Short Review: The Chemistry and Pulping of Acacia

Acacia mangium Willd. is a fast-growing dicotyledonous tree, native to northern Australia and Southeast Asia,[1] where it has been planted because of its high silvicultural performance and its ability to grow in degraded soils.[2] *Acacia mangium* is a well-known nitrogen-fixing tree, being used for land rehabilitation, particularly in eroded and nitrogen-deficient soils. As reported by Udarbe,[3] the general pattern of growth is evaluated with Mean Annual Increment in the range of 10 - 29 m^3/ha/yr. The basic density of 8 years old *Acacia mangium* plantation is 409 kg/m^3 which yields an annual wood production of 4 to 12 tons/ha/year.[4] Tree form is relatively good, but there is a tendency for persistent branching which affects wood quality if pruning is not done at an early age. Grown at an initial escapement of 3 m by 3 m the stand closes canopy in 2 to 3 years with the height at about 8 m. When grown for pulp logs on a rotation of 5 to 7 years, pruning and thinning are not necessary. Planting escapement may be reduced to 2.5 m by 2.5 m to take advantage of the fast initial growth. For saw log production the rotation is estimated to be between 12 to 15 years. *Acacia mangium* forms a symbiotic relationship with bacteria *Rhizobium* that fixes nitrogen to enhance the tree growth.[5]

Acacia mangium is also a fast-transpiring tree species with high daily water consumption. A study on the water consumption of *Acacia mangium* in the Malaysian state of Sabah, Borneo was reported by Cienciala to vary from 10 to 130 kg/day depending on the sapwood area.[6] The soil in the area of this study consisted of two main types and several intermediate forms. The two main types were Haplic Acrisol with clayish topsoil and Gleyic Podzol with sandy topsoil. Both soil types formed on frequently inter-layered dark shale, siltstones and sandstones. The air temperature was mostly between 22 and 32 °C and daily average around 26 °C. Air humidity fluctuated from 100 to less than 60 % and daily mean was mostly above 80 %. The mean daily transpiration (tree sap flow and tree transpiration can be considered equal on daily basis under non-limiting soil water condition) was a function of sapwood area as shown in Fig 1.

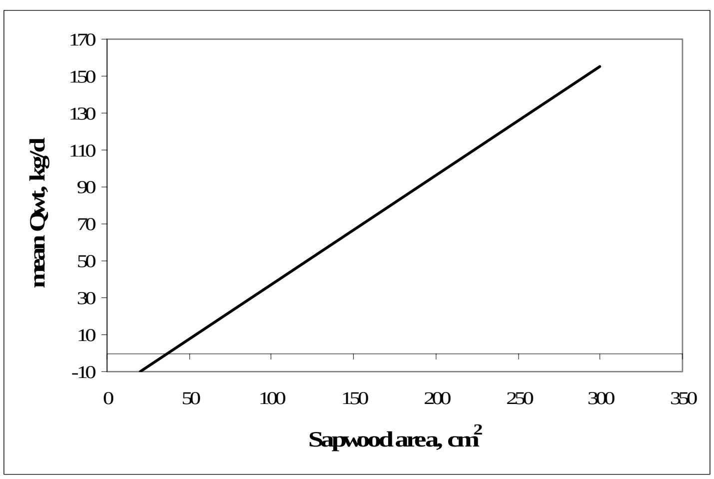

Fig.1. Mean daily tree sap flow (Qwt) against the sapwood area of *Acacia mangium* tree.[6]

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A study by Mackensen at PT.IHM (Perusahaan Terbatas Indonesia Hutani Manunggal) in East Kalimantan, Indonesia, showed that fertilization costs for *Eucalyptus deglupta* were generally higher than for *Acacia mangium*, i.e. 13 – 32 % and 9 – 16 % of overall investment costs, respectively.[7] Those range covered from low-, medium- to high-impact management which depended on nutrient losses due to burning of residual phytomass, leaching below root deep, erosion and harvesting techniques. The soil pH in this area was 4.5 - 4.8 and characterized by sand, silt and clay sediment.

