

Studies on Bleaching of Alkoxygen Delignified Pulp of *Cajanus cajan*

Dharm Dutt*, J S Upadhyaya, C H Tyagi, R S Malik and Anurag Yadav

Indian Institute of Technology Roorkee (Formerly University of Roorkee), Saharanpur Campus

Department of Paper Technology (Formerly Institute of Paper Technology) Post Box No. 83 Saharanpur 247 001, India

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The proposed study was undertaken to assess the suitability of *Cajanus cajan* using alkoxygen delignification process. Molecular oxygen is a specific oxidising agent for lignin but has limitations because of its low solubility in cooking liquors. The problem of mass transfer of oxygen should be far less than that of woods, because of more loose and open structure and low specific gravity of *Cajanus cajan*, makes it possible for dissolved oxygen to diffuse easily to accomplish the alkoxygen delignification. The effect of cooking variables like oxygen pressure (0, 0.5, 0.8, 1.0 and 1.2 MPa), alkali charges (16, 18 and 20 per cent as NaOH), cooking time (60, 90, 120, and 150 min) and cooking temperature (155, 160, 165, and 170°C) on pulp yield, kappa number and screen rejects were studied. The alkoxygen delignification of *Cajanus cajan* led to significant increase in screened pulp yield, faster rate of delignification and substantial drop in kappa number due to carbohydrate stabilization. The results of these studies revealed that optimum process condition for alkoxygen delignification process of *Cajanus cajan* includes the following: Alkali charge = 18 per cent (as NaOH), Temperature = 165°C, Time = 120 min and Oxygen pressure = 1.0 Mpa. The unbleached pulp of kappa number 30 and brightness 29.8 per cent, (Elrepho) shows good response towards bleaching. To attain stable and high brightness, the pulp was bleached with chlorine dioxide and oxygen. The properties of CEDED, and C(EO)DED bleached pulps were compared with CEHH bleached pulp.

Introduction

It has been known for many years that oxygen in alkaline medium can be used as a delignifying agent in pulp bleaching. Although molecular oxygen is considered as a specific oxidizing agent for lignin degradation and solubilization reactions, the drawback for its low solubility in cooking liquor causes a serious problem in mass transfer in a heterogeneous system composed of gas 'oxygen', liquid 'water' and solid 'fibres', which exist during pulping operations. Oxygen must cross the gas liquid interface, diffuse through the liquid film surrounding the fibre and finally diffuse into the fibre wall before reacting surface. Depending on the conditions the rate of oxygen transport can limit the rate of the overall process, because of the inherent slowness of the diffusion phenomenon involved¹. The mass transfer problem is aggravated by the low solubility of oxygen in aqueous sodium hydroxide^{2,3}. Typically, 24-times as much oxygen is consumed during bleaching at 15 per cent consistency as can be present in the liquid phase at any one time and at 27 per cent consistency, 50-times

as much. Obviously the process must facilitate the transfer of oxygen into and through the liquid phase. Ensuring that the partial pressure of oxygen in the gas phase and the gas liquid interfacial area are both sufficiently large can do this. Even at the very high oxygen pressure, useful mass transfer of molecular oxygen into the fibre wall, where oxidation reaction should take place is difficult to obtain in one stage pulping⁴.

Studies have been carried out to develop the two-stage approach for wood pulping to produce high yield pulp of superior quality comparable to Kraft. These generally involve a first more or less mild cooking stage followed by mechanical defibration. The coarse pulp thus obtained is suitable for subsequent alkaline oxygen treatment, due to its higher exposed surface area^{5,7}. Unfortunately the two stage pulping process is rather cumbersome and is likely to involve high capital cost. Thermo-chemical fibres, instead of wood chips, have been used for alkali-oxygen delignification process with one-stage alkali-oxygen treatment to develop a new pollution-free alternative method to the existing Kraft process. But some strength deficiencies due to mechanical attrition

* Author for correspondence

are caused in the pressurized refiner, which itself is an operation and high in energy consumption.

The transition metals in pulp, such as Mn, Cu and Fe in unbleached pulp promote random cleavage⁸. They catalyze the formation of reactive oxygen based radicals, such as hydroxyl radicals, that dominantly attack the cellulose chain⁹⁻¹¹. Magnesium, salts and sodium silicate are good stabilizers. It is believed to function by precipitating as magnesium hydroxide, which absorbs the metal ion and making them unavailable for catalysis of peroxide decomposition¹² or by forming complex with them¹³.

