pulp was high, and the high screened pulp yield of SAS pulp was partly due to stabilization of hemicelluloses (xylan and glucomannan), and partly due to the mild alkaline cooking conditions, which preserve the hemicellulose in pulp (Khristova et al. 2006). The retarded delignification in SAS cooking may be due to the rapid decrease in the cold pH already in the early stages of cooking. Most of the chemicals of the cooking liquor charged were consumed as the digester temperature rose up to the maximum temperature. This is why the cooking method is referred to as neutral sulphite (NS) or semi alkaline sulphite (SAS) cooking.

The most interesting aspects of the SAS pulping process are its ability to produce brighter pulp with high screened pulp yield. The brightness of unbleached pulp of kenaf, true hemp, and roselle varied between 40-50% (ISO). Kenaf, true hemp, and roselle produced screened pulp yield values of 63.0% (kappa number 41.0), 62.5% (kappa number 41.2),
63.0% (kappa number 41.0), 62.5% (kappa number 41.2), and 64.0% (kappa number 41.5) respectively, at total alkali dose 15% (as Na_2O), alkali ratio 0.80, Na_2SO_3 charge 10.40% (as Na_2O), Na_2CO_3 dose 2.60% (as Na_2O), maximum cooking time 120 min, and maximum cooking temperature 170 ^oC, liquor to wood ratio of 4.5:1, and AQ dose 0.075% (on oven dry chips basis). These raw materials may be cooked together due to identical pulping conditions.

Table 2 reveals the bleaching conditions and results of CEHH bleaching of kenaf, true hemp, and roselle. Because of the rather high kappa number, the chlorine consumption was slightly higher. A pulp brightness level of 80.5% (ISO) for kenaf, 80.8% (ISO) for true hemp, and 79.5 % (ISO) for roselle were obtained as a result of CEHH bleaching. Pulp viscosity (CED 0.5%) of all the three pulp samples fell within the range 11.40 to 11.78 cps. As the degree of polymerization at given a kappa number is regarded as a measure of selectivity of the delignification (Gevert and Lohmander 1997), the AS-AQ pulp showed better bleaching selectivity than the soda and soda-AQ pulps, which declined in the following order: AS-AQ> soda-AQ>soda pulp.

Both unbleached and bleached SAS-AQ pulps of kenaf, true hemp, and roselle were more readily beaten up to a desired beating level (Tables 3 and 4). This implies that a shorter time is required to beat SAS-AQ pulps, thereby requiring less energy during beating and refining due to retention of more hemicelluloses in comparison to soda and kraft pulps (Dutt et al. 2008, 2009, 2010; Upadhyaya et al. 2008). Bleaching did not markedly change the paper making properties of SAS pulps. All the strength properties increased up to a certain level of ^{o}SR, and after that the strength properties showed a declining trend as a result of over-beating or higher slowness values except tear index. Therefore, tearing energy required to pull out the fibers from the mesh were higher. Further, cutting action, external and internal fibrillations, and brushing action tended to bring the tear index down, whereas all other properties depending upon hydrogen bonding improved with pulp beating. It is obvious from these results that kenaf, true hemp, and roselle pulps should not be beaten to a slowness range beyond, 52, 50, and 42 ^{o}SR, respectively.

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Table 1. Pulping Conditions and Characteristics of Kenaf, True Hemp, and Roselle during Semi-Alkaline Sulphite-AQ Pulping