A study by Cole[8] on the growth of twelve *Acacia* species on acid soil in Hawaii showed that *Acacia mangium* ranked the best in the growth rate among the others at both low and high soil fertility level. The species under the study were *A. mangium, A.crassicarpa, A.cincinnate, A. leiocalyx, A. leptocarpa, A. auriculiformis, A. orites, A. implexa, A. angustissima, A. polystachya,* and *A. koa.* The low fertility is defined as 14-14-14 plus micronutrient 143 kg/ha, while high fertility is 14-14-14 plus micronutrient 143 kg/ha, lime 8 Mg/ha, P 200 kg/ha, K 77 kg/ha.

Acacia mangium has been tested and found suitable for furniture making, general purpose industrial timber (not exposed to the weather), plywood and other panel products, pulp and paper and other related products, charcoal and wood pellets. In recent years, this hardwood species has been recognized as an excellent source of short cellulose fibers for papermaking.[9] Extensive plantations are now growing in Southeast Asia, particularly Indonesia, supplying wood to the pulp and paper industry.[10] In Indonesia, *Acacia mangium* has become the dominating plantation pulpwood during the last ten years because *Eucalyptus* plantations have not been successful. Many large scale pulp mills have been built in Indonesia based on *Acacia* plantations. *Acacia* pulp is very interesting from a quality point of view and fairly similar to *Eucalyptus camadulensis* in terms of fiber morphology. Environmentally *Acacia* species are attractive because of their ability to fix nitrogen from air to improve soil fertility. *Acacia* species have been studied and used for pulpwood in many countries like Australia, Brazil, South Africa, Indonesia, Vietnam, and Malaysia.[11] The interesting properties of *Acacia mangium* fibers together with its easy adaptation to tropical humid climates suggest that extensive *Acacia mangium* plantations soon will spread to other regions of the world such as South America, competing seriously with other tropical hardwood fiber sources.

In terms of species numbers *Acacia*, as currently defined, is the second largest genus in the *Pea* family, i.e. the *Leguminosae* (*Astragalus* is the largest).[12] This genus contains in excess of 1380 species. This is a conservative number as it does not include many of the undescribed taxa (an estimated 100+ species in Australia and 20 species in America). *Acacias* grow in tropical, subtropical and warm temperate parts of the world and are found in the African region (144 species), Asia (89 species), the Americas (about 185 species) and the Australian region (993 species).[13]

As reported by FAO 2001, the global forest plantation distribution is described as follows: Asia-Pacific 61 %, North & Central America 17 %, South America 9 %, Europe 6 %, Africa 4 %, and Western Asia 3 %.[13] Forest in Asia-Pacific region covers approximately 699 million hectares. Of this area, some 113.2 million hectares are forest plantations, or 16 % of the total forest resource. This is considerably higher than the global average of plantations, which stand at around 5 %. The five countries that from Asia rank among the top ten plantation countries in the world: China (46.7 million hectares), India (32.6 million hectares), Japan (10.7 million hectares), Indonesia (9.9

million hectares), and Thailand (4.9 million hectares). The distribution of species in Asia-Pacific: *Tectona* 5 %, *Acacia* 7 %, *Hevea* 8 %, *Eucalyptus* 10 %, Unspecified 13 %, *Pinus* 14 %, other coniferous 18 %, and other broad leaved 25 %.

Acacia mangium is a very promising hardwood plantation species which can grow in degraded soil and can be used for land rehabilitation due to its ability to fix the nitrogen. *Acacia mangium* growth rate is the fastest among the other acacia species in both low and high fertility. *Acacia mangium* wood has been found suitable for many different applications, and thus becoming dominant plantation species.

2.1.2. The chemistry

Acacia mangium wood, a prominent fast-growing plantation species used in the pulp and paper industry, has been studied to quantify and structurally characterize the lignin, xylan and cellulose by Pinto.[14] Table 1 summarizes the general chemical composition of *Acacia mangium* wood.