During the past few years, considerable attention has been paid to pollution abatement of pulping process. Stringent pollution limits are forcing pulp and paper industries to lower the cooking kappa number. A major part of effort has been focused on bleaching. Environmental concerns in the paper industry have led to a need to reduce the kappa number of pulps entering the bleach plant in order to reduce the BOD, COD, colour, and AOX level of the effluent discharged. This goal can be achieved in two ways:

- Extended delignification can be achieved by doing front end and back end modification in conventional cooking process to lower cooking kappa number without destroying the pulp strength or losing of pulp yields.
- Introduction of a separate oxygen delignification stage between cooking and bleaching.

The effect of the above options helps in penetration of cooking liquor over 5mm thick chip particles, which remains poorly delignified in conventional cooking process. Another effect of above option is maximum removal of lignin by oxygen delignification process with the result that load to the recovery boiler is increased. This means lower pollution load and also saving of bleaching chemicals.

***Cajanus cajan* As A Raw Material**

Cajanus cajan is commonly known as 'Tauhar' in Hindi. It is an important eco-friendly leguminous edible crop, often grown for green manure or for cover on plantation and is about 3–5m in height. The estimated annual collectable yield of *Cajanus cajan* is 3.29–3.40 t/ha. Its crop provides pulpable raw material having bulk density around 180–190 kg/m³. The average production was 14.58 to 15.30 mt in 1981–1986 (ref.14).

Due to shortfall of cellulosic fibrous raw material in India, attention has been paid on utilization of agro-based residues as a source of raw material for papermaking. *Cajanus cajan* is a promising raw material and can be used as a supplement raw material. The present investigation on *Cajanus cajan* was studied in two parts. The objective of the first part was to reduce kappa number by alkali-oxygen delignification. The second part focuses on the bleaching studies to improve upon the brightness stability. A comparison of strength properties has been made among CEHH, CEDED, and C(EO)DED bleached pulps.

Experimental Procedure

The *Cajanus cajan* was collected from places in the vicinity of Saharanpur. The material was chopped manually, air-dried and then analysed for its morphological characteristics and chemical composition as per Tappi standard methods. The results are summarized in Table 1 and 2.

Pulping Studies

The purpose of pulping studies was to optimize the pulping conditions necessary to obtain pulp of low kappa number. Pulping studies were carried out in a WEVERK rotary electrically heated digester of capacity 0.02m³ using different alkali charges in the range of 12–18 per cent (as NaOH), oxygen pressure of 0.0, 0.5, 0.8, 1.0, and 1.2 MPa, at 155, 160, 165 and 170 °C, respectively, maximum pulping time of 60, 90, 120 and 150 min and liquor to wood ratio of 3.5: 1. At the end of cooking the pulp was properly washed and screened. Kappa number, pulp yield, and screen rejects were measured in each case. The results are reported in Tables 3–5.

Bleaching Studies

The alkali-oxygen delignified pulp of brightness 29.8 per cent (Elrepho) and kappa number 30 was bleached using CEDED and C(EO) DED bleaching sequences. The results were compared with CEHH bleaching sequence and are reported in Table 6.

Pulping Evaluation Studies

The bleached pulps were beaten in PFI mill with a beating pressure of 1.8 kg/cm², a freeness level of 40°SR and laboratory hand-sheets of 60 g/m² were prepared on British sheet former. These hand-sheets were evaluated as per the BIS method for their different physical strength properties at 27 ± 2 °C and a

Table 1 — Morphological characteristics of *Cajanus cajan*

Sl No.	Particulars	Unit	<i>Cajanus cajan</i>	Bamboo (14)
1	Colour		Light brown	Light brown
2	Density	kg/m ³	480	521
3	Fiber length, L variation	Mm	0.312 – 0.910	1.5 – 4.4
4	Fiber width, D variation	μm	10.87 – 32.76	—
5	Lumen width, d variation	μm	4.10 – 22.64	—
6	Cell-wall thickness, W variation	μm	1.62 – 5.44	—
7	Flexibility coefficient, $^{d}/l_D \times 100$	—	68.03	40.5
8	Ratio of cell-wall thickness to fibre width, $^{2W}/l_D$	—	0.320	0.593
9	Muhlestepl ratio, per cent	—	61.5	—
10	Ratio of length to width, $^{L}/D$	—	34.60	72.0
11	Ratio of cell-wall thickness to lumen width, $^{W}/d$	—	0.23	0.74