Particulars	Total alkali, 13% (as Na_2O)					Total alkali, 15% (as Na_2O)					Total alkali,17 % (as Na_2O)				
Alkali ratio,%	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
*Na_2SO_3, % (as Na_2O)	7.80	9.10	10.40	11.70	12.35	9.00	10.50	12.00	13.50	14.25	10.20	11.90	13.60	15.30	16.15
*Na_2CO_3, % (as Na_2O)	5.20	3.90	2.60	1.30	0.65	6.00	4.50	3.00	1.50	0.75	6.80	5.10	3.40	1.70	0.85
White liquor pH	11.6	10.8	10.5	10.0	9.6	11.3	10.9	10.5	10.2	9.7	11.5	10.9	10.6	10.2	9.7
Kenaf															
Pulp yield, %	74.0	70.7	66.8	67.0	70.1	72.2	68.0	65.1	66.8	68.2	70.0	67.2	63.4	65.6	66.9
Screened pulp yield, %	69.4	66.7	63.6	63.4	66.1	68.9	65.1	63.0	64.0	65.2	67.2	65.1	61.9	63.5	64.6
Rejects, %	4.6	4.0	3.3	3.6	4.0	3.3	2.9	2.0	2.8	3.0	2.8	2.1	1.5	2.1	2.3
Kappa number	68.2	57.3	46.2	50.0	53.8	63.8	52.2	41.0	43.8	48.0	56.7	47.2	38.0	42.1	46.5
Spent liquor pH	8.4	8.3	8.2	8.0	7.7	8.4	8.3	8.10	7.9	7.7	8.5	8.4	8.1	7.9	7.7
Roselle															
Pulp yield, %	73.5	68.8	66.1	66.7	69.8	71.6	67.7	64.6	66.6	68.1	69.7	66.9	63.0	65.2	67.1
Screened pulp yield, %	69.0	64.7	63.0	62.9	65.7	68.4	64.9	62.5	63.7	64.9	66.7	64.7	61.4	63.2	64.6
Rejects, %	4.5	4.1	3.2	3.8	4.1	3.2	2.8	2.1	2.9	3.2	2.0	2.7	1.6	2.0	2.5
Kappa number	67.6	55.5	46.8	50.0	53.4	62.4	50.7	41.2	44.0	47.4	57.0	48.4	38.5	41.8	45.5
Spent liquor pH	8.4	8.3	8.1	7.9	7.7	8.4	8.4	8.0	7.9	7.7	8.4	8.4	8.2	7.8	7.7
True hemp															
Pulp yield, %	75.2	71.1	68.1	69.8	71.9	73.1	70.0	66.2	67.6	69.2	69.5	66.5	62.8	66.0	67.8
Screened pulp yield, %	70.7	67.1	64.7	66.1	67.6	69.9	67.3	64.0	64.7	66.2	66.8	64.4	61.4	64.0	65.4
Rejects, %	4.5	4.0	3.4	3.7	4.2	3.2	2.8	2.2	2.9	3.0	2.8	2.1	1.4	2.0	2.4
Kappa number	66.7	56.2	47.0	49.5	53.7	60.8	51.4	41.5	43.8	48.6	56.4	46.5	38.7	41.0	44.8
Spent liquor pH	8.4	8.4	8.1	8.0	7.8	8.4	8.3	8.1	7.9	7.7	8.5	8.35	8.2	7.9	7.7

*on oven dry chips basis, AQ dose= 0.075% (on oven dry basis), liquor to raw material ratio = 4.5:1, time from ambient temperature to 105 ^oC = 45 min, time from 105 ^oC to 170 ^oC = 45 min, time at 170 ^oC= 120 min

Table 2. Bleaching Conditions and Results of Semi-Alkaline Sulphite-AQ Pulps of Kenaf, True Hemp, and Roselle

Particulars	Kenaf	Roselle	True hemp
Unbleached pulp kappa number	41.0	41.2	41.5
Chlorination stage (C)			
Chlorine applied as available Cl_2 on pulp %	7.00	7.00	7.00
Chlorine consumed as available Cl_2 on pulp %	6.95	6.96	6.95
Final pH	1.80	1.85	1.80
Extraction stage (E)			
NaOH applied on pulp %	1.50	1.50	1.50
Initial pH	11.20	11.20	11.15
Final pH	9.80	9.85	9.80
Hypochlorite 1st stage (H_1)			
Hypochlorite applied as available Cl_2 on pulp %	2.00	2.00	2.00
Hypochlorite consumed as available Cl_2 on pulp %	1.96	1.95	1.95
Final pH	7.90	7.85	7.90
Hypochlorite 2nd stage (H_2)			
Hypochlorite applied as available Cl_2 on pulp %	1.00	1.00	1.00
Hypochlorite consumed as available Cl_2 on pulp %	0.91	0.92	0.92
Final pH	7.80	7.85	7.85
Total Cl_2 applied on the pulp %	10.00	10.00	10.00
Total Cl_2 consumed on the pulp %	9.82	9.83	9.82
Bleaching losses, %	10.50	10.35	10.80
Bleached pulp yield, %	52.45	52.13	53.20
Brightness (ISO),%	80.50	80.80	79.50
Viscosity CED (0.5%), cps	11.50	11.40	11.78

Bleaching conditions	C	E	H_1	H_2
Consistency, %	3	10	10	10
Temperature, ^oC	25±2	60±2	45±2	45±2
Time, min	40	60	90	90

