Ecologically friendly alkaline pulping of pigeon pea stalks from Sudan

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Abstract: Pigeon pea stalks, agricultural residues from Gezira state –Sudan were pulped with alkaline sulphite, alkaline sulphite anthraquinone (AS-AQ) and alkaline sulphite anthraquinone with methanol- ASAM. The objective of present work was to optimize alkaline processes for pigeon pea stalks and to reach delignification suitable for bleaching. With active alkali charge 16-19% as Na_2O demonstrated total yields 50.4-52.7% viscosities 833-886 ml/g for alkaline sulphite process. AS-AQ produced pulps with total yields 40.2-50.1%, viscosities 722-932 ml/g and brightness 27-44% when active alkalis charges 16-20%. ASAM pulping gave good to excellent physical properties, total yields 47.6-51.7%, screened yields 46.9-48.3%, viscosities 981-1032 ml/g, when active alkali charge 15-19% and methanol 15% were applied.

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Introduction

Diversity of pulp and paper raw materials in Sudan will point this country as a promising land for pulp and paper industry. It includes non-woody plants, agricultural residues, recycled paper as well as hard wood species [1-3]. Pigeon pea stem is agricultural residues normally not used after cultivation of peas. It is an erect perennial legume shrub often grown as an annual reaching (1-4 m) in height, widely distributed in Africa, yield of dry seeds average 400-570 kg/ha. India was the primary center of origin, pigeon pea has strong woody stem, predominantly a crop of tropical areas mainly cultivated in semi arid regions of India and Kenya [4-6]. Pigeon pea (*Cajanus Cajan*) is an important crop in semi-arid, tropical and subtropical farming systems, providing high quality vegetable protein, animal feed, and firewood [7]. Pigeon pea, a multi-purpose species, is extensively used as food grain and green manure crop for soil fertility amelioration in local cropping systems. Recently, pigeon pea root exudates have been found to contain phenolic compounds (e.g. piscidic acid), which chelate Fe to free P in Fe bound P in soils for crop uptake [8].

The methanol extract of *Cajanus Cajan* seeds were fractionated into petroleum ether, chloroform, and methanol. The methanol fraction significantly decreased fasting blood glucose, and lipid profiles ($p<0.001$) on streptozotocin-induced mice compared to control [9]. Antioxidant activities of the aqueous and ethanol extracts of pigeon pea (*Cajanus Cajan*) leaves, as well as petroleum ether, ethyl acetate, *n*-butanol and water fractions and the four main compounds separated from the ethanol extract, cajaninstilbene acid (3-hydroxy-4-prenylmethoxystilbene-2-carboxylic acid), pinostrobin, vitexin and orientin, were examined by a DPPH radical-scavenging assay and a β-carotene-linoleic acid test. In the DPPH system, the antioxidant activity of the ethanol extracts was superior to that of the aqueous extracts [10]. Methanol extract of the pod surfaces of *Cajanus cajan*, a feeding stimulant for fifth-instar *Helicoverpa armigera*, was shown to contain four main phenolic compounds. Three of these were identified as isoquercitrin, quercetin, and quercetin-3-methyl ether, by comparing UV spectra and HPLC retention times with authentic standards. The fourth compound was isolated by semi-preparative HPLC and determined to be 3-hydroxy-4-prenyl-5-methoxystilbene-2-carboxylic acid (stilbene) by NMR spectroscopy and mass spectrometry [11]. The methanol extract of *Bassia latifolia* bud and *Cajanus Cajan* seed produce anti-fertility activity on mature female mice [12]. The findings suggest a possible/potential antiperoxidative role for *Cajanus Cajan* plant extract in hepatic system [13]. The extracts of *Cajanus Cajan* showed wider zones of inhibition against *Candida albicans* than other plant extracts [14].

The AS/AQ process, by using a split addition of alkali charge to ensure a rather even alkali profile throughout the cook, produces pulp with strength properties that are equal or even slightly superior to those of Kraft pulp [15]. The most meaningful advantage of ASAM pulping in comparison to the Kraft process is the easy bleachability of the pulps [16]. *Cajanus Cajan* as a short fibered plant could be mixed with long fibered wood species for production of paper with good properties increased the pulp yield. The best and economic processes suitable for pulping *C. cajan* stalks were found to be soda-AQ and specially alkaline sulfite anthraquinone with methanol.(ASAM) due to its high selectivity in dissolving lignin and preserving cellulose and hemicelluloses [2].

Physical properties, anatomical features, fiber dimensions, morphological indices and chemical composition of pigeon pea were presented in previous study [2]. However extensive cookings with alkaline sulphite, alkaline sulphite with anthraquinone and alkaline sulphite with anthraquinone with addition of methanol processes were carried out in present work. The objectives of present work are: i) To optimize the best pulping conditions by alkaline sulphite (AS), alkaline sulphite with anthraquinone (AS-AQ), alkaline sulphite anthraquinone with methanol (ASAM) processes. ii) To reach the best delignification rate for an easy bleachable pulps without chlorine compounds (low kappa number).