Table 2 — Proximate chemical analysis of *Cajanus cajan*

Sl No.	Parameters	Per cent
1	Cold water solubility	3.42
2	Hot water solubility	5.10
3	Alcohol-benzene solubility, $^{V}/V$ 1:2	4.14
4	1 per cent NaOH solubility	19.66
5	Lignin	18.72
6	Pentosan	15.97
7	Hemi-cellulose	25.24
8	α-cellulose	72.86
9	β-cellulose	47.31
10	γ-cellulose	11.56
11	Holo-cellulose	13.50
12	Ash	1.72
13	Silica	0.56
14	Acetyl content	2.18
15	Methoxyl content	3.55

relative humidity level of 65 ± 2 per cent. The pulp evaluation results are reported in Table 7.

Results and Discussion

Table 1 shows the morphological characteristics of *Cajanus cajan* and comparison with bamboo. The morphological studies reveal that the fibre length of *Cajanus cajan* is comparatively lower than bamboo. The lumen diam of *Cajanus cajan* fibre is higher, whereas the cell wall thickness is lower than that of bamboo. It can be concluded that the thin walled and wide lumen fibres of *Cajanus cajan* collapse easily when made into paper sheets and thus may result into a more compact stronger sheet due to good fibre bonding. On delignification, it produces more flexible fibres offering more surface contact area with better inter-fibre bonding.

Table 2 shows the results of proximate chemical analysis of *Cajanus cajan*. It indicates that *Cajanus cajan* has moderate quantity of solubles, i.e., hot water solubility 5.10 per cent and alcohol-benzene solubility 4.14 per cent, thereby creating less hindrance during pulp processing and paper making. This plant has lower lignin content and comparatively higher carbohydrate fraction in comparison to other agro-based cellulosic fibrous raw materials. Therefore, it requires lesser cooking chemicals and shorter cooking cycle.

Table 3 — Effect of alkali charge and oxygen pressure on pulp yield, screen rejects and kappa number during alkoxygen delignification of *Cajanus cajan*

Alkali charge, per cent as NaOH	Oxygen pressure, Mpa	Pulp yield, per cent	Screening rejects, per cent	Screened yield, per cent	Kappa number
16	0.0	51.5	1.85	49.6	57
	0.5	53.5	1.30	52.2	54
	0.8	54.3	1.15	53.2	51
	1.0	51.1	1.08	50.3	49
	1.2	46.1	1.02	45.1	41
18	0.0	49.6	1.45	48.2	41
	0.5	50.8	0.95	49.8	38
	0.8	51.6	0.82	50.8	33
	1.0	51.1	0.75	50.4	30
	1.2	47.8	0.65	47.1	26
20	0.0	46.9	0.63	46.3	37
	0.5	48.4	0.28	48.1	33
	0.8	49.9	0.21	49.8	29
	1.0	48.3	0.13	48.1	27
	1.2	45.3	0.11	45.2	25

Fixed cooking parameters — Alkali charge as NaOH, 18 per cent, Time from room temp to 105°C, 45 min, Time from 105°C to 165°C, 45 min, at 165°C, 120 min and liquor to wood ratio, 3.5 : 1

Table 4 — Effect of time on pulp yield, screen rejects and kappa number during alkoxygen delignification of *Cajanus cajan*

Time at maximum Temperature, min	Pulp yield, per cent	Rejects, per cent	Screened pulp yield, per cent	Kappa number
60	56.5	8.60	47.9	44
90	51.8	2.30	49.5	36
120	51.1	0.75	50.3	30
150	48.2	0.37	47.8	28

Fixed cooking parameters — Alkali charge as NaOH, 18 per cent, Oxygen pressure 1.0 Mpa, Time from room temp to 105°C, 45 min, Time from 105°C to 165°C, 45 min, Time at temp 165°C, 120 min and liquor to wood ratio, 3.5 : 1

Table 5 — Effect of temperature on pulp yield, kappa number and screening Rejects during alkoxygen delignification of *Cajanus cajan*

Temperature, °C	Pulp yield, per cent	Rejects, per cent	Screened pulp yield, per cent	Kappa number
155	52.1	2.35	49.8	41
160	53.4	1.20	42.2	35
165	51.1	0.75	50.3	29
170	49.4	0.45	48.9	28