Therefore, tearing energy required to pull out the fibers from the mesh were higher. Further, cutting action, external and internal fibrillations, and brushing action tended to bring the tear index down, whereas all other properties depending upon hydrogen bonding improved with pulp beating. It is obvious from these results that kenaf, true hemp, and roselle pulps should not be beaten to a slowness range beyond, 52, 50, and 42 ^oSR respectively. The strength characteristics of the bleached pulps (Table 4) followed the pattern of the unbleached pulps (Table 3). The high tensile and burst indexes, double fold numbers, and good tear resistance of the unbleached kenaf, true hemp, and roselle pulps were only moderately reduced in the CEHH bleaching. It seems that the fibre weakening during bleaching of the AS-AQ pulp, indicated by the viscosity reduction, was to some extent compensated by the improved stiffness, combined with the enhanced bonding ability due to the preservation of hemicelluloses. Thus, the bonding strength

Table 3. Properties of Unbleached Semi-Alkaline Sulphite-AQ Pulps of Kenaf, True Hemp, and Roselle

Plant species	Beating time, min	Beating level, °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 folds, numbers
Kenaf	0	17	4	0.62	1.52	20.15	7.60	1200	18
	5	30	11	0.65	3.46	58.70	8.50	550	160
	10	41	18	0.70	4.60	69.58	7.68	160	380
	15	52	24	0.73	4.78	71.25	7.25	130	420
	20	64	45	0.77	4.50	70.60	6.94	100	540
Roselle	0	17	4	0.63	1.38	21.82	7.78	1100	20
	5	29	12	0.66	3.12	59.78	8.60	500	190
	10	40	18	0.69	4.65	69.85	7.60	150	400
	15	50	26	0.75	4.80	70.50	7.22	120	450
	20	65	48	0.79	4.56	69.90	6.88	100	550
True hemp	0	18	4	0.65	2.98	38.90	8.78	1000	62
	5	28	11	0.69	4.26	69.55	9.45	450	300
	10	35	20	0.74	4.88	75.76	8.25	120	650
	15	42	28	0.79	5.30	78.60	6.95	100	920
	20	57	45	0.82	5.48	77.35	6.65	90	1020

ability due to the preservation of hemicelluloses. Thus, the bonding strength properties of the AS-AQ bleached pulp were still higher than those of bleached soda, soda-AQ, kraft, and kraft-AQ pulps (Dutt et al. 2008, 2009, 2010; Upadhyaya et al. 2008). After bleaching, the beatability of the three pulps was strongly accelerated. The higher tear and bonding strength properties were reflected in the higher runnability factor (Dutt et al. 2005). In addition to brightness, opacity is an important property of many grades of papers. SAS pulps have high scattering coefficient. This is because the fibers are stiff and uncollapsed, which provides a large optically area, but they have good bonding ability due to high local plasticity and good bonding strength.

Table 5 shows the Bauer McNett classification results for the SAS-AQ pulp of kenaf, true hemp, and roselle. The +20 fraction of fibers in SAS-AQ pulps of all the three raw materials varied between 18.2 and 20.7%, and after bleaching this fraction was drastically reduced to the range 5.4 to 7.9%. These results indicate that the decline in this fraction was greater during CEHH beaching. The –20+60 fraction showed a maximum percentage of fibers, and the percentage change in this fraction was less during bleaching. However, the –60+80 fraction was slightly increased during bleaching. The increase in the –120 fraction during bleaching may contribute to fluff generation in the dryer section

Table 4. Properties of Bleached Semi-Alkaline Sulphite-AQ Pulps of Kenaf, True Hemp, and Roselle

Plant species	Beating time, min	Beating level, °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 folds, nos	Brightness, %	Opacity, %
Kenaf	0	18	4	0.63	1.18	18.48	7.12	5	900	80.0	93.0
	5	31	12	0.65	3.05	57.80	8.02	30	260	76.0	87.5
	10	42	20	0.71	4.32	66.20	7.10	160	150	74.0	84.0
	15	53	258	0.75	4.56	68.80	6.52	250	120	72.5	82.5
	20	65	50	0.80	4.48	67.50	6.12	310	90	70.5	81.0
Roselle	0	18	4	0.64	1.20	20.02	7.02	5	850	80.0	92.5
	5	32	13	0.67	3.14	55.28	8.16	35	250	76.0	88.0
	10	41	19	0.72	4.52	64.80	7.20	180	140	73.5	86.0
	15	54	26	0.78	4.90	68.25	6.78	260	110	72.0	83.0
	20	64	51	0.81	4.68	67.85	6.20	320	80	71.0	81.0
True hemp	0	19	4	0.65	2.42	36.90	8.76	35	800	79.5	92.0
	5	29	14	0.69	4.75	68.76	9.00	210	210	75.5	87.5
	10	35	22	0.76	5.00	77.00	8.12	420	130	73.0	83.0
	15	42	32	0.79	5.40	79.20	7.08	600	110	72.0	82.0
	20	56	47	0.83	5.56	79.98	6.58	720	80	70.5	80.5

