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Encouraging Invasive *Acacia* Control Strategies by Repurposing Their Wood Biomass Waste for Pulp and Paper Production

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Abstract: Concerns on the expanding infestation of several *Acacia* species in the southern Mediterranean European countries have triggered an ever-growing requirement for costly targeted control actions. Valorizing biomass waste produced could help promote and better finance these actions. For that purpose, wood wastes from invasive control actions were tested regarding their pulp and paper potential, aiming to entice cellulose industries to partake in future conservation actions. Wood waste from the five most pervasive *Acacia* species was studied (*Acacia dealbata* Link, *Acacia longifolia* Willd, *Acacia mearnsii* De Wild, *Acacia melanoxylon* R.Br, and *Acacia saligna* Labill) regarding physical and chemical characteristics, and a central composite design was used to optimize alkali charge and reaction temperature on pulping yield and delignification. Bleached kraft pulps were produced with each species' optimized conditions and for an equitable mixture of all species. Optimized pulp yields (52.6%–53.5%) and pulp polymerization degree (2867–3690) of *Acacia* species were higher than those of *Eucalyptus globulus* Labill (used as reference). Optimized bleached pulps were refined and fiber, pulp, and handsheet properties determined. *Acacia dealbata* and *A. longifolia* presented high specific wood consumption and lower handsheet strength properties, pointing to overall lower pulping potential, while *A. melanoxylon* and *A. mearnsii* characteristics were equal to or higher than those of *E. globulus*. *A. saligna* pulp and handsheet characteristics appear more suited for tissue paper. The *Acacia* mixture achieved acceptable characteristics, enabling the indiscriminate use of *Acacia* wood regardless of the species. As a shortcoming, the *Acacia* pulps showed the worst optical characteristics, with brightness dropping substantially with beating (64%–76%) when compared to *E. globulus* (81%).

Keywords: *Acacia dealbata*; *Acacia longifolia*; *Acacia mearnsii*; *Acacia melanoxylon*; *Acacia saligna*; kraft pulping; response surface methodology; wood characteristics; fiber characteristics; handsheet properties

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1. Introduction

Acacia is a genus with more than 1300 species identified, mostly endemic to Oceania [1]. They are widely spread as intentional or invasive populations. These species have a rapid growth rate, high biomass production, robust seed banks, and the capacity to fix nitrogen, competing with native plants for limited resources such as water, light, and nutrients [2,3]. Consequences from the presence of these species in the ecosystems include a possible decrease in water availability, an increase in wildfire frequency and severity, and changes in soil nutrient levels [4,5].

In southern Europe Mediterranean countries (Portugal, Spain, France, Italy), the most predominant Acacias (*A. cyclops*, *A. dealbata*, *A. longifolia*, *A. karro*, *A. mearnsii*, *A. melanoxylon*, *A. pycnantha*, *A. retinodes*, and *A. saligna*) have invasive species status [1,6]. Portuguese legislation (DL nº 92/2019) considers all *Acacia* spp. invasive aliens. They were introduced for purposes such as ornamentals, sand and soil stabilizers, flood and landslide prevention, wind breakers, helping restore dune ecosystems, and forestry [2,4,7].

In Portugal alone, the distribution of *Acacia* spp. covers almost all territory, with an area of 16,000 ha in 2015, sometimes with more than one species simultaneously, doubling between 2005 and 2015, and with estimations that climate change will further drive this proliferation [8–10].

Control initiatives from local authorities generate significant amounts of biomass waste, mainly used for energy production [6]. Nevertheless, the costs associated with such prolific species' management and control actions hinder their efficacy and upscale. Finding purpose and valorizing the residual biomasses (wood, bark, leaves, stumps, flowers, pods) from the different *Acacia* species could contribute to a long-term control strategy [6,11–14].

Currently, there are several uses for different *Acacia* species and plant parts: bark, mostly from *A. mearnsii*, is used for tannin production; leaves and pods are used as fodder; flowers are used for fragrances by the perfume industries; and wood is mostly used for solid wood products (mostly *A. mangium*, *A. melanoxylon*, and *A. auriculiformis*), as biofuel (either as is or for pellet and briquette production) or as raw material for pulp and paper production (mostly from *A. mangium*, *A. auriculiformis*, *A. crassicarpa*, and *A. mearnsii*) [15].

One field of interest in using *Acacia* wood is pulp and paper production. Some species are already used industrially for this purpose, mostly in Africa, East Asia, South America, and Australia, where dedicated cultures can be grown or through the use of native forest species [16,17]. As for the vast majority, including some that infest European countries, little is known regarding their possible use as pulpwood raw material. *A. mearnsii* already has an implemented industry for tannin production from the bark that sees wood as the sidestream. The knowledge gathered for this species is therefore higher, already being used for bleached hardwood kraft pulp production, with characteristics also considered suitable for dissolving and semi-chemical pulps [16]. As for the other European infesting species, only a few works regarding pulping exist and only for *A. dealbata* and *A. melanoxylon* [13,18–20].

Determining the suitability for pulp and paper production requires deep knowledge of the raw material's structural and chemical characteristics, pulping and bleaching's main variables that influence delignification and their effect on fibers, and final product (pulp and paper) characteristics. Factors like wood density, extractive content (related to pitch problems), delignification chemical charges and yields, paper strength, and optical properties are all essential to determine raw material viability, possible product value, and best-suited end-use.

An experimental design can be used to minimize the workload required to determine the influence of several parameters at the same time. Response surface methodology (RSM) is counted as one of the most simple and robust while still providing accurate models for several response variables simultaneously, with the least amount of factor levels.