The lignin content of *Acacia mangium* wood was shown to be 27.6 %, a value above the range of lignin contents typically found in hardwoods, 20 – 26 %, and was found similar to *Eucalyptus urograndis* (see Table 2).[15] This can be explained, at least partially, by the presence of polyphenolic extractives (see Fig 2) that were not removed by ethanol/toluene extraction of wood.

Table 1. Chemical composition of *Acacia mangium* wood

	Relative abundance, % dry wood [a]
Ashes	0.22
Extractives	
Ethanol/Toluene	4.46
Dichloromethane	1.32
Methanol/water	4.05
Lignin	
Klason lignin	27.1
Acid soluble lignin	0.54
Holocellulose	70.9
Cellulose (Kurschner-Hoffer)	46.5 [b]
Pentosans	13.3
Neutral monosaccharides [c]	
Rhamnose	0.3
Arabinose	0.2
Xylose	10.9
Mannose	1.0
Galactose	0.6
Glucose	48.0
Uronic acids	7.6

[a] Extractive-free wood, except for extractive content, [b] Corrected for pentosans content, [c] Determined as anhydrous monosaccharide.

The high lignin/polyphenolic extractives content of *Acacia mangium* wood contributes to the high chemical consumption required to chemically delignify this wood and to the low pulp yield, when compared to those of other hardwoods.[16] Hardwood lignin is a complex macromolecule composed of dehydropolymerized units derived from syringylpropane (S) guaiacylpropane (G), and p-hydrophenylpropane (H). The relative proportions of S, G, and H units and the nature and relative abundance of linkages between them are highly variable, influencing the reactivity of lignin during pulping and bleaching processes.[17] The S/G/H proportion of several hardwoods and unbleached kraft pulp residual lignin is summarized in Fig 3.

Table 2. Compositions of hardwoods and unbleached kraft pulp

Species	*E. globulus*	*E. urograndis*	*E. grandis*	*B. pendula*	*A. mangium*
	Wood composition, %				
Lignin (Klason)*	22.1	27.9	26.7	21.5	27.6
Glucomanan	53.4	52.1	50.9	44.5	51.6
Xylan	14.2	11.4	12.4	23.6	11.9
Rhamnose	0.3	0.2	0.3	0.8	0.3
Arabinose	0.4	0.4	0.4	0.7	0.2
Mannose	1.1	0.7	0.7	2.1	1.0
Galactomanan	1.5	1.2	1.0	0.8	0.6
	Unbleached pulp composition, % (wood basis)				
Lignin (Klason)*	1.3	1.0	1.2	1.3	1.2
Glucomanan	45.0	40.2	40.5	38.8	42.2
Xylan	10.6	6.8	6.6	12.4	6.7
Rhamnose	0.1	0.2	0.2	0.1	0.2
Arabinose	0.1	0.1	0.0	0.1	0.0
Mannose	0.1	0.1	0.1	0.3	0.2
Galactomanan	0.4	0.1	0.1	0.1	0.0

* Uncorrected for polyphenolics content

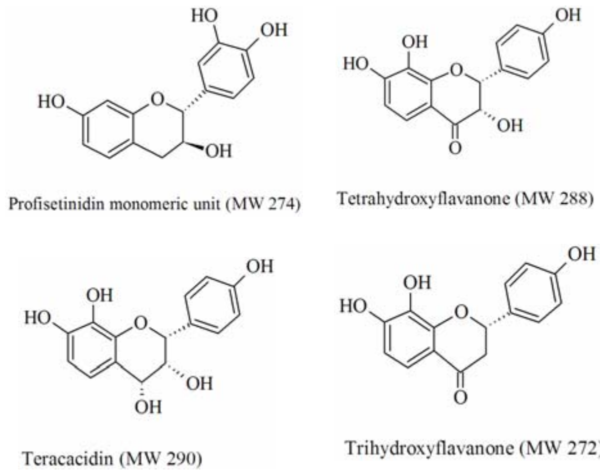

Fig.2. Structure of polyphenols found in *Acacia mangium*.[18]