of paper machines or during printing of paper (Dutt et al. 2007a), and this problem may be solved by increasing the refining of pulp or use of wet end bonding additives (Dutt et al. 2007b).

Table 5. Bauer McNett Fiber Classification of Semi-Alkaline Sulphite-AQ Pulps at Optimum Pulping Conditions

Mesh size	Kenaf pulps		Roselle pulps		True hemp pulps	
	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
+20	18.5	5.4	18.2	5.6	20.7	7.9
–20+60	48.2	38.2	47.9	38.0	49.8	38.6
–60+80	14.0	25.3	13.9	25.5	11.8	22.0
–80+120	6.8	12.2	7.4	11.8	7.2	10.4
–120	12.0	18.5	12.1	19.0	10.2	20.8

The effect of different proportions of Na_2SO_3 and Na_2CO_3 (molal basis) on pulp yield, delignification, and physical strength properties at constant sodium charge were studied (Table 6).

Table 6. Pulping Conditions and Results of NSSC-AQ Pulping and Pulp and Paper Evaluation Properties of Kenaf, True hemp, and Roselle

Time at temp, min	Cooking liquor total Na_2O as Na_2CO_3,: Na_2SO_3,	Weight ratio of Na_2SO_3:Na_2CO_3	Kenaf		Roselle		True hemp	
			Screened pulp yield, %	Spent liquor pH	Screened pulp yield, %	Spent liquor pH	Screened pulp yield, %	Spent liquor pH
60	100:0	0.00	80.0	8.7	79.5	8.6	81.0	8.7
	80:20	0.30	78.5	8.5	78.0	8.5	79.3	8.5
	60:40	0.79	76.8	8.2	77.1	8.2	76.8	8.3
	40:60	1.78	75.5	8.0	75.4	8.1	75.0	8.0
	30:70	2.77	76.0	7.8	75.8	7.7	76.5	7.5
	20:80	4.75	77.2	7.5	77.5	7.3	77.3	7.2
	0:100	–	78.0	7.3	78.0	7.1	79.0	7.1
90	100:0	0.00	79.2	8.6	78.6	8.5	80.2	8.6
	80:20	0.30	76.5	8.4	76.2	8.3	77.2	8.4
	60:40	0.79	74.0	8.2	73.8	8.1	74.2	8.0
	40:60	1.78	72.0	8.0	72.0	8.0	73.5	7.9
	30:70	2.77	72.5	7.8	74.2	7.7	74.5	7.6
	20:80	4.75	73.8	7.6	75.0	7.4	76.0	7.2
	0:100	–	75.0	7.2	76.5	7.1	77.2	7.0
120	100:0	0.00	78.0	8.6	77.5	8.5	78.5	8.5
	80:20	0.30	74.2	8.4	73.5	8.3	74.5	8.4
	60:40	0.79	72.0	8.2	71.2	8.1	71.4	8.2
	40:60	1.78	70.8	7.8	71.8	7.7	73.0	7.7
	30:70	2.77	72.0	7.4	72.8	7.3	75.0	7.3
	20:80	4.75	72.9	7.3	73.7	7.1	76.6	7.1
	0:100	–	74.2	7.2	75.0	7.0	77.8	7.0

Total alkali as Na_2O charge = 8% (on oven dry chips basis), time from 30 ^oC to 105 ^oC = 45 min, time from 105 ^oC to 160 ^oC = 45 min, liquor to raw materials ratio = 4.5:1, maximum pulping temperature = 160 ^oC.

