Melia dubia Valorization at 4, 5- and 6-year Age for Pulp and Paper Production

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Abstract: Melia dubia, a fast-growing hardwood tree, has been identified as a potential pulpwood species which can be cultivated under agroforestry scheme in diverse climatic and geographical conditions. This study explores 4, 5- and 6-year harvests of M. dubia for pulp and paper production with an aim to choose the most suitable harvesting age. All the three harvests of M. dubia were subjected to physicochemical analysis, fiber characterization, kraft pulping and OD_0EopD_1 bleaching (O = oxygen delignification, D = chlorine dioxide, Eop = extraction fortified with peroxide and oxygen). The unbleached and bleached pulps were evaluated for chemical characteristics and physical strength properties. The black liquor properties, heavy metal contents in pulp and SEM characteristics of pulps as well as hand sheets were also analyzed. The basic densities of M. dubia trees were found in the range of 433 – 490 kg/m^3. The 5-year-old harvest exhibited the lowest ash (0.65%) and alcohol benzene extractives (1.75%) while the highest holocellulose (82.55%) and pentosans (16.60%). Fiber length (1152.8 µm) and fiber diameter (24.34 µm) of the 6-year-old harvest was the highest among all. Kraft pulping of M. dubia harvests resulted in 51 – 51.66% screened yield with kappa number, intrinsic viscosity and brightness of unbleached pulps in ranges 14.15 – 15.6, 658.2 – 785 cm^3/g and 32 – 32.7% ISO respectively. Their OD_0EopD_1 bleaching produced pulps with brightness 85.07 – 90.40% ISO, intrinsic viscosity 440.56 – 455.50 cm^3/g, tensile index 66.36 – 68.43 Nm/g, tear index 4.14 – 5.24 mNm^2/g, burst index 4.15 – 4.32 kPam^2/g etc. This study confirmed the papermaking suitability of all the three harvests of M. dubia; however, the five years was rated as the best age at which M. dubia should be harvested for pulp and paper.

Keywords: Agroforestry, Harvesting Age, Kraft Pulping, ECF Bleaching, Pulp and Paper

1. Introduction

The limited forest resources and growing wood demand has created a paucity of wood for pulp and paper industry. To counter the issue, the wood-based pulp and paper mills have initiated plantations under agroforestry/farm forestry scheme. The concept of agroforestry is shaping perspectives in forest management by reducing the pressure on available natural forests. Agroforestry is widely practiced worldwide in meeting the demand for wood for producing pulp and paper. It is considered very important in Central America, South America, Southeast Asia, and Africa. It has been estimated that due to agroforestry plantations 46% of global agricultural land is under more than 10% tree cover. In the last 25 years about 6 lac acres of pulpwood plantations has carried out successfully in India [1]. Different pulp and paper mills have planted different plants species according to the different climatic zone under agroforestry. In agroforestry, the short rotation wood plantation is preferred to long rotation plantations. This facilitates in meeting the required wood demand of pulp and paper mills in short duration.

Major tree species raised for pulp and paper production under agroforestry scheme are *Eucalyptus camaldulensis*, *Eucalyptus tereticornis*, *Casuarina equisettifolia*, *Casuarina junghuniana*, *Dalbergia sisoo*, *Gmelina arborea*, *Tectona grandis*, *Acacia mangium*, *Acacia crassicarpa*, *Populous deltoides*, *Pinus roxburghi* etc. Recently, *M. dubia* has been identified as a potential hardwood for pulp and paper production under agroforestry scheme [2]. *M. dubia* is a deciduous perennial tree which belongs to *Meliacea* family. *Melia composite Willd* and *Melia superba Roxb* are its biological synonyms. Due to its fast growth, multiple uses and high economic returns it is popularly termed as a money-spinning tree. The ground breast height of 5-year *M. dubia* in favorable and rain fed conditions has been observed to be 82 cm and 48 cm respectively [3]. It can attain a height up to 20 m with spreading crown, bole length 9 m and girth 1.5 m [4]. It has high carbon assimilation potential and helps to reduce the greenhouse effect. The plantation of *M. dubia* in adverse climatic conditions and on degraded land has been found to change the pH of the soil from alkaline to neutral and improve groundnut and masoor crop production [5]. It can be potentially grown as intercrop among coconut, black gram, green gram, and turmeric. It can be used as bund plant for casuarina, banana, drumstick, sugarcane plantation and mango orchards. It can also be grown as a shade tree for coffee and tea plantations. The tree is indigenous to India but also found in Sri Lanka, Myanmar, Malaysia, Java, China and Australia [6].

The harvesting age of a tree has a direct influence on its physiochemical, pulping and bleaching characteristics. The harvesting age for a tree depends on its end use and varies from species to species. From pulp and papermaking point of view several properties of a tree such as bulk density, basic density, cellulose content, solubility (hot water, cold water, 1% NaOH, alcohol benzene), lignin, ash, pentosan etc. highly depends on its harvesting age. The variations in these parameters have been clearly observed in a different age of Eucalyptus, Leucaena, Acacia etc. [7] – [9]. However, studies on the acquiescence of *M. dubia* for pulp and paper production in different age gradation are very limited in the literature. Some studies highlight its Kraft pulping followed by CEHH bleaching (C=chlorination, E=extraction, H=hypo) [10] as well as D_0EopD_1 bleaching (D=Chlorine dioxide, Eop=Extraction with peroxide in the presence of oxygen) [11]. The aim of this study is to select the best harvesting age of *M. dubia* through physicochemical analysis, kraft pulping, elemental chlorine free (ECF) bleaching, fiber morphology, and fiber fractionation.

2. Materials and Methods

2.1 Processing of raw materials

Melia dubia 4, 5- and 6-year harvest was collected from a nearby agroforestry farm and were named as MD4, MD5, and MD6 respectively. The wood logs were manually debarked to remove the upper dark layer of ~2 cm. The debarked logs were cut into thin logs and then inserted into a wood chipper to get chips. The chips were first classified in different classes depending upon their size. The wood chips were classified into five classes as knots (45 mm), oversized chips (13 mm), accepted chips (8 mm), pin chips (3 mm) and fines using a laboratory chip classifier. The results were expressed as the percentage of total mass of all fractions. The accepted chips were processed further for making ~ 100 g dust (mesh size 40) using a machine (Willy Mill) in the laboratory as well as for pulping experiments.