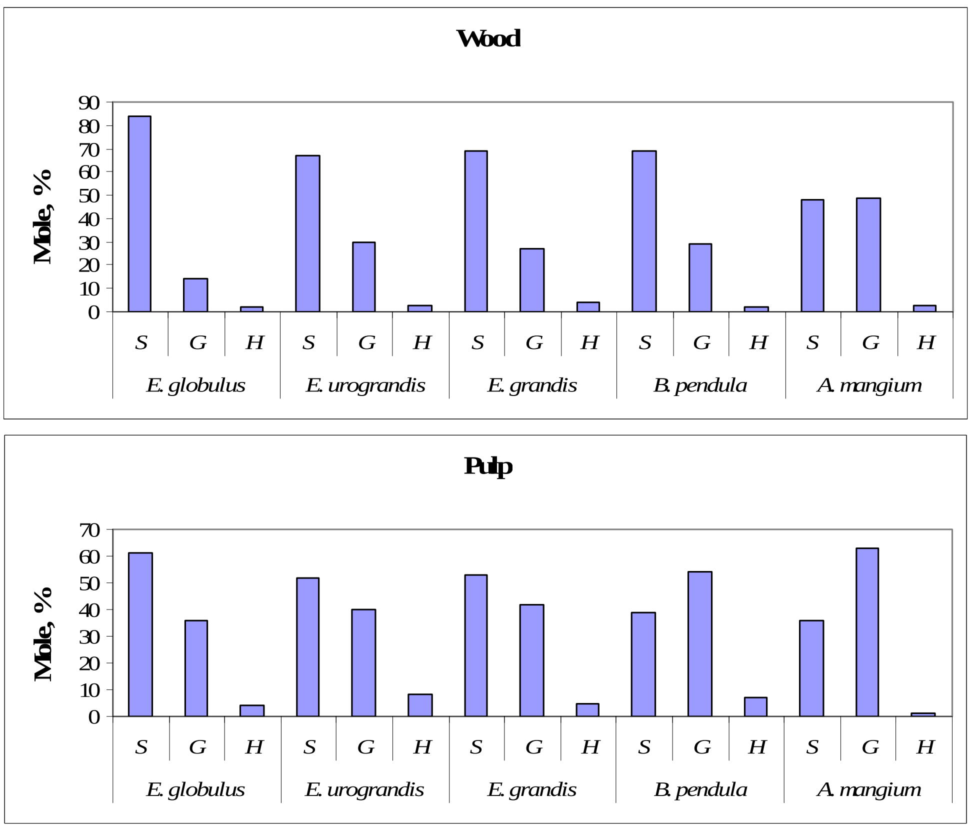

Fig.3. Molar percentages of syringyl (S), guaiacyl (G), and p-hydroxiphenyl (H) units (determined by ^{13}C NMR spectroscopy) in (top) wood and (bottom) pulp lignins

Acacia mangium had the highest surface coverage (24 %) of extractives compared to those of *Betula pendula*, *Eucalyptus globulus*, *Eucalyptus urograndis* and *Eucalyptus grandis* that had 10, 7, 6 and 5 %, respectively.[19] The main component of the extractive was saturated fatty acids (docosanoic, tetracosanoic, hexacosanoic and octacosanoic acids) that were very stable under the condition of ECF bleaching.[20]

2.1.3. Fiber and sheet properties

Three bleached hardwood kraft pulps have been studied on the fiber and sheet properties by Mohlin i.e. one *Acacia mangium* (Indonesia origin), and two *Eucalyptuses* of Brazillian (A) and Iberian (B) origin.[21] The main difference between the *Acacia* and the *Eucalyptus* was that the *Acacia* had thinner fiber walls and fewer defects (kink) as shown in Table 3 and Table 4.