Fixed cooking parameters — Alkali charge as NaOH, 18 per cent, Oxygen pressure 1.0 Mpa, Time from room temp to 105°C, 45 min, Time from 105°C to max temp, 45 min, Time at temp max temp, 120 min and liquor to wood ratio, 3.5 : 1

The effect of variables such as, oxygen pressure, alkali charge, temperature, and cooking time was studied to obtain pulp of desired kappa number. Table 3 shows the results of alkali oxygen delignification of *Cajanus cajan* at alkali charges of 16, 18, and 20 per cent (as NaOH) with and without oxygen at pressures of 0.0, 0.5, 0.8 and 1.2 MPa at fixed cook-

ing variables i.e., at 165°C, time at maximum temperature; 90 min, time at temperature; 120 min and liquor to wood ratio of 3.5: 1. Table 3 shows that oxygen has a considerable effect on the cooking variables. It is thus evident that on increasing oxygen pressure from 0.0 to 1.0 MPa the screened pulp yield increases. Further, on increasing oxygen pressure be-

Table 6 — Bleaching conditions and results of alkoxygen delignified pulp of *Cajanus cajan*

Sl No.	Particulars	CEHH	CEDED	C(EO)DED					
1	Chlorination stage, (C)								
(i)	Chlorine, per cent	4.70	4.70	4.70					
2	Extraction stage, (E ₁)								
(ii)	Alkali, per cent (as NaOH)	2.30	2.30	—					
(iii)	Brightness, per cent, Elrepho	36.00	36.00	—					
3	Alkali Oxygen stage, (O)								
(i)	Alkali, per cent on o.d. pulp basis	—	—	2.3					
(ii)	Oxygen pressure, Mpa	—	—	1.0					
(iii)	MgSO ₄ , per cent	—	—	1.0					
(iv)	PH	—	—	11.2					
(v)	Kappa number	—	—	15.0					
(vi)	Brightness, per cent elrepho	—	—	58.0					
4	Hypochlorite stage, (H ₁)								
(i)	Hypochlorite, per cent	1.82	—	—					
(ii)	Brightness, per cent Elrepho	68.00	—	—					
(iii)	Copper number	1.77	—	—					
5	Hypochlorite stage, (H ₂)								
(i)	Hypochlorite, per cent	0.92	—	—					
(ii)	Brightness, per cent Elrepho	77.40	—	—					
(iii)	Post colour number	3.90	—	—					
(iv)	Viscosity (cuprammonium) cps	9.15	—	—					
(v)	Copper number	0.98	—	—					
6	Chlorine dioxide, (D ₁)								
(i)	Chlorine dioxide, per cent	—	1.2	1.2					
(ii)	Brightness, per cent Elrepho	—	81.5	82.6					
(iii)	Post colour number	—	2.0	2.4					
(iv)	Viscosity (cuprammonium) cps	—	10.0	10.6					
7	Extraction stage, (E ₂)								
(i)	Alkali, percent as NaOH	—	0.5	0.5					
(ii)	Brightness, per cent Elrepho	—	79.8	81.5					
8	Chlorine dioxide, (D ₂)								
(i)	Chlorine dioxide, per cent	—	0.6	0.6					
(ii)	Brightness, per cent Elrepho	—	86.3	88.2					
(iii)	Post colour number	—	0.7	0.5					
(iv)	Viscosity, cps (cupramonium)	—	10.1	10.1					
(v)	Copper number	—	0.15	0.13					
Bleaching conditions		C	E ₁	O	H ₁	H ₂	D ₁	E ₂	D ₂
Consistency, per cent		2.8	10.1	5.0	10.5	45 ± 2	9.0	10.2	9.0
Temp, °C		27 ± 2	70 ± 2	90 ± 2	45 ± 2	120	70 ± 2	45 ± 2	70 ± 2
Time, min		30	120	90	60	11.0	120	90	120
pH		2.4	11.2	11.5	11.0	11.4	3.5	11.5	3.5

beyond 1.0 Mpa, results in a slight decrease in pulp yield. The maximum carbohydrate yield is obtained at oxygen pressure of 1.0 MPa.