2.2 Physico-chemical characterization

M. dubia in different harvest age was characterized for bulk density using SCAN-CM 46:92 and basic density using SCAN-CM 43:95. The chemical analysis was performed to evaluate ash (TAPPI T 211 om-02); cold and hot water solubility (TAPPI T 207 cm-99); 1% NaOH solubility (TAPPI T 212 om-02); alcohol benzene solubility (TAPPI T 204 cm-97); holocellulose [12]; acid insoluble lignin (TAPPI T 222 om-02); Pentosan (TAPPI T 223 cm-01); and alpha, beta and gamma cellulose (TAPPI T 203 cm-99). Kraft pulp was also characterized for the above-mentioned chemical properties using the same standards.

2.3 Kraft pulping procedure

The kraft pulp for 4, 5- and 6-year *M. dubia* was prepared in series digester having 6 bombs (STALSVETS, Alfa Aval Group, Sweden) to obtain target kappa number 15±1. The 300 g oven-dried sample of accepted chips was taken for kraft pulping. The typical Indian paper mill conditions used for kraft pulping of hardwoods i.e. temperature 160°C, time 90 min., solid to liquid ratio 1:3.5, cooking chemical 16% as Na_2O, and sulphidity 20% were implanted in this study. The cooking schedule consisted of 30 min heating from ambient temperature to 100°C, 90 min heating from 100°C to 160°C and a further 90 min heating at 160°C. The calculated volume of white liquor and water was added to the bombs, which were tightly screwed and placed in digester containing oil bath. The cooked material was washed on 26 cm Büchner funnel fitted with terylene filter cloth, to remove the black liquor from the pulp. The chips were further disintegrated for 10 min in laboratory disintegrator. The pulp was finally washed on Büchner funnel with hot water until the filtrate is colorless. The pulp was further screened in Somerville vibratory screen using the mesh of 0.25 mm to remove the rejects. The pulp was disintegrated for 10 min diluted to approximately 0.5% stock concentration, agitated by hand and one-litre aliquots were poured on to the screen plates. The pulp feeding was done carefully and was regulated to avoid blocking of the screen. The screen rejects were collected and dried in an oven for determination of percent rejects and screened pulp yield.

2.4 Black liquor characterization

The black liquor obtained after kraft pulping was characterized for pH, total dissolved solids (TAPPI T 650 pm-84), residual active alkali (TAPPI T 625 cm-85), organics and inorganics.

2.5 Oxygen delignification and ECF bleaching procedure

The kraft pulp obtained from each *M. dubia* harvest was bleached using ECF sequence D_0EopD_1 followed by oxygen delignification. Firstly, oxygen delignification was performed using the series digester having six bombs attached with an oxygen cylinder. The oxygen pressure 5 kg/cm^2, pulp consistency 8%, temperature 90^{o}C, time 90 min, NaOH 1.5% w/w was used for oxygen delignification. The chemicals used in ECF bleaching were chlorine dioxide in initial stage 2.5%, NaOH 2%, H_2O_2 1.5%, and chlorine dioxide in final stage 1%. The polythene bags and hot water bath (Julabo TW 20, Germany) were used for bleaching. The pulp was thoroughly washed in Büchner funnel with tap water using vacuum pump after each stage of the bleaching. The pH of the pulp was maintained by using H_2SO_4 and NaOH. Bleaching conditions are presented in **Table 1**.

Table 1: ECF bleaching conditions

Parameters	*Unit*	D_0	*Eop*	D_1
Consistency	%	8	8	8
Reaction time	min.	60	75	180
Reaction temperature	^{o}C	70	80	75
End pH	-	3.2	12	3.5

2.6 Pulp characterization

The unbleached and bleached pulps were characterized for kappa number (TAPPI T 236 om-99), CED viscosity (SCAN C 15:62), brightness (ISO 2470) and freeness (ISO DP 5269). Atomic absorption spectrophotometer- AAnalyst-800 (Perkin Elmer) was used for heavy metal analysis.

2.7 Hand sheets characterization

The unbleached and bleached hand sheets of 60 gsm were prepared with British sheet former machine according to the ISO 5269-1:2005 standard to measure apparent density (ISO 534:1988E), burst index (ISO 2758), tensile index (ISO 1924), tear index (ISO 1974), opacity (ISO 2471) and light scattering coefficient (ISO 9416).

2.8 Fiber classification and morphology

The Bauer McNett fiber classification of unbleached pulp was done according to TAPPI T 233 cm-82 standard. The fiber dimensions were measured with the help of Morfi Fibre Analyser (Morfi v9.6) and photomicrographs of fibers were clicked using motorized research microscope B×61 (Olympus) according to testing procedure IS 5285-1998.

2.9 Scanning electron microscope (SEM) analysis

SEM analysis was performed using MIRA 3 TESCAN microscope. For clicking the 3D image of pulp, the sample was initially mounted on double stick electrically conductive carbon tape and coated with gold/palladium in a vacuum chamber.

3. Results and Discussions

3.1 Chips classification

Chips classification is done to maintain the uniformity in chip size and shape during pulping so that the penetration of the pulping liquor, water and heat remains uniform and consistent [13]. The oversized chips, knots, accepted chips, pin chips and fines in the 4-year harvest were 22.5%, 2.5%, 66%, 8%, and 1% respectively. In 5-year harvest, these were 15.5%, 3%, 73%, 7.5% and 1% respectively while in the 6-year harvest, these were 16.5%, 4.5%, 71.5%, 6.5% and 1% respectively. In 5-year harvest, the percentage of accepted chips is the highest while the percentage of oversized chips is the lowest in comparison to 4- and 6-year harvests. Though the fine percentage is the same in all the harvests, the knots are the highest in the 6-year harvest. It has been observed in previous studies that knots and oversized chips decrease the brightness and strength of the pulp [14]. The thickness of the chips is the most critical dimension in the kraft pulping process. Due to the nature of the impregnation process, the delignification of wood strongly depends on the thickness of chips. Variation of the delignification stage within the chips results in less homogeneous pulp and results in reduced pulp yield and pulp strength properties. Short chips usually increase the number of broken fibers. Pulp obtained from an accepted fraction of chips has better uniformity and pulp quality with low rejects. Hence, in this study, all the investigations on *M. dubia* harvests have been performed using the accepted fraction of chips.