The NSSC-AQ pulping was conducted at a total chemical charge of 8% (as Na_2O) using varying ratios of sulphite-to-carbonate for different cooking times from 60 to 120 min at 160 °C (Table 7). For a shorter cook (60 min delignification time) used for corrugating medium, the maximum delignification was achieved at a chemical ratio of 60% of Na_2SO_3 and 40% of Na_2CO_3. The lowest pulp yield was obtained with a combination of Na_2SO_3 and Na_2CO_3 rather than with 100% Na_2SO_3 or 100% Na_2CO_3. For cooks conducted at a cooking time of 90 min while keeping other conditions constant, maximum delignification was achieved with a little higher ratio of sulphite-to-carbonate (70:30). These results also indicate that after a maximum degree of delignification, the pulp yield again increased irrespective of the time at temperature, which can be explained on the basis that the rate of delignification decreases after the desired proportion of sulphite to carbonate in the liquor has been reached.

Table 7. Pulping Conditions and Results of NSSC-AQ Pulping and Pulp and Paper Evaluation Properties of Kenaf, True Hemp, and Roselle

Plant species	Cooking liquor total (as Na_2O)	Weight ratio of Na_2SO_3:Na_2CO_3	Time at 160 °C, min	Spent liquor	Kappa no.	°SR	Apparent density, g/mm³	Burst index, kPam²/g	Tear index, mNm²/g	Tensile index, Nm/g	Brightness, % (ISO)	Concora crush resistance, lb
	Na_2CO_3,: Na_2SO_3,			Na_2CO_3, g/L								
Kenaf	100:0	0.00	120	0.0	132	40	0.67	2.34	5.80	35.92	22.5	48.5
	40:60	1.78	60	4.9	125	41	0.68	2.45	6.02	40.12	27.0	51.6
	30:70	2.77	120	5.4	102	40	0.66	3.28	6.52	45.20	31.5	70.0
	0:100	–	120	11.2	115	40	0.64	2.60	5.75	38.45	36.0	63.5
Roselle	100:0	0.00	120	0.0	130	41	0.66	2.42	5.62	33.82	22.0	50.5
	40:60	1.78	60	5.3	122	42	0.67	2.58	5.90	39.60	29.0	53.8
	30:70	2.77	120	6.0	100	40	0.65	3.42	6.62	46.80	33.5	72.0
	0:100	–	120	11.8	112	39	0.67	2.52	5.88	40.50	38.0	65.2
True hemp	100:0	0.00	120	0.0	138	40	0.69	2.80	5.50	38.50	24.0	51.0
	40:60	1.78	60	5.5	132	40	0.72	2.98	5.84	44.82	33.0	54.5
	30:70	2.77	120	6.4	105	41	0.70	4.12	6.26	51.80	36.5	75.0
	0:100	–	120	11.5	122	39	0.68	3.00	5.90	45.20	40.5	67.0

Total alkali as Na_2O charge = 8% (on oven dry chips basis), time from 30°C to 105°C = 45 min, time from 105 °C to 160 °C = 45 min, liquor to raw materials ratio = 4.5:1, maximum pulping temperature = 160 °C.

A similar trend was observed at a cooking time of 120 min. The pulps that were obtained at a sulphite-to-carbonate ratio of 70:30 showed better mechanical strength properties in comparison to pulps obtained with 100% Na_2SO_3 or 100% Na_2CO_3 (Table 7). The strength properties of pulps obtained at 100% sulphite showed better values than pulps obtained at 100% carbonate. The pulps cooked for 120 min, obtained at optimum proportions of sulphite-to-carbonate ratio of 70:30, were evaluated for strength properties at different beating levels (Table 8).

Table 8. Effect of Beating on NSSC-AQ Pulp Properties from Kenaf, True hemp, and Roselle

Plant species	Beating time, min	^{o}SR	Drainage time, s	Apparent density, g/cm^3	Burst index, kPam^2/g	Tensile index, Nm/g	Tear index, mNm^2/g	Double folds numbers	Brightness, % (ISO)	Porosity (Bendtsen), mL/min
Kenaf	0	19	4	0.61	1.00	24.36	6.52	14	44.0	1000
	5	32	10	0.64	2.85	41.80	7.02	60	41.5	380
	10	43	17	0.67	3.46	52.75	6.48	100	40.0	160
	15	52	24	0.70	3.80	58.20	5.90	140	36.0	100
Roselle	0	19	4	0.59	1.10	26.10	6.84	18	44.0	950
	5	31	12	0.63	3.05	42.84	7.16	80	42.5	360
	10	42	18	0.68	3.65	53.25	6.60	110	40.5	140
	15	53	26	0.72	4.12	59.75	6.02	160	37.0	90
True hemp	0	18	5	0.62	2.80	29.20	6.74	28	44.0	900
	5	28	13	0.65	3.86	48.55	7.20	110	42.5	300
	10	38	17	0.69	4.52	55.65	6.80	160	41.0	120
	15	45	25	0.73	4.90	61.25	6.42	205	38.0	90