Materials and Methods

Stalks of Pigeon pea were collected from Gezira state characterized with clay soil. They were randomly selected according to TAPPI standards [17]. Stalks were transported to National Centre for Research (NCR) in Khartoum state. Leaves and debris were separated, and then stalks were chopped into 2-4 cm length. Chips were air dried under sun; the moisture content was determined 4-6%, kept in air tight polythene bags until used. The pulping was carried out in batch mode in a high- pressure stainless steel vessel. The optimization of cooking was applied in small digester while cookings were done at different chemical charges of alkaline sulphite (AS), alkaline sulphite with anthraquinone (AS-AQ) and alkaline sulphite-anthraquinone with methanol (ASAM).

Pulping experiments were carried out in a 7l laboratory scale batch reactor with forced circulation of cooking liquor and pressure control [18-20]. The cooking conditions were kept constant, time to reach maximum temperature 90 min, time at maximum temperature 120 min, AQ dose added during AS-AQ and ASAM processes was 0.1% on oven dry weight pigeon pea stalks, liquor to raw material ratio was 4:1 and methanol added during ASAM cookings was 15% volume by volume of white liquor. After cooking the black liquors were analyzed for total solids, residual alkali and pH. The pulps produced were extensively washed and screened through 100 mesh slot screen, and then the amount of screened yields and rejects were obtained as percentage of oven –dry pigeon pea stalks. The determination of kappa number, freeness, and viscosity was done according to TAPPI standards T236 om-99, T227-0m99 and T230-0m-99 respectively. The beating was applied in valley beater according to T200-sp-01, consistency was determined according to T240-0m-02; sheets were formed for physical tests of pulp according to T205-sp-02 and sheets were tested according to T220-sp-01.

Results and Discussion

A good delignification medium must have nucleophilic species to promote the cleavage of lignin and an to dissolve the lignin fragments. The addition of water is able to promote the delignification reaction [21]. The application of alkaline process (AS) with active alkali range 16-19% as Na_2O resulted in screened yields 38.2-43.1% , total yields 50.4-52.7%, brightness 22-31% and viscosities 833-886 ml/g (Table 1).

Table 1: Pulping conditions and unbleached pulp evaluation for alkaline sulphite pulping of *Cajanus Cajan* stems

Cook Code	active alkali as Na_2O, %	Maximum Temperature (^{0}C)	Screened Yield, %	Total Yield, %	Viscosity mlg^{-1}	Brightness %
CAS1	16	170	38.2	52.7	833	22
CAS2	17	170	40.4	51.3	876	25
CAS3	18	170	42.5	50.8	884	30
CAS4	19	170	43.1	50.4	886	31

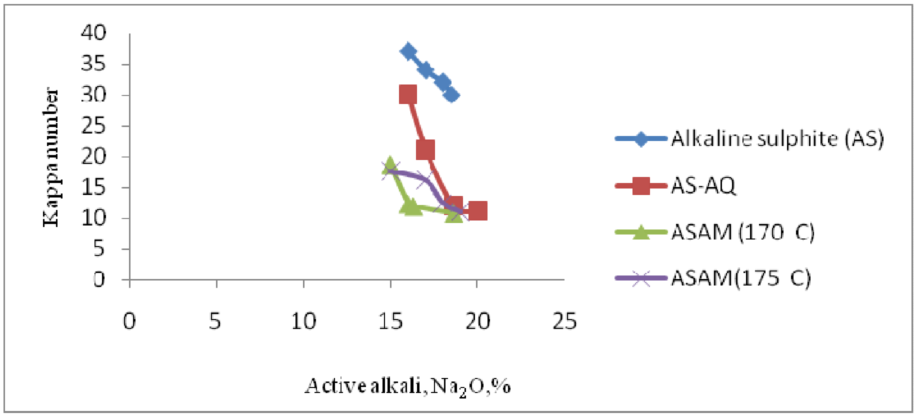

Figure 1. Plot Kappa number vs. active alkali as Na_2O during pigeon pea (*Cajuns Cajan*) alkaline pulping.

The pulp yield and residual lignin decrease with the intensification of splitting processes of α and β – ether alkylaryl bonds of lignin macromolecules and transfer of lignin decomposition products and also the extractive and mineral contents into cooking solution [22]. Table 1 reflected that, with an increase of active alkali during alkaline sulphite was associated with an increase in viscosity, brightness and screened yields, although the vice versa pattern in total yield, thus with an increase of active alkali there was decrease in total yields as result of reduction rejects with an increase in active alkali. On other hand Kappa numbers were decreased with an increase in active alkali (figure 1) as well as rejects (Figure 2). However with an increase of Kappa numbers the total yields were increased (Figure 3). The black liquor analysis showed that, with an increase of active alkali and decrease of Kappa was associated with an increase of total solids, residual active alkali and pH which is very important in chemical recovery (Figure 4).