3.2 Physico-chemical properties of *M. dubia* harvests

The physicochemical analysis is a predetermination process to check the suitability of lignocellulosic material for pulping and bleaching. The results of physicochemical analysis of *M. dubia* at 4, 5- and 6-year age gradation are shown in **Table 2**.

It can be seen from this table that *M. dubia* in 4 year exhibits the highest ash, hot water solubility, alcohol benzene solubility, lignin while the lowest basic density, bulk density, 1% NaOH solubility and pentosan. *M. dubia* in 5 year shows the lowest ash, alcohol benzene and lignin while the highest pentosan and holocellulose. *M. dubia* in 6 year reveals the highest basic density, bulk density, and 1% NaOH solubility while the lowest hot water solubility, cold water solubility and holocellulose. Alpha, beta and gamma cellulose are almost the same in all the three ages. Literature has classified ash, hot water solubility, cold water solubility, NaOH solubility, alcohol benzene extractives, and lignin as non-beneficial attributes since their low values are sought while holocellulose, alpha cellulose, pentosans and bulk density as a beneficial attribute since their higher values are desirable from pulp and papermaking point of view [15] – [16].

Table 2: Physico-chemical properties of *Melia dubia* at 4, 5- and 6-year age

Parameters	*MD4*	*MD5*	*MD6*
Physical property (kg/m^3)			
Basic density	433.33	481	490
Bulk density	198	215	224
Chemical property (%)			
Ash	0.85	0.65	0.73
Hot water solubility	4.32	4.12	3.2
Cold water solubility	0.54	0.56	0.4
1% NaOH solubility	19.03	19.73	19.82
Alcohol Benzene solubility	2.30	1.75	1.82
Klason lignin	27.8	26.27	26.5
Holocellulose	81.96	82.55	80.75
Alpha cellulose	49.37	49.56	49.81
Beta cellulose	17.26	17.67	17.70
Gamma cellulose	13.12	13.32	13.34
Pentosans	14.55	16.60	16.34

An increasing trend in basic and bulk density of *M. dubia* exists with an increase in age. Generally, an immature wood is known to be of lower density than mature wood because the proportion of lower density material formed early in the life of a tree is reduced by the formation of higher density materials in older trees [17] Such an impact of age on wood density has also been previously reported in *Eucalyptus* species, *Pinus taeda*, *Tectona grandis*, *Acacia auriculiformis* etc. [18] – [21] The density of wood influences the strength and physical characteristics of paper sheets. The amount of wood needed to produce one tonne of air-dried pulp is also calculated from density and pulp yield. Less ash content is preferred in lignocellulosic raw materials to avoid the corrosion and scaling problem [22] – [23]. The solubility of the raw material in water, 1% NaOH, alcohol benzene negatively affects the pulp yield, paper quality and drainage characteristics of the paper machine [24] – [25]. Lower values of solubility in water indicate that the raw material has lower soluble carbohydrate content in chips which has advantages in terms of resistance to degradation and optimal chemical use in the pulping process. The higher extractive content has its negative share in terms of alkali neutralization in the pulping process as well as pitch generation.

The lignin content influences the alkali consumption during pulping and affects bleachability, hardness, and color of pulp. The lignin content in *M. dubia* was found like *Eucalyptus globulus* (27.68%) and *Eucalyptus grandis* (27.10%) [26] – [27]. The amount of holocellulose shows total carbohydrate content in a lignocellulosic raw material. The higher holocellulose content indicates that with milder pulping conditions the pulp yield levels could be significantly improved. The holocellulose in *Melia dubia* is higher than other industrial hardwoods such as *Eucalyptus globulus* (80 .47%), *Eucalyptus grandis* (72.80%), and *Leucaena* (76.58%) [26] – [28]. The alpha, beta and gamma cellulose provide information about the aging and response to refining operations. The alpha cellulose indicates the undegraded, high molecular cellulose content in pulp, beta indicates the degraded pulp and gamma indicates the hemicellulose [29] – [30]. The alpha cellulose in the present study is higher than the *Eucalyptus grandis* (44.20%) [27], *Casuarina* (46.2%) [31] but less than the *Leucaena* (58.70%) [28]. The amount of pentosans also reveals the presence of hemicellulose in hardwood. The hemicellulose helps in retaining the strength in pulp during refining, so pentosans should be high in a lignocellulosic raw material. The hemicellulose usually degrades during cooking and its retention is desired after cooking as it acts as an amorphous layer around the fiber and protects the fiber from mechanical distractions while providing strength and enhancing the pulp yield.

3.3 Kraft pulp characteristics

Properties and heavy metal contents of kraft pulps obtained from *M. dubia* at 4, 5- and 6-year age gradation have been enumerated in **Table 3**. All the kraft pulps exhibited almost same but increasing kappa number, total yield and screened yield irrespective of tree age. However, rejects and brightness showed a decreasing trend with age while intrinsic viscosity initially exhibited an increasing trend up to the 5-year and later got decreased in the 6-year. The increase in pulp yield with age has also been observed in *Eucalyptus dunni* at 2, 4 and 6 years [32]. The large degradation of carbohydrates reduces the pulp yield. Though the reduction in rejects of kraft pulp with tree age is contrary to *Pinus radiate*, no obvious explanation can be provided for this behavior [33]. It might be possible due to the variation of the amount of heartwood and presence of some portion of barks and knots in cooking chips. The similar effect of tree age on intrinsic viscosity was observed in kraft pulping of the *White joban* tree with age 3, 5 and 7 years wherein intrinsic viscosity increased up to 5 years and then got decreased in the 7-year [34]. It was observed that the presence of hemicelluloses decreases pulp viscosity due to its lower degree of polymerization as compared to cellulose.

The heavy metal contents show variation across the tree age in kraft pulps. The iron, magnesium, zinc, nickel decreased with age while cadmium, copper, calcium increased with age. The overall metal content in *M. dubia* in 4, 5, 6 year exhibited the following decreasing trend: Ca > Mg > Cu > Zn > Fe > Ni > Mn > Pb > Cd. The metal ions enter the pulping process with the raw materials since trees absorb various heavy metals from soil and water among which Fe, Mn, Zn, Cu, and Ni are essential for tree growth [35]. The metal ions also reach to pulps through process chemicals and make-up water.