Table 3. Fiber dimensions, fiber kink and fiber coarseness for unrefined bleached hardwood kraft pulps

Pulp	Fiber length, mm	Fiber width, μm	Fiber kink, #/fiber	Fiber coarseness, mg/m
Acacia	0.65	14.1	0.22	0.46
[a]*Eucalyptus* A	0.74	14.9	0.53	0.60
[b]*Eucalyptus* B	0.71	15.1	0.47	0.59

[a]*Eucalyptus* A: Brazillian origin, [b]*Eucalyptus* B: Iberian origin

Table 4. Result of microscopy measurement of cross sectional dimensions of unrefined bleached hardwood kraft pulps

Pulp	Wall thickness, μm	Wall perimeter, μm	Lumen perimeter, μm	Wall area, μm^2
Acacia	2.0	38.5	23.0	53.7
[a]*Eucalyptus* A	2.7	39.4	18.0	70.4
[b]*Eucalyptus* B	2.5	38.9	19.1	66.5

[a]*Eucalyptus* A: Brazillian origin, [b]*Eucalyptus* B: Iberian origin

Acacia mangium can be readily pulped by either the kraft or NSSC (Neutral Sulfite Semi-Chemical) process to produce good quality pulp for fine papers or packaging materials respectively. Test of *Acacia mangium* cooking by CSIRO (Commonwealth Scientific and Industrial Research Organization) has shown that yields of screened pulp of over 50 % can be obtained by the kraft process and as high as 75 % by the neutral sulphite process. Subsequent tests by CSIRO have shown that kraft pulping and papermaking properties of *Acacia mangium* compared very favorably with those of plantation-grown *Gmelina arborea* and *Eucalyptus deglupta*. *Acacia dealbata* and *Acacia melanoxylon* were also reported to exhibit better kraft pulping performance than *Eucalyptus globules.*[22] An added advantage is the higher basic density of *Acacia mangium* wood.

Due to chemical composition and structure of lignin and extractive (see section 2.1.2.), *Acacia mangium* required the most drastic pulping conditions to get a similar Kappa number and also consumed the most amount of chlorine dioxide during bleaching stages to get a similar brightness compared to those other four hardwoods as shown in Table 5.

Table 5. Kraft pulping conditions,[a] pulp yield, and ClO_2 consumption during bleaching by a chlorine dioxide based sequence (DEDED)[b]

Wood species	active alkali % Na_2O/wood	unbleached pulp Kappa number	unbleached pulp yield, %/wood	ClO_2 consumption %/pulp
E. globulus	16	18.9	55.6	4.4
E. urograndis	20	18.4	49.6	5.3
E. grandis	19	16.1	50.6	5.4
B. pendula	18	18.5	49.8	7.2
A. mangium	24	16.0	51.1	7.4

[a]Kappa number 16-19   [b]Final brightness 90 %

A study by Malinen et al on the cooking of different age of *Acacia mangium* from eastern Thailand showed that the yield decreased rapidly when age of wood increases as shown in Table 6.[4] At Kappa number 20, the pulp yield dropped from 52 to 50 % and the pulp viscosity dropped from 1,200 to 1,000 ml/g along with increasing age.

Table 6. Unbleached kraft pulp properties of *Acacia mangium* from eastern Thailand

Species age	Effective alkali, %	Kappa number	Screened yield, %	Viscosity, ml/g	HexA, meq/kg
4 year	16	24.6	53.5	1269	57.7
	18	18.2	51.4	1072	62.6
	19	18.2	52.7	1121	60.6
	20	16.5	51.3	955	47.8
	21	14.9	50.8	904	40.2
	22	17.1	50.9	927	43.4
	23	12.8	49.7	713	24.8
6 year	16	27.3	53.3	1264	64.5
	18	20.3	51.9	1096	64.6
	19	20.5	52.4	1212	68.1
	20	18.6	49.9	992	48.9
	21	16.7	50.1	965	46.8
	22	17.6	49.9	1059	51.0
	23	15.1	48.8	818	34.4
7 year	16	29.0	53.3	1274	57.0
	18	20.1	50.9	1058	60.4
	19	18.2	50.4	1035	58.3
	20	17.3	48.4	913	46.0
	22	18.6	48.2	883	39.0
	23	16.9	49.5	878	39.9
8 year	16	29.0	53.4	1218	-
	18	19.7	50.2	1029	-
	20	19.0	48.0	928	-
	22	16.3	47.5	784	-
	23	15.3	47.7	808	-