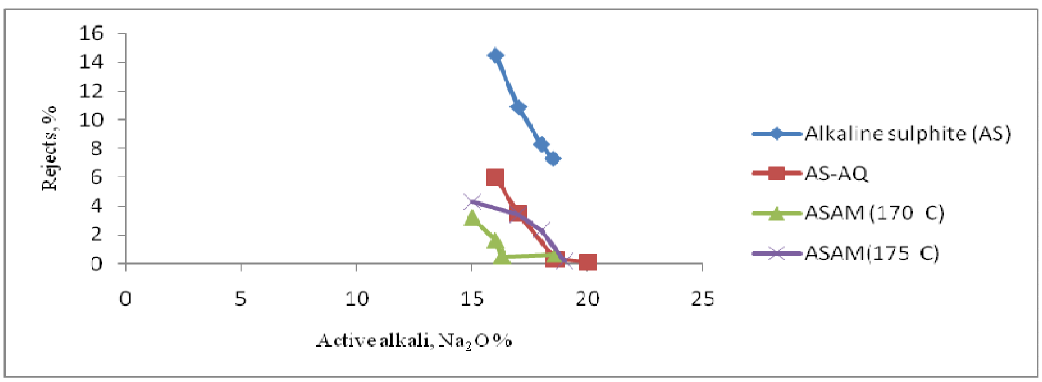

Figure 2. Plot rejects vs. active alkali during pigeon pea (*Cajuns Cajan*) alkaline pulping

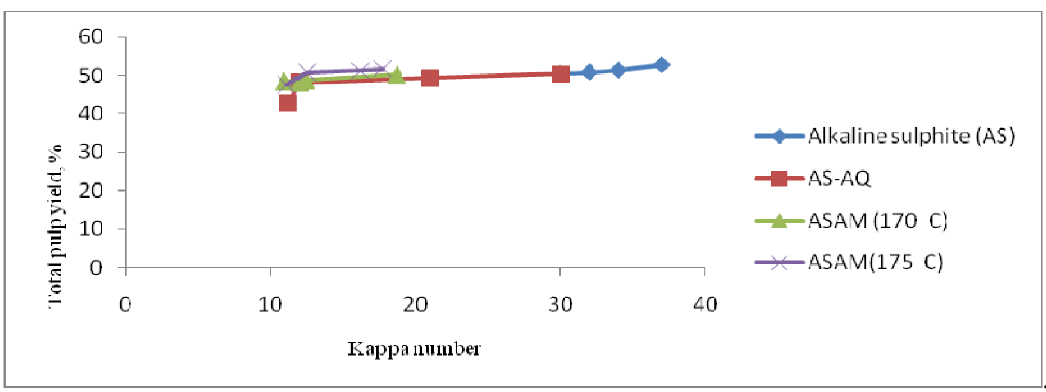

Figure 3. Plot total pulp yield vs. Kappa number during pigeon pea (*Cajuns Cajan*) alkaline pulping.

Anthraquinone (AQ) dispersion can be enhanced by dissolved lignin in alkaline solution. This dispersion of AQ in lignin-enriched solution is a relatively slow process, which takes about 30-60 min to achieve a maximum. Enhancing the dispersion leads to increase adsorption on the chips [23]. In alkaline sulphite with anthraquinone (Table 2), viscosities were highly increased compared to the corresponding ones in alkaline process (Table 1), this is also associated with an increase brightness, screened yields and total yields when using active alkali charges 16-20%.

Table 2: Pulping conditions and unbleached pulp evaluation for alkaline sulphite – anthraquinone (AS-AQ pulping of *Cajanus Cajan* stems

Cook Code	active alkali as Na_2O, %	Maximum Temperature (^0C)	Screened Yield, %	Total Yield, %	Viscosity mlg^{-1}	Brightness %
CASAQ1	16	170	44.3	50.3	975	25
CASAQ2	16.5	175	45.9	50.1	932	27
CASAQ3	17	170	45.8	49.2	823	30
CASAQ4	17.5	175	46.9	48.5	893	29
CASAQ5	16.3	170	44.4	50.4	986	27
CASAQ6	18.6	170	47.9	48.1	757	37
CASAQ7	19	170	45.9	47.5	744	40
CASAQ8	20	170	42.6	42.7	731	42
CASAQ9	20	175	40.2	40.2	722	44