The metal ions present in pulp have an influential effect on bleachability, especially when bleaching is carried out with oxygen and hydrogen peroxide. Magnesium has a more effective impact in peroxide stage since it acts as a protector in hydrogen peroxide bleaching. Manganese causes reflectance in chlorine dioxide stage. Cadmium is considered very toxic and was found very low in the present study. Calcium causes a scaling problem in the digester and black liquor evaporators still important to enhance the brightness during bleaching [36]. Iron leads to colorisation of pulp and final paper products [37] and has an impact on pulp viscosity. Iron in D_o stage causes depolymerization of carbohydrates which reduces the viscosity of the pulp [38]. During kraft pulping the metal ions get reduced and converted into insoluble hydroxides as well as sulfides and get attached to the fibers. The removal of metals ions before bleaching is preferred to reduce their negative impacts. Acid washing of pulp is preferred for this purpose.

Table 3: Properties and heavy metal content of *M. dubia* kraft pulps

Parameters	*MD4*	*MD5*	*MD6*
Kappa number	14.15	15.1	15.6
Total yield, %	51.30	51.63	51.86
Rejects, %	0.30	0.25	0.20
Screened yield, %	51	51.38	51.66
Intrinsic viscosity, cm^3/g	658.2	785	766.6
Brightness, % ISO	32.7	32.1	32
Iron, ppm	30.12	28.94	27.2
Manganese, ppm	0.58	0.54	0.54
Magnesium, ppm	1432	1431	1430
Zinc, ppm	74.51	70.2	68.4
Nickel, ppm	7.66	7.23	6.56
Lead, ppm	0.18	0.17	0.19
Cadmium, ppm	0.03	0.04	0.05
Copper, ppm	118.0	119	119.5
Calcium, ppm	2487	2543	2674

3. 4 Black liquor properties

Table 4 shows the properties of black liquor obtained after kraft pulping of 4, 5, and 6-year harvests of *M. dubia*. All the black liquors are alkaline in nature with pH 12.85 – 12.90. The black liquor obtained from kraft pulping of 5-year *M. dubia* shows the highest residual active alkali 7.56 gpl as Na_2O. The residual active alkali shows the presence of free $NaOH+Na_2S$ content after pulping. A certain level of residual active alkali is essential to keep the black liquor colloidally stable. Liquors with low levels of residual active alkali get precipitated at low solids concentration during evaporation, which eventually increases black liquor viscosity.

The total dissolved solids were found in the range 16.27 – 19.05 %. The total dissolved solids increase with age and were the highest in the 6-year. The total solids of black liquor represent the sum of total dissolved solids and total suspended solids present in the black liquor. This measures the amount of solids remaining after removal of water and other non-aqueous volatile materials normally lost in evaporation. The total alkali was found higher in the 5-year in comparison to the 4 and 6-year. The total alkali measures all organic and inorganic sodium salts present in the black liquor. It broadly includes NaOH; Na_2CO_3, organically bound sodium and sodium silicates in the black liquor. Total alkali determination accounts for total recoverable sodium present in the black liquor. The organic and inorganic in black liquor represent the sulfated ash and the total recoverable sodium present in black liquor. The organics found in black liquor in the present study are in the range 70.69 – 74.72% and is the highest in the 6-year. The inorganics are in the range of 25.28 – 29.31% with the highest level in the 4-year. The percentage of organics increases with age while that of inorganics decreases with age.

Table 4: Black liquor properties of *Melia dubia*

Parameters	*MD4*	*MD5*	*MD6*
pH	12.90	12.85	12.90
Residual active alkali, gpl as Na_2O	7.28	7.56	6.32
Total dissolved solids, %	16.27	16.64	19.05
Total alkali, gpl as Na_2O	35.96	37.2	34.87
Organics, % w/w	70.69	72.24	74.72
Inorganics, % w/w as NaOH	29.31	27.76	25.28

3.5 Oxygen delignified and bleached pulp characteristics

Table 5 shows the properties of oxygen delignified and bleached pulp in each bleaching stage of D_0EopD_1 sequence. Oxygen delignification of kraft pulp is carried out to reduce the bleach chemical demand which results in the reduction of chlorinated organic compounds in bleach plant effluents [39]. This stage utilizes pressurized oxygen and sodium hydroxide to remove substantial fractions of lignin from the kraft pulp. It can be seen from the table that the highest yield and the highest brightness while the lowest kappa number and the lowest intrinsic viscosity has been observed for kraft pulp of *M. dubia* in 5-year age.

The reduction in kappa number is 47.75%, 46.35%, and 45.64% respectively in oxygen delignified pulps of 6, 5- and 4-year harvest. The loss in intrinsic viscosity is 3.91%, 20.58%, and 15.26% respectively in oxygen delignified pulps of 4, 5- and 6-year harvest. The formation of hydroxyl radicals during oxygen delignification causes cleavage of lignin, cellulose, and hemicellulose which reduces the yield, kappa number and intrinsic viscosity of the kraft pulp [40] – [41]. The attack of oxygen on cellulose causes the reduction in viscosity while the sodium reaction with lignin reduced the kappa number of the pulp [42]. However, there is no severe yield loss during oxygen delignification across all the years as the yield remains high 97.6 – 98.4%. It may be attributed to the conversion of reducing end group in the cellulose chain to the stable oxidized form in presence of oxygen which stops the peeling reaction that is considered responsible for yield loss [43]. It is quite clear from these behaviors that the 5-year kraft pulp of *M. dubia* is more responsive towards oxygen delignification.