Table 3 gives alkali oxygen delignification of *Cajanus cajan* at different alkali charges with varying oxygen pressures. As far as the effect of delignifica-

Table 7— Mechanical strength properties of CEHH, CEDED and C(EO)DED bleached pulps of *Cajanus cajan*

Parameters	CEHH	CEDED	C(EO)DED
Burst index, kPam ² /g	4.06	4.85	4.98
Tear index, mNm ² /g	3.50	4.10	3.80
Tensile index, Nm/g	53.76	57.21	57.98
Folding endurance, no	28	36	38

tion is concerned, it can be observed that an increase in caustic soda charge from 16 to 20 per cent (as NaOH) kappa number decreases from 57 to 25, depending upon the oxygen pressure. Alkali charge has great influence on the pulp yield. An increase in alkali charge, results in substantial yield loss. The screened pulp yield obtained at an alkali charge of 18 per cent (as NaOH) and oxygen pressure of 1.0 MPa appears to be the most reasonable, while considering the kappa number and pulp yield values. Both screen rejects and kappa number decrease continuously as a result of an increase in either alkali charge or oxygen pressure.

Table 4 shows the results of alkali-oxygen pulping to study the effect of cooking time on pulp yield and kappa number. The cooks were made for 60, 90, 120 and 150 min while keeping all other variables constant. The results indicate that as the cooking time increases, both the screen rejects and kappa number decrease, it means that as the time of cooking increases the amount of lignin removal also increases. A cooking time of 120 min may be taken as an optimum pulping time at which optimum pulp yield is obtained at low kappa number.

Table 5 shows the results of alkali-oxygen pulping, carried out at 155, 160, 165 and 170 °C respectively, while keeping all other variables constant. The results indicate that an increase in cooking temperature improves delignification. As temperature increases, both pulp yield and screen rejects show declining trend. The optimum pulp yield with low kappa number and screen rejects was obtained at 165 °C.

Based on the above results, it can be concluded that optimum conditions for alkali oxygen delignification of *Cajanus cajan* are as follows:

Alkali charge	= 18 per cent as NaOH,
Temperature	= 165 °C,
Time	= 120 min,
Oxygen pressure	= 1.0 Mpa,
Liquor to wood ratio	= 3.5 : 1.

Table 6 shows the bleaching results of alkali-oxygen delignified pulp of *Cajanus cajan*. The final brightness of CEHH, CEDED, and C(EO)DED pulps was observed to be 77.4, 86.3 and, 88.20 per cent (Elrepho), respectively. The post colour number of CEHH pulp is on the higher side, i.e., 3.92 units as compared to CEDED and C(EO)DED pulps, i.e., 0.7 and 0.5, respectively. The reason is that the hypochlorite oxidises cellulose into oxycellulose (Copper number 0.98) and introducing carbonyl groups into the cellulose molecule which result in colour reversion in paper and thereby drop in viscosity of 9.8 cps was observed¹⁶.

In CEDED pulp the post colour number is around 0.25 and viscosity is 10.1 cps, because chlorine dioxide removes lignin by selective oxidation without causing much carbohydrate degradation and it is reflected in terms of Copper number, i.e., 0.25 units. In C(EO)DED bleached pulp, the pulp brightness of around 88.2 per cent, (Elrepho) with less brightness reversion i.e. PC number 0.5 units and copper number 0.18 units has been observed. Oxygen removes most of the lignin and destroys chromophoric groups in lignin structure in (EO) stage of Table 6. Chlorine dioxide further improves the brightness stability by rupturing carbohydrate molecule near carbonyl groups, dissolving the smaller fragments and thus eliminating the carbonyl groups in the chain.

Conclusions

The proposed study ascertains that the alkali oxygen delignification of *Cajanus cajan* is comparatively a better process. The lignin in this plant material is much more sensitive to the action of oxygen and results in pulp with higher degree of delignification. The delignification is easier than wood chips due to the more open and loose structure of *Cajanus cajan* chips. There is no diffusion problem of dissolved oxygen into this non-woody plant because of its more open and loose structure and low specific gravity. Based on experimental results, it can be concluded that optimum set of parameters for alkali oxygen delignification of *Cajanus cajan* may be considered as follows: Alkali charge = 18 per cent as NaOH, Oxygen pressure = 1.0 Mpa, Maximum temp = 165 °C, Time at maximum temperature = 120 min and liquor to wood ratio = 3.5 : 1.

A brightness level of 86.3 - 88.2 per cent, (Elrepho) can be achieved with CEDED and C(EO)DED

bleaching sequences without much adverse effect on viscosity, colour reversion and strength properties. High brightness pulps of *Cajanus Cajan* can be used as a supplement for expensive imported pulps for making cultural papers with good optical properties.

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