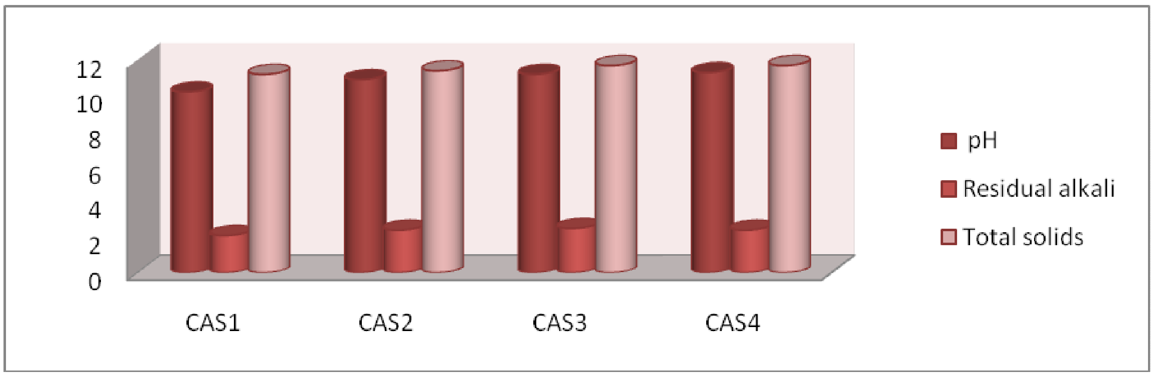

Figure 4. Black liquor analysis for pigeon pea (*Cajuns Cajan*) alkaline sulphite cooking.

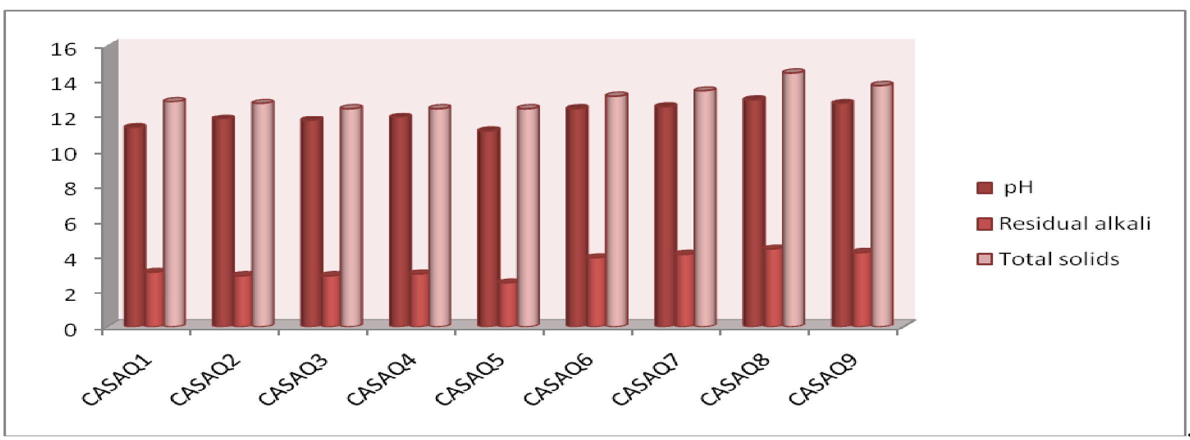

Figure 5. Black liquor analysis for pigeon pea (*Cajuns Cajan*) alkaline sulphite anthraquinone (AS-AQ) cookings

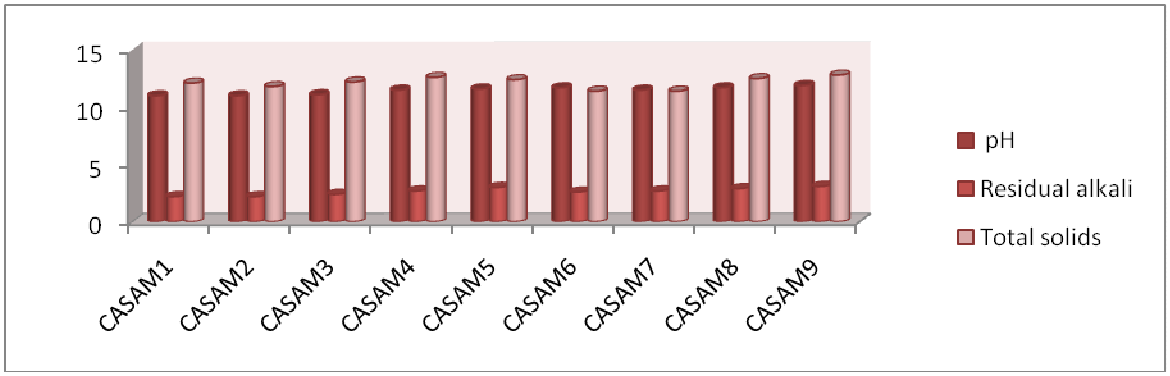

Figure 6. Black liquor analysis for pigeon pea (*Cajuns Cajan*) alkaline sulphite anthraquinone with methanol ASAM cooking.