The chlorine dioxide is highly selective in nature and reacts frequently with lignin without affecting cellulose fibers. The lignin in the pulp gets oxidized and solubilized and hence the pulp brightness improves. The carbohydrate degradation in the pulp is low which improves the yield of pulp and enhance the strength property of fibers. In D_0 stage the brightness shows an increase of ~ 8 % in *M. dubia* kraft pulp of all the three harvests. The 4, 5 and 6-year kraft pulp shows respectively 19.95%, 25.92%, and 23.83% reduction in kappa number along with 10.23%, 12.66 % and 6.03% decrease in intrinsic viscosity. The highest brightness has been observed in 5-year pulp but with the lowest viscosity. The Eop stage removes the chlorinated and oxidized lignin remaining in the pulp. The alkali-soluble lignin is removed with sodium hydroxide, oxygen, hydrogen peroxide [44]. It helps to reactivate the remaining lignin for next oxidation stage

Table 5: Properties of *M. dubia* bleached pulps

Bleaching stages	Results		
	MD-4	MD-5	MD-6
Oxygen Delignification			
Brightness, %ISO	44.27	45.83	44.29
Kappa number	8.12	8.10	8.14
Viscosity, cm^3/g	632.45	623.37	649.62
Yield, %	97.6	98.4	97.84
D_0 Stage			
Brightness, %ISO	52.16	53.75	52.30
Kappa number	6.5	6	6.2
Viscosity, cm^3/g	623.24	604.88	615.34
Eop Stage			
Brightness, %ISO	76.15	82.06	74.87
Kappa number	3.8	2	3.1
Viscosity, cm^3/g	559.24	528.25	578.26
D_1 Stage			
Brightness, %ISO	85.07	90.40	86.58
Viscosity, cm^3/g	455.50	440.56	450.45
Total yield, %	95	95.6	95.2

The addition of oxygen during extraction removes the lignin effectively and reduces the effluent color and consumption of chlorine dioxide in the next stage while the use of hydrogen peroxide improves the brightness in the pulp [45]. Post Eop stage brightness increased by 23.99 %, 28.31 % and 22.57 %, kappa number reduced by 41.53 %, 66.66 %, 50 % and intrinsic viscosity also reduced by 10.26 %, 12.67 % and 6.03 % in 4, 5 and 6 year respectively. The 5-year pulp shows the highest brightness and the lowest kappa number after Eop stage. In final D_1 stage, the brightness increased by 8.92%, 8.34%, and 11.71%, while the intrinsic viscosity reduced by 18.55%, 16.60% and 22.10% respectively in 4, 5- and 6-year age. The 5-year *M. dubia* kraft pulp revealed the highest brightness, and the lowest viscosity as compared to 4- and 6-year bleached pulps. The final bleached yield was almost similar ~ 95 % in all the cases.

3.6 Strength and optical properties of hand sheets

The physical strength and optical properties of unbleached and bleached hand sheets of *M. dubia* at 4, 5- and 6-year age are listed in **Table 6** and **Table 7** respectively. The apparent densities of the unbleached and bleached hand sheets of *M. dubia* decrease with increase in age though the decrease is not too prominent. Also, the values of apparent densities decrease by 10 – 12.79% after bleaching. The highest decrease of 12.79% was observed in 4-year harvest followed by 10.84% and 10% in 5 and 6 years respectively. The apparent density of paper influences its physical, chemical and electrical properties. It also affects absorptivity and printability of paper. The increase in apparent density increases the tensile and burst index of the paper sheet. However, the presence of fines in the pulp alters the apparent density and the pulp having more fines appears with low apparent density [46]. The apparent density of the pulp depends on freeness and increases with higher freeness [47]. The apparent densities reported in this study were evaluated at 400 ml CSF (Canadian Standard Freeness). Typical values of apparent densities lie in the range from 0.5 g/cm^3 for a bulky paper to 0.75 g/cm^3 for highly bonded sheets [48].

Table 6: Physical strength and optical properties of the unbleached pulp of *M. dubia* at 4, 5- and 6-year age

Properties	*Unbleached pulp*		
	MD4	*MD5*	*MD6*
Apparent density, g/cm^3	0.86	0.83	0.80
Tensile index, Nm/g	83.95	75.90	74.17
Tear index, mNm^2/g	6.13	7.58	8.36
Bursting index, kPam^2/g	6.04	5.57	5.26
Light scattering coefficient, m^2/kg	27.56	26.65	26.51
Opacity, %	97.96	98.75	99.54

Table 7: Physical strength and optical properties of the bleached pulp of *M. dubia* at 4, 5- and 6-year age

Properties	*Bleached pulp*		
	MD4	*MD5*	*MD6*
Apparent density, g/cm^3	0.75	0.74	0.72
Tensile index, Nm/g	68.43	67.39	66.36
Tear index, mNm^2/g	4.14	5.13	5.24
Bursting index, kPam^2/g	4.15	4.21	4.32
Light scattering coefficient, m^2/kg	26.67	26.59	26.38
Opacity, %	82.20	81.23	83.79

Tensile indices obtained for unbleached and bleached hand sheets of *M. dubia* in 4, 5- and 6-year age gradation are in the ranges 74.17 – 83.9 Nm/g and 66.36 – 68.43 Nm/g respectively. The tensile indices decrease with increase in age as well as decrease 10.52 – 18.48% after bleaching. With a one-year increase in age of *M. dubia* tensile indices of its unbleached hand sheets decrease by ~ 3.5% while that of bleached hand sheets decrease by ~ 1.33 – 2.70%. The highest decrease of 18.48% in the tensile index after bleaching was found for the 4-year while the 5- and 6-years harvest exhibited 11.21% and 10.52% respectively. The tensile index reduces as the pulp gets delignified and hence it's directly proportional to the lignin content in the pulp [49]. The highest and lowest tensile strength of pulps respectively in 4- and 6-year age of *M. dubia* can be correlated to the corresponding highest and lowest lignin content which is indicated by their kappa numbers. The tensile property of the pulp also depends on the mechanical and chemical treatments during bleaching stages [50]. Tensile index of a paper is an important property which represents the paper strength. The durability and potential end-use performance of paper is also indicated through the tensile index. The standard requirement of the tensile index for news print and stationary grades paper are 45-60 Nm/g and 40-70 Nm/g respectively [48].

The tear indices of *M. dubia* unbleached and bleached pulps vary between 6.13 – 8.36 mNm^2/g and 4.15 – 4.32 mNm^2/g respectively. This decrease in tear index values lies in the range 32.46 – 37.32%. Tear depends on the fibre length of the pulp and increases as the fiber length increases [50]. It can be seen later in the manuscript that *M. dubia* exhibits the highest fiber length in the 6-year (1152.8 µm) followed by the 5-year (990.13 µm) and the 4-year (856 µm). Hence, the tear index values of its unbleached and bleached pulps follow the same order i.e. 6-year > 5-year > 4-year. Tear index shows the flexibility in fibers. It is a significant factor that influences the property of various grades of papers such as cover papers, wrapping papers, packaging papers, bond papers etc. The burst indices of *M. dubia* unbleached and bleached pulps lie in the range 5.26-6.04 kPam^2/g and 4.15-4.50 kPam^2/g respectively. Around, 17.87 – 31.29% decreases in burst indices were found after bleaching. Bursting index represents the pressure tolerated by the paper. Tear, tensile and burst indices showed a linear increasing relation with each other for the bamboo pulp [51] – [52] however, in case of *Populous alba*, tear index decreased with increase in tensile index [47]. Similar findings of a decrease in tear index with an increase in the tensile index have been observed in *M. dubia* across all the harvests subjected to investigation.