Total alkali as Na_2O charge = 8% (on oven dry chips basis), time from 30^{o}C to 105^{o}C = 45 min, time from 105 ^{o}C to 160 ^{o}C = 45 min, liquor to raw materials ratio = 4.5:1, maximum pulping temperature = 160 ^{o}C.

The results show that maximum values of strength properties were obtained at a beating level of 42±2 ^{o}SR. The energy consumption was very dependent on pulping conditions. All of the studied variables reduced defibration energy consumption. Na_2SO_3 charge was the most important factor in wood softening by lignin sulphonation. The temperature effect was also considerable, as a consequence of an increase in reaction rate. The amount of Na_2CO_3 affects the energy requirement due to the softening of the hemicellulosic material (Area and Valade 1995). Burst and tensile indexes, apparent density, and double-fold numbers increased with increasing beating level up to a certain limit, while porosity and brightness decreased with increasing beating level. Initially, tear index increased due to removal of primary walls, which exposed secondary wall layers and resulted in hydrogen bonding. Therefore, tearing energy required to pull out the fibers from the mesh increased slightly. Further, cutting action, external and internal fibrillations, and brushing action tended to decrease the tear index.

CONCLUSIONS

SAS-AQ pulping process offers many advantages including high pulp yield, better mechanical strength properties comparable to kraft pulp, avoidance of foul odours of liquor and condensates, and good light scattering coefficient. In spite of several advantages, the SAS-AQ process bears with many drawbacks, which include longer cooking times required to achieve low kappa number in the pulps. Kenaf, true hemp, and roselle produced screened pulp yields of 63.0% (kappa number 41.0), 62.5% (kappa number 41.2) and 64.0% (kappa number 41.5) respectively, at a total alkali dose 15% (as Na_2O), alkali ratio 0.80, Na_2SO_3 charge 10.40% (as Na_2O), Na_2CO_3 dose 2.60% (as Na_2O), maximum cooking time 120 min and maximum cooking temperature 170 ^oC, liquor to wood ratio of 4.5:1 and AQ dose 0.075% (on oven dry chips basis). A pulp brightness level of 80.5% (ISO) for kenaf, 80.8% (ISO) for true hemp, and 79.5 % (ISO) for roselle were obtained as a result of CEHH bleaching. Pulp viscosity (CED 0.5%) of all the three pulp samples were between 11.40 and11.78 cps. A minimum beating time was required to beat SAS-AQ pulps, due to retention of hemicelluloses, in comparison to soda and kraft pulps. Kenaf, true hemp, and roselle pulps showed optimal mechanical strength properties at a beating level of 52, 50 and 42 ^oSR respectively. Good mechanical strength properties were obtained due to improved stiffness combined with bonding ability and preservation of hemicelluloses.

In the NSSC-AQ pulping process, the carbonate component serves as an additional chemical or as partial replacement for the sulphite and is found to have appreciable pulping effect. Increasing sulphite-to-carbonate ratio shortens the cooking time, and affects the mechanical strength properties. With high pulp yield from a short cooking cycle (60 min), the maximum strength properties were achieved at sulphite-to-carbonate ratio of 60:40. The NSSC-AQ process also provides an opportunity for saving in sulphur. For bleaching grade pulps of longer cooking duration addition of carbonate-to-sulphite in the ratio of 30:70 showed a higher rate for degree of delignification. In addition to its corrosion inhibiting properties Na_2CO_3 must be considered as an effective pulping agent when used in combination with Na_2SO_3 in the NSSC-AQ process.

The pulping conditions of SAS-AQ and NSSC-AQ pulping process for kenaf, true hemp, and roselle were identical. Therefore, these raw materials may be cooked together. Mixed cooking of these raw materials may be helpful to minimize the demand for wood fiber resources.

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Article submitted: June 9, 2010; Peer review completed: July 22, 2010; Revised version received: August 10, 2010; Corrected version accepted: August 11, 2010; Published: August 11, 2010.