Table 3. Pulping conditions and unbleached pulp evaluation for alkaline sulphite – anthraquinone with methanol - ASAM pulping of *Cajanus Cajan* stems, AQ pulping of *Cajanus Cajan* stems

Cook Code	active alkali as Na_2O, %	Maximum Temperature (^0C)	Screened Yield, %	Total Yield, %	Viscosity mlg^{-1}	Brightness %
CASAM1	15	175	47.5	51.7	1032	39
CASAM2	15	170	46.9	50.1	1021	37
CASAM3	16	170	47.2	48.8	1010	39
CASAM4	16	175	48.2	51.7	1015	42
CASAM 5	18.6	170	47.9	48.5	981	42
CASAM6	16.3	170	47.7	48.2	996	41
CASAM7	17	175	47.8	51.2	1025	40
CASAM8	18	175	48.3	50.7	1019	41
CASAM9	19	175	47.6	47.6	1011	43

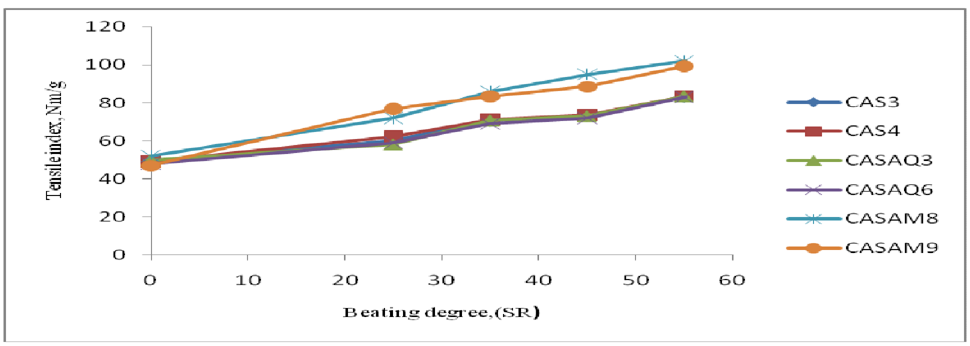

Figure 7. Tensile index vs. beating degree of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps.

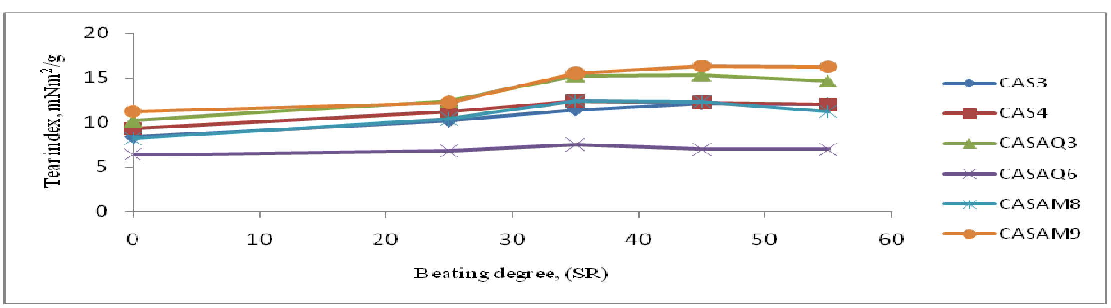

Figure 8. Tear index vs. beating degree of unbleached of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps.

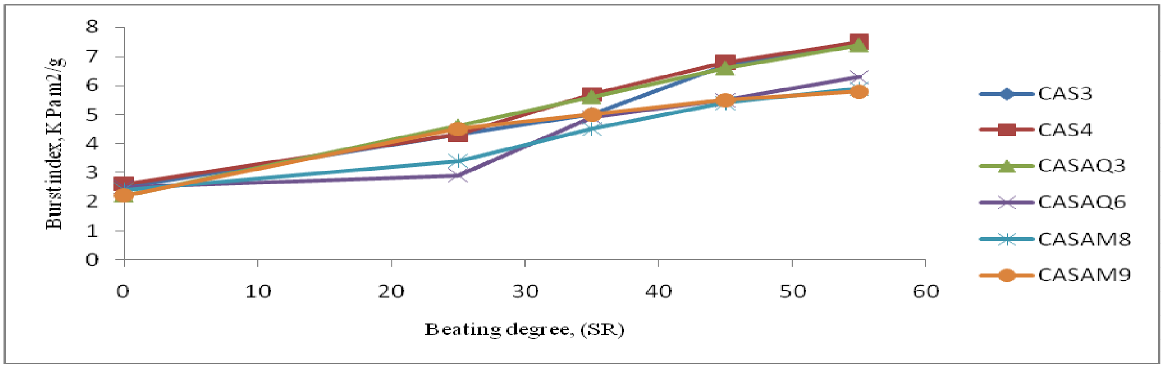

Figure 9. Burst index vs. beating degree of unbleached of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps.