The optical properties such as light scattering coefficient and opacity were also found for *M. dubia* unbleached and bleached hand sheets. The relative amount of light scattering within the layer is called light scattering coefficient of a sheet. It is basically related to the visual appearance of the paper sheets. The light scattering coefficient of unbleached and bleached hand sheet of *M. dubia* have been respectively found in ranges 26.51 – 27.56 m^2/kg and 26.38 – 26.67 m^2/kg. No significant changes have been found in light scattering coefficients after bleaching.

Opacity is an important property for printing and writing grade paper. It is the ability of paper to prevent the printed images or text from being appeared at the reverse side. It is measured as a percent of light absorbed by a sheet of paper and is a function of paper thickness, amount of filler(s), pulp brightness, and beating degree [53]. 97.96 – 99.54% and 82.20 – 83.23% opacity have been found for unbleached and bleached hand sheets of *M. dubia*. The decrease in opacity after bleaching may be attributed to the removal of lignin after bleaching. The basis weight of the hand sheets also impacts the opacity and light scattering coefficient of the paper. Light scatters more if it passes through denser paper [54]. The value of opacity should be > 88 % for stationery and between 90 – 94% for newsprint paper [48]. The opacity values obtained in this work for pure pulp can be increased by adding fillers according to the product.

3.7 Fibre morphology and classification

Figure 1 (a, b, c) illustrates the microscopic images of *M. dubia* unbleached pulp of the 4, 5- and 6-year respectively. The fibers and vessels appear to increase in length and diameter with age. The long and short fibers are cylindrical in shape with smooth walls. The fibers appear uniform with a broader middle part and gradual pointed tapering ends. The fiber diameter shows a small change with an increase in *M. dubia* age. The vessel appears cylindrical in shape with an increase in length and diameter with respect to age. The frequency of vessels appears more in the 4-year as compared to the 5 and 6-year. The percentage of fibers is anticipated to enhance while the proportion of the other cell types reduce with the advancement of age [55].

Different morphological and anatomical parameters of *M. dubia* fibers at 4, 5- and 6-year age gradation are shown in **Table 8**. It can be observed from this table that the fiber length, fiber diameter, cell wall thickness, vessel length, and vessel diameter increase with an increase in harvest age while the lumen diameter decreases with increase in harvest age. Runkel ratio which is a derived factor also shows an increasing trend with increasing harvest age because it is directly proportional to cell wall thickness while indirectly proportional to lumen diameter.

Table 8: *M. dubia* fiber dimension at 4, 5- and 6-year age

Parameters	*MD4*	*MD5*	*MD6*
Fibre length, µm	856	990.13	1152.8
Fibre diameter, µm	22.73	23.42	24.34
Lumen diameter, µm	14.03	13.92	13.58
Cell wall thickness, µm	4.35	4.75	5.38
Vessel length, µm	187.46	200.13	208.26
Vessel diameter, µm	70.62	76.29	98.49
Runkle ratio	0.66	0.69	0.80

The fiber length, fiber width, vessel length, and vessel width increase with an increase in growth rings and radius of the tree with age while the fiber lumen diameter decreases with increase in the radius of the tree. The vessel length and vessel diameter show increase with an increase in basic density. Fiber length is one of the most important characteristics of papermaking fibers. The long fibers frequently form bonds with other fibers and make a strong network as compared to short fibers. Fiber length positively influences the tensile strength of paper. Fiber length is correlated to the lignin content in the pulp. The higher content of lignin in pulp reflects shorter fibers and vice versa [49]. In 6 year harvest the fiber length is higher in comparison to 4 and 5 years and hence the lignin content in its pulp is the lowest as evident in **Table 2**. The thickness of the cell wall is important in pulp refining. The thicker walls provide more flexibility of fibers during refining. Fiber length, fiber diameter, and cell wall thickness have a positive impact while lumen diameter has a negative impact on wood density and mechanical strength properties [56]. Fibers having Runkle ratio > 1 is not preferred for papermaking due to less flexibility, low stiffness, and poor bonding ability. The fibers with Runkle ratio < 1 produce good quality pulp and paper, as these collapse easily and provide more surface area for bonding [57]. Vessels cause problems in the final uses of the paper. During printing, the vessels attach to the surface of the rollers in the printing machine and produce a series of points on the paper sheet which are not covered by ink [58].