The kraft cooking condition was as follows: sulfidity 35 %, liquor to wood ratio 4, time from room temperature to 80 °C 15 minutes, cooking temperature 165 °C, time from 80 to 165 °C 60 minutes, time at 165 °C 80 minutes, and various effective alkali from 16 to 23 % as NaOH. *Acacia mangium* of seven and eight year old had clearly lower yield, probably because of heart rot in the wood as indicated by its high 1 % NaOH solubility, 8.2, 13.7, and 16.7 % for four, seven, and eight year old, respectively. The contents of hexenuronic acids (HexA) in unbleached kraft pulps dropped rapidly with lowering kappa number.

A pilot scale pulping study on seven year old *Acacia mangium* by Bahar et al was performed.[23] The pulps were bleached according to CEHH sequence. The results showed that optimum physical properties of bleached *Acacia mangium* pulp obtained at 15.0 % active alkali, 22.5 % sulfidity, 165 °C, and cooking time for 1.5 + 2.0 hours. The cooking results were shown in Table 7.

A kraft cooking study on three different *Acacia* species of six and nine year old was recently conducted which showed that *Acacias* were easily pulped using the conventional kraft process with acceptable pulp yields, i.e. 50 % total yield with Kappa number of 20. The kraft cooking condition was as follows: active alkali 15.0 % (as Na_2O of oven dry chip), wood to liquor ratio of 1:4, sulfidity 25.0 %, maximum temperature 170 °C, and time at temperature 50 minutes. The physical properties of unbleached kraft pulp were show in Table 8. In general, the physical properties of six year old Acacia were better than nine year old Acacia.

Table 7. Pilot scale kraft cooking results of *Acacia mangium*[22]

Active alkali, %	Max. temp., °C	Screened yield, %	Kappa number
17.0	170	41.2	11.3
15.0	170	48.3	14.4
13.0	170	44.5	17.6
17.0	165	47.5	12.7
15.0	165	42.1	15.3
13.0	165	41.3	21.0

Note: liquor to wood ratio 4, time to reach maximum temperature 1.5 hours, time at maximum temperature 2.0 hours, sulfidity 22.5 %

Table 8. Physical properties of unbleached kraft pulp of three *Acacia* species[24]

Species	Age (year)	Tensile Index (Nm/g)	Burst Index ($kPa.m^2/g$)	Tear Index ($mN.m^2/g$)
A. mangium	6	61.1	6.4	10.7
	9	63.4	6.0	8.8
A. crassicarpa	6	58.1	6.1	9.8
	9	62.2	5.8	8.7
A. auriculiformis	6	61.8	6.5	11.2
	9	62.7	6.2	10.5

2.3. Oxygen delignification

Oxygen delignification is a well established technique in industrial application for delignifying unbleached pulps during the last decade. The main benefit of this process is environmental. Currently most systems installed are based on the medium consistency (10 - 14 %) process. The oxygen delignification reaction is usually conducted for 15 to 90 minutes under pressure of 400 to 1000 kPa and at the temperature of 90 – 110 °C [4, 34]. Due to the severe carbohydrates degradation at higher degree of delignification, the delignification degree for conventional kraft pulp is normally in the range of 35 – 50 %. The typical conditions of oxygen delignification for Acacia and mixed hardwood (MHW) are shown in Table 9.

Table 9. Commercial oxygen delignification operating conditions for *Acacia* and mixed tropical hardwood (MHW)

	Acacia	MHW
Temperature, °C	87-90	87-90
O_2 charge, kg/ADT	14-17	14-17
NaOH charge, kg/ADT	14-16	16-18
pH	10.8-11.0	10.8-11.0
Consistency, %	12	12
Reaction time, minutes	120	120
Starting Kappa number	12 – 13	13 - 14

For further details see Professor Ragauskas

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