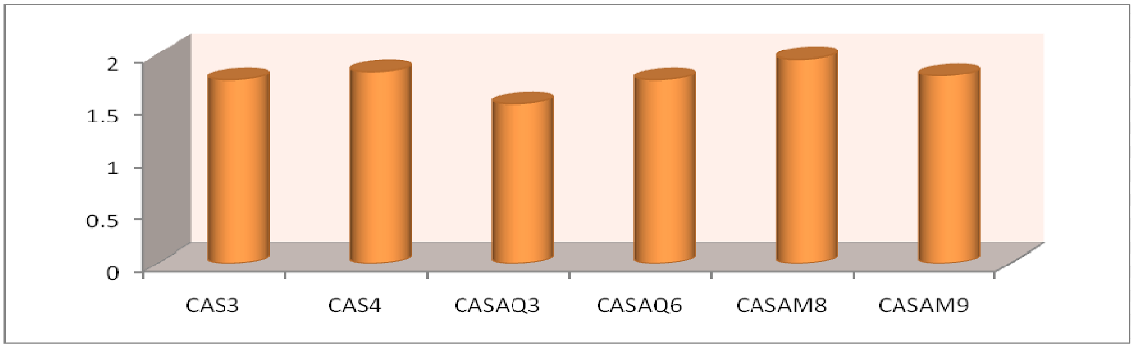

Figure 10. Fold Kohler (log) of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps.at beating degree, 45 (SR).

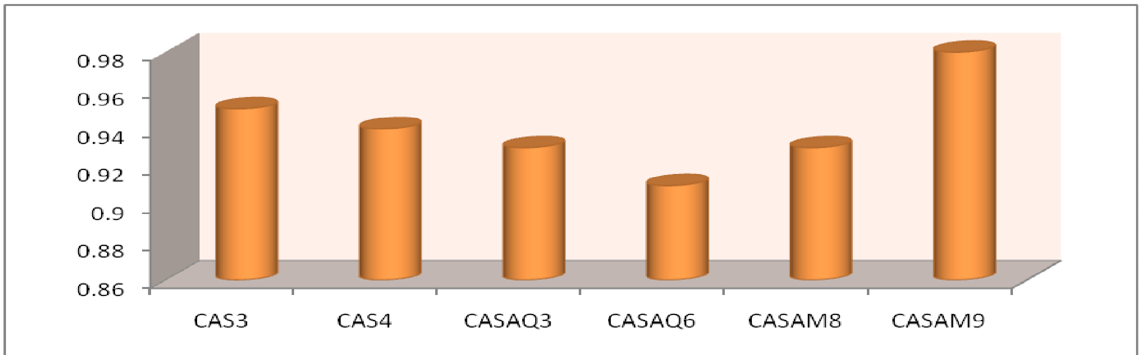

Figure 11. Apparent density, g /cm^3, of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps. at beating degree, 45 (SR).

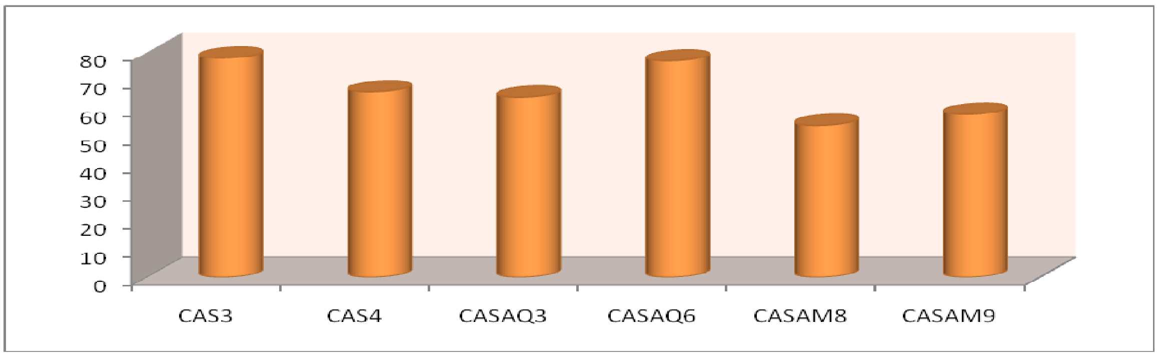

Figure 12. Porosity Bendsten ml/min, of unbleached pigeon pea (*Cajuns Cajan*) alkaline pulps.at beating degree, 45 (SR).