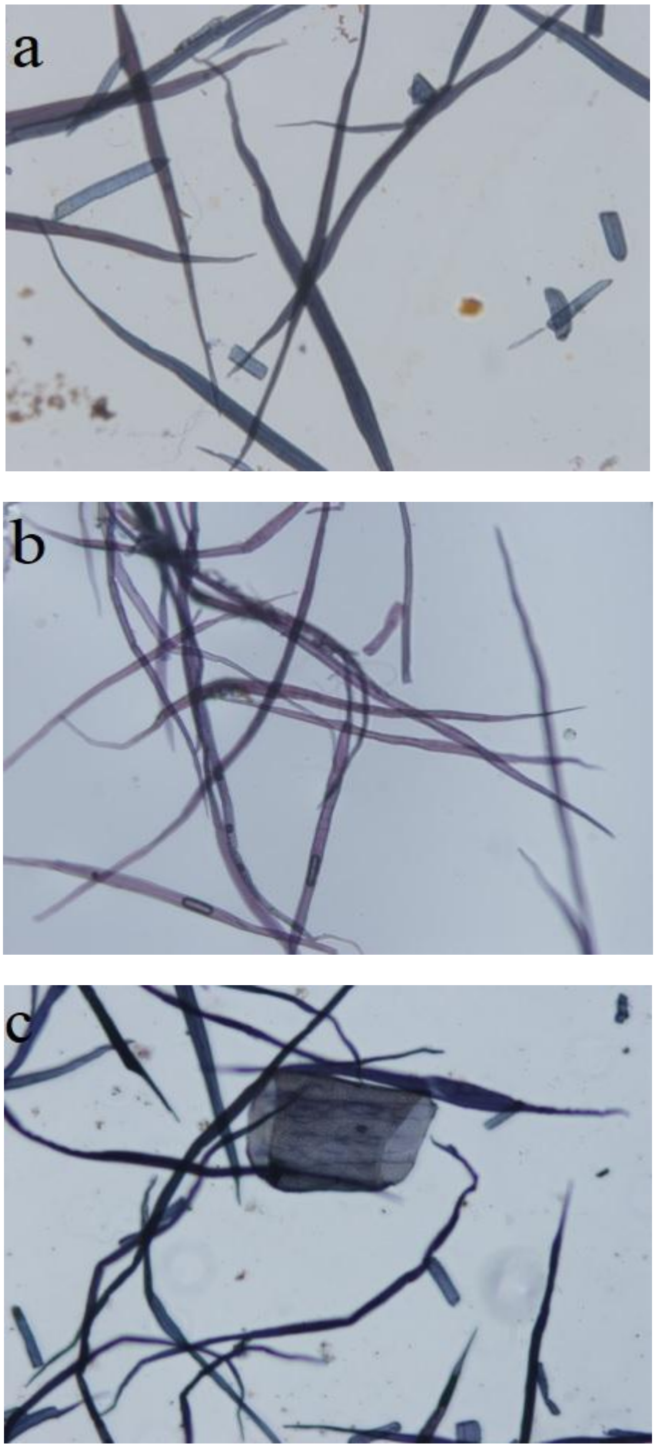

Figure 1: Photomicrographs of *M. dubia* unbleached pulp of a) 4-year, b) 5-year, c) and 6-year at 10X magnification

The Bauer McNett fiber classification in +30, +50, +100, +200 and -200 mesh screen for *M. dubia* unbleached pulps based on weighted average length of fibers in the 4-year harvest were 9.5%, 64.8%, 12.9%, 6.3%, and 6.5% respectively. In the 5-year harvest these were 8.5%, 64.7%, 13.8%, 6.3% and 6.7% respectively while in the 6-year harvest these were 8.6%, 63.8%, 14.9%, 6.5% and 6.2%

respectively. The fibers retain according to their length at different mesh openings in the Bauer McNett classifier. The long fibers retain at +30 mesh screen, short fibers retain at +50 to +200 mesh screen and fines retain at -200 mesh screen [59]. The number of vessels and parenchymatous cells increase when pulps cross from +28 to -150 mesh while the number of fibers decreases [60].

It is obvious that in all the harvests of *M. dubia* the fibers percentage show the following order: +50 (64-65%) > +100 (13-15%) > +30 (9%) > -200 (6-7%) > + 200 (6%). Although the fibers in *M. dubia* are not long but come under short fiber as the maximum retention is on +50 mesh screen. The pulp screen retention is almost similar in 4, 5 and 6 years. The fibers passing through + 200 mesh screen has a huge impact on mechanical properties of pulp. The fibers < 200 mesh fraction show higher water swellability and result in a higher density of hand sheets and mechanical properties [61].

3.8 Surface morphology of pulp and hand sheets

The SEM micrographs of unbleached pulp and bleached hand sheets of *M. dubia* in 4, 5- and 6-year harvests at different magnifications are shown in **Fig. 2 (a, b, c)** and **Fig. 3 (a, b, c)** respectively. The unbleached pulps show uneven surface and intact heterogeneous fibers with rectangular shapes. Fibers show limited crossovers and network contain plenty of voids. The removal of lignin during pulping has led to the creation of voids in fibers. These voids are more prevalent in 5-year harvest which indicates better delignification during cooking in comparison to 4 and 6 years. The random appearance of voids on the surface of unbleached fibers gives a good indication of appropriate consumption and reactivity of chemicals during bleaching. Some thinly layered wreckages have also been observed to be loosely attached with the surface of unbleached kraft fibers [62]. These wreckages can be attributed to the fractions of middle lamellae and a certain amount of lignin present on the surface of unbleached fibers [63].

The fibers of bleached pulp hand sheets appear flat and smooth. After bleaching and preparation of hand sheets, the fibers got flattened and the voids which were created during pulping got filled up to a certain extent. The fibers collapsed and got strongly bound with other fibers resulting in more contact area in comparison to unbleached pulps. The smoothness in 5-year bleached fibers appears high as compared to 4- and 6-year fibers. Some fibrillation in the bleached pulp fibers also appeared which may be attributed to the creation of porous fiber wall due to the removal of lignin during bleaching [62]. Some gel-like substance was visible among the fibers which connected the fibers with each other [64]. The 6-year bleached fibers appear denser in comparison to the 4 and the 5-year which eventually impacted the strength properties.

4. Conclusion

This study explored the effect of harvesting age of *M. dubia* at 4, 5 and 6 year on its pulp and papermaking potential. A significant effect of age was reflected on its physicochemical properties, morphological features, pulping characteristics, bleachability and paper characteristics.