The increase of active alkali charges at fixed maximum temperatures 170 ^{0}C was resulted in total yields 42.7-50.4%, screened yields were 42.6-45.8, and viscosities were 722-975 ml/g, brightness 25-42. At maximum temperature 175 ^{0}C, total yields were 40.2-50.1%, screened yields were 40.2-46.9%, viscosities were 722-932 ml/g and brightness 27-44%, it seemed that during cooking of pigeon pea stalks using alkaline sulphite with anthraquinone (AS-AQ), the increase in temperature had adverse affect on viscosity, although this associated with better brightness and decrease in screened yields and total yields, demonstrated the suitability of maximum temperature 170 ^{0}C for cooking of pigeon pea stalks with AS-AQ process. Figure 1 showed that the Kappa number decrease with an increase of active alkali charge, rejects were decreased with an increase of active alkali charge used (Figure 2) and total yields were increased with an increase of Kappa numbers (Figure 3). The analysis of black liquor of AS-AQ cookings was showed the same pattern of alkaline sulphite process (Figure 5).

Methanol and anthraquinone are added to digesting to aid delignification and inhibit cellulose degradation. Depending upon the pulp properties required the methanol added should be in the range of 10 to 20% by volume of the white liquor [24]. Production of ASAM pulps by applying active alkali charges 15-19% as Na_2O, two maximum temperatures 170 and 175 ^{0}C, 0.1% AQ dose on oven dry weight of pea pigeon pea stalks and methanol as 15% volume by volume of white liquor (Table 3). The viscosities were improved to 981-1032 ml/g, initial brightness were increased to 37-43% compared to those of AS-AQ pulps. In general total yields were increased 47.6-51.7%, as well as screened yields 46.9-48.3%. When applying low active alkali charge 15% as Na_2O at maximum temperature 175 ^{0}C, the viscosity was at highest level 1032 ml/g and, good initial brightness 39% and highest total yield 51.7%.
When applying active alkali charge 18.6% as Na_2O during ASAM pulping with maximum temperature 170 ^{0}C resulted in lowest viscosity 981ml/g with good initial brightness 42%, more or less very good screened yield 47.9% and total yield 48.5% (Table3). However at higher alkali charge 19% and higher maximum temperature 175 ^{0}C, the viscosity was decreased 1011ml/g with good initial brightness 43% (Table 3). During cooking with ASAM process, it seemed an increase of maximum temperature to 175 ^{0}C resulted in more or less similar Kappa numbers to those when temperature 170 ^{0}C was used (Figure 1). However rejects were reduced to minimum when ASAM cookings were applied compared to alkaline sulphite and alkaline sulphite-AQ cookings (Figure 2). On the other hand cookings with high maximum temperature 175 ^{0}C showed better total yields than cookings with maximum temperature170 ^{0}C (Figure 3).

Sulphite liquor burning and chemical recovery, after stripping and recovery of residual methanol are more complicated than for the Kraft process [24], the black liquor analysis of ASAM cookings were demonstrated in (Figure 6).

In general the physical properties of pulps were good to very good especially for pulps produced with ASAM process [Figures 7-12]. The tensile strengths were increased with the degree of beating, although all pulps reflected similar strengths, but ASAM pulps were much higher due to the high bonding strength between fibres as a result of perseveration of carbohydrate specifically the Pentosans [Figure 7]. It seemed the tear index very high for most pulps although AS-AQ pulps were the least and ASAM pulps were the highest [Figure 8], however burst index was showed in [Figure 9]; the burst indices of AS-AQ and alkaline sulphite pulps were higher than those of ASAM pulps. The burst strengths were increased with an increase in beating degree. On other hand the fold Kohler indicated the superiority of ASAM pulp compared to other studied processes [Figure10]. The highest apparent density and least porous pulps were presented by CASAM9 [Figures 11 and 12].

Conclusion

The digesting of pigeon pea stalks with alkaline processes was reported, and indicated it suitability for production of paper for writing and printing grades
In ASAM pulping, the effect of anthraquinone and methanol was clearly known in improvement of viscosity, total yield, screened yield, brightness and development of physical pulp properties when compared to alkaline sulphite and alkaline sulphite anthraquinone (AS-AQ) processes.
Pigeon pea stalks could be delignify to bleachable Kappa numbers with both AS-AQ and specifically ASAM process with good to excellent pulp properties.

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References

1- Elzaki, O. T Khider, T. O. Omer, S.H. and Shomeina, S.K. 2012. Environment friendly alkaline pulping of *Albizia lebbeck* from Sudan. Nature and Science, 10(4):76-82.

2- Elzaki, O. T Khider, T. O. and Omer, S.H 2012. Pulp and papermaking characteristics of *Cajanus Cajan* from Sudan. American-Eurasian Journal of Agricultural and Environmental Science, 12 (2): 159-163.
3- Khider, T. O. Omer, S.H. and Elzaki, O.T. 2012. Pulping and Totally Chlorine Free (TCF) Bleaching of *Acacia mellifera* from Sudan. World Applied Sciences Journal, 16 (9): 1256-1261.
4- Valenzuela, H and Smith, J. 2002. Pigeon pea. Sustainable Agriculture Green manure Crops. SA.GM-8.
5- Van der Maesen, L.J.G.1983. World Distribution of Pigeon pea. ICRISAT, Information Bulletin No.14.
6- Singh, F. and Oswalt, D.L. 1992. Pigeon pea Botany and Production Practices. Skill Development Series No.9. ICRISAT. Human Resource Development Program.
7- Subharani, S. Singh, T.K. 2011. Assessment of spatial distribution of pod borer, *Cydia ptychora* (Meyrick) on pigeon pea. Journal of Ecology and Natural Environment vol. 3(11):360-364.
8- Yeboah, E J.O. Fening and Ampontuah, E.O. 2009. The Use of Pigeon Pea (Cajanus Cajan) for Amelioration of Ultisols in Ghana. Soil Research Institute Academy, 28:401-410.
9- Habib, A. Anisuzzaman, A. Islam Khan, R. and Gafur, A. 2010. Chemical and Pharmacological characterization of hypolipidemic compound from *Cajanus Cajan*. Bangladesh Journal Pharmacology 5: 34-38.
10- Nan Wu , Kuang Fu , Yu-Jie Fu , Yuan-Gang Zu , Fang-Rong Chang, Yung-Husan Chen, Xiao-Lei Liu, Yu Kong, Wei Liu and Cheng-Bo Gu. 2009. Antioxidant Activities of Extracts and Main Components of Pigeon pea [*Cajanus Cajan* (L.) Millsp.] Leaves. Molecule, 14: 1032-1043.
11- Green, P.W.C. Stevenson, O.C. Simmonds, M.S.J. Sharma, H.C. 2003. Phenolic compounds on the pod-surface of pigeon pea, Cajanus Cajan, mediate feeding behavior of Helicoverpa armigera larvae. Journal of Chemical Ecology, Vol. 29(4): 811-821.
12- Bandyopadhyay, S 2010. Anti-Fertility Activity of Methanol Extract of *Bassia latifolia and Cajanus Cajan* in Female Albino Mice Ovaries. Iranian Journal of Pharmacology and Therapeutics 9: 83-87.
13- Adeboye, O.A. and Olaniyi. M.O. 2011. Hepatoprotective effect of *Cajanus Cajan* on tissue defense system in D-galactosamine-induced hepatitis in rats. Turkish Journal of Biochemistry, 36:237-241.
14- Ezeifeka, G.O. Orji, M.U. Mbata, T.I. and Patrick, A.O. 2004. Antimicrobial activities of *Cajanus cajan*, Garcinia kola, Xylopia aetiopica on pathogenic microorganisms. Biotechnology,3 (1):41-43.
15- Sixta, H. 2006. Handbook of Pulp. Wiley- VCH Verlag GmbH &Co. KGaA, Weinheim.
16- Kordsachia, O. Wandianger, B. and Patt, R. 1992. Some investigations on ASAM pulping and chlorine free bleaching of Eucalptus from Spain. Holz als Roh- und Werkstoff 50:85-91.
17- TAPPI. 2002. TAPPI Test Methods. TAPPI Press, Atlanta.
18- Shatalov, A,A. and Pereira, H. 2006 Papermaking fibers from giant reed (Arundo donex L.) by advanced ecologically friendly pulping and bleaching technologies. BioResources 1(1), 45-61.
19- Khider, T. Omer, S. and Taha, O. 2012. Alkaline Pulping of *Typha domingensis* Stems from Sudan. World Applied Sciences Journal, 16 (3): 331-336.
20- Khider, T. Omer, S. and Taha, O. 2011. Alkaline Pulping with Additives of Southern Cattail Stems from Sudan. World Applied Sciences Journal 15 (10): 1449-1453, 2011.
21- Jahan, M. S. Sabina Rawsn, D.A. Chowdhary, D .A. N. and Al-maruf, A. 2008. Alternative pulping process for producing dissolving pulp from jute. BioResource 3(4):1359-1370.
22- Barbash, V. Trembus, I. and Nagorna, j. 2012. Pulp obtaining from corn stalks. Chemistry and Chemical technology, vol. 6(1) : 83-87.
23- Chai, X.S. Samp, J. Hou, Q. X. Yoon, S.H. and Zhu, J.Y. 2007. Possible mechanism for anthraquinone species diffusion in alkaline pulping. Ind. Eng. Chem. Res. 46:5245-5249.
24- Hentges, R.A. Hunter, W.D. and Jackson, M. 1993. The ASAM process: a concept for environmentally friendly and higher quality pulps. TAPPI Conference, TAPPI Proceedings: 689-699.

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