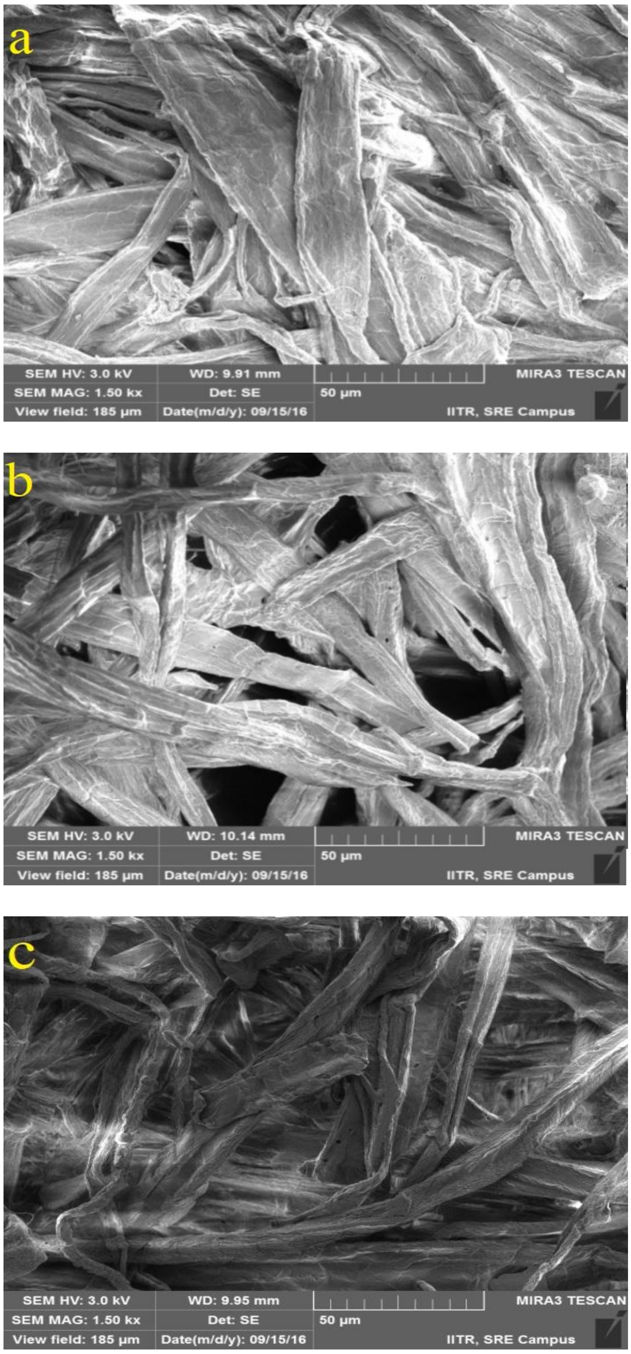

Figure 2: SEM micrographs of *M. dubia* unbleached pulp of a) 4-year, b) 5-year, c) 6-year

The chemical properties of 5-year wood were found dominating over 4 and 6-year due to low lignin (26.27%), low ash (0.65%) and high holocellulose (82.55%). The fiber length (990.13 μm), fiber diameter (23.42 μm), vessel length (200.13 μm) and vessel diameter (76.29 μm) and Runkle ratio (0.69) of the 5-year harvest were greater than that of the 4-year but smaller than that of the 6-year. During kraft pulping 5-year-old *M. dubia* showed high intrinsic viscosity (785 cm^3/g) and moderate pulp brightness (32.10), kappa number (15.10), screened pulp yield (51.63 %) in comparison to 4- and 6-year.

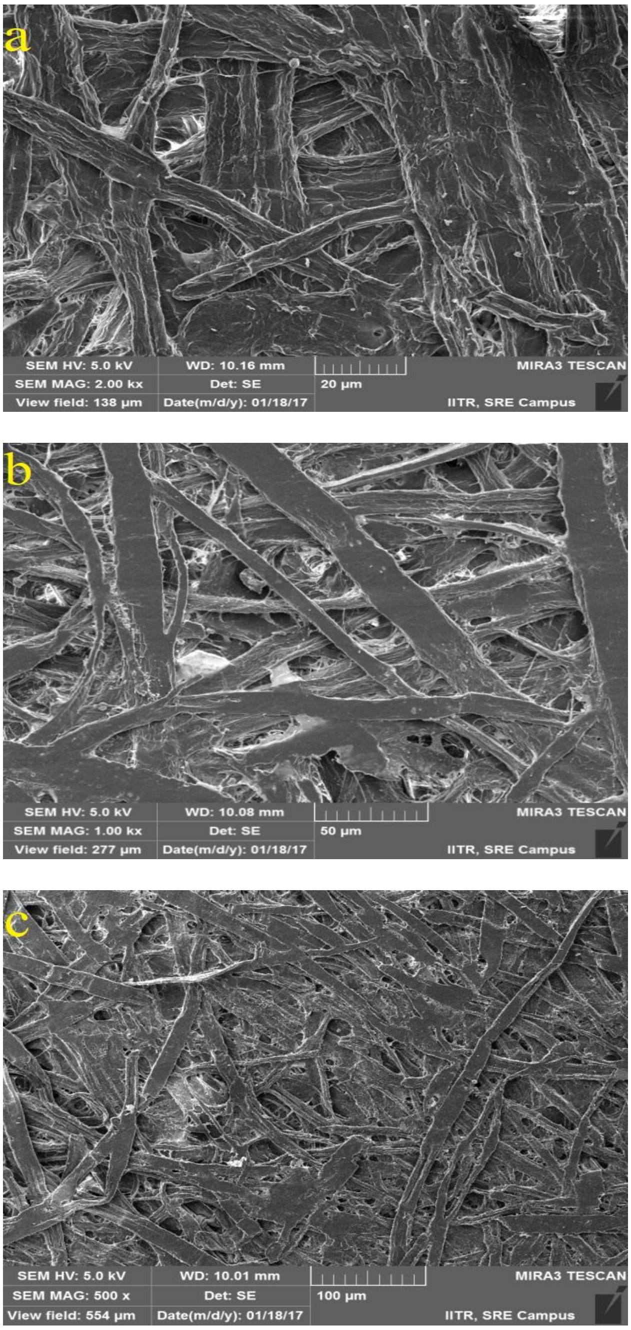

Figure 3: SEM micrographs of *M. dubia* bleached hand sheets of a) 4-year, b) 5-year, c) 6-year

The 5-year-old *M. dubia* was found more responsive towards oxygen delignification with high yield 98.4%, high brightness 45.85 % and low kappa number 8.10. After D_0EopD_1 bleaching, the final yield (95.6%) and brightness (90.40% ISO) was higher for the 5-year-old *M. dubia* pulp. The scanning electron micrographs of pulp obtained from 5-year wood depicted smoother fibers with close bonding with other fibers as compared to pulp of 4- and 6-year wood. Although, the 5- and 6-year-old *M. dubia* exhibited almost similar properties during pulp and papermaking processes, the 5-year harvesting age is acceptable. This will curtail investment of extra time and revenue till the 6-year. These investments till the 6-year will not turn into profitability. The results confirmed the feasibility of *M. dubia* as an alternative raw material for pulp and paper production. This study provides complete know-how of pulp and papermaking properties of *M. dubia* towards its feasible utilization as an industrial crop.

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