This work studied the pulpwood potential of five *Acacia* species' wood residues, collected upon invasive species control actions, for bleached kraft pulp and paper production (*A. dealbata*, *A. longifolia*, *A. mearnsii*, *A. melanoxylon*, and *A. saligna*), focusing on wood characteristics, pulping process optimization, and bleach pulp and paper characteristics, to ascertain their viability for that purpose.

2. Materials and Methods

2.1. Sampling

Wood from 5 different *Acacia* species, at least three trees for each, was used to conduct this study. *A. longifolia* and *A. melanoxylon* were collected from the fields of Monte da Lua, at Parques de Sintra, Sintra, Portugal. *A. dealbata*, *A. mearnsii*, and *A. saligna* were collected from fields of the School of Agriculture, University of Lisbon (ULisboa), at Tapada da Ajuda, Lisboa, Portugal. The trunk logs were manually debarked, and the wood was allowed to air-dry for several weeks before further processing. Discs at breast height were obtained, containing both heartwood and sapwood. Wood chips for pulping were obtained through a knife-mill and sieved through a 10 mm × 10 mm mesh. The smaller than typical industrial sized wood chips (25 mm × 25 mm × 4 mm) will lead to temperature and diffusion deviations from the industrial process but were necessary for this laboratorial experiment. From this point forward, *A. dealbata*, *A. longifolia*, *A. mearnsii*, *A. melanoxylon*, and *A. saligna* will be abbreviated to Ad, Al, Am, Amx, and As, respectively. *Eucalyptus globulus* (henceforth Eg) wood chips were provided by the Navigator company, collected at the Setúbal pulp mill, Portugal, and knife-mill and sieved through a 10 mm × 10 mm mesh, so as to have the same wood chip sizes as that of the *Acacia*.

2.2. Wood Properties

Wood's apparent and basic density were determined in 2 cm edge wood cubes, with at least 10 pieces (with both heart and sapwood) being used. Apparent density was determined in air-dry blocks with moisture content at 11%–13% (ASTM D2395) [21], and basic density was determined as the oven-dry mass of the cube divided by the "green" volume (measured after blocks' submersion in water for a couple of weeks).

For the chemical analysis, wood chips of each species were further milled and sieved with the 40–60 mesh fraction used.

Extractive content was determined through Soxhlet apparatus (125 mL, Linex, Vilabo, Lisboa, Portugal) using sequentially increasing polarity solvents: n-hexane, ethanol, and water. Ash content was determined by the Tappi standard method T 211 om-02 [22]. Insoluble and soluble lignin were determined in the extractive free material according to the Tappi standard methods T222 om-88 and UM250 om-83 [22], respectively.

Determination of the neutral monosaccharide, uronic acid, and acetyl group (through acetate determination) contents in wood was based on the monomers present in the hydrolysate from the lignin analysis by separation through a Dionex ICS-3000 High-Pressure Ion Chromatography (Thermo Fisher Scientific, Waltham, MA, USA), using an Aminotrap plus Carbopac SA10 column (Thermo Fisher Scientific, Waltham, MA, USA), as described elsewhere [23].

Cellulose and hemicellulose contents were estimated using the neutral monosaccharides, using the anhydrous correction factor 0.88 (132/150) for pentoses and 0.9 (162/180) for hexoses and assuming simplistically that all glucose would be the result of cellulose hydrolysis and the remaining from the hemicelluloses (acetates assumed to be mainly resulting from acetyl groups in hemicelluloses).

All analyses were performed in triplicate and reported as average percentages regarding dried material.

2.3. Kraft Pulping

Kraft pulping was conducted in stainless-steel microdigesters (Ca 100 mL) under rotation in an oil bath. The cooking conditions were as follows: 10 g of wood, liquid-to-wood ratio of 4:1, and 25% sulfidity. The reaction was considered to occur under isothermal conditions, for 60 min, beginning counting after 5 min to reach the bath temperature.

The factors studied were active alkali (AA, as Na_2O), ranging from 16% to 24%, and temperature (T, °C), ranging from 151 °C to 179 °C. After cooking, the digesters were cooled in an ice bath until room temperature. The solid residues were washed, defibrated, further washed, and recovered by vacuum filtration. The pulp was dried at 50 °C and stored before further tests.

2.3.1. Experimental Design and Statistical Analysis

Response surface methodology was used to determine the minimum necessary points required to correlate the effects of active alkali (AA) and temperature (T) and the response variables' yield (Y) and Kappa number (K). The design chosen was the central composite design with 4 factorial points, 4 axial points, and a central point. Although this methodology uses a normalization of the process variables, as they have different range intervals and units, it was only presented the equations of the natural values. The experimental results were fitted into a second-order polynomial equation using multiple regression analysis through the least square method. Whenever a coefficient proved non-significant to the model, it was excluded and the model was simplified. Each response variable led to a specific model correlating the predicted response variable to the independent variables. The statistical significance of each model and respective coefficients was determined by analysis of variance. Experimental design and statistical analysis were performed with Statistica® 6.0 software.

2.3.2. Scale-Up

For scale-up purposes, Kraft pulping was conducted in a stainless-steel batch reactor (Ca 5 L) with fluid recirculation, under the optimized cooking conditions previously established for each *Acacia* species. The different reactor types (recirculation vs. rotation) will surely give different responses even if the conditions are approximate to those in the smaller digesters. In addition to the 5 *Acacia* species, two more pulps were produced using similar reaction conditions (average conditions of AA and T determined for all 5 *Acacia*, AA = 17% and T = 169 °C). One was the equitable mixture of all *Acacia* species (20% of each), and the other was the comparative species *E. globulus*. The heating time to temperature and the isothermal period for each batch was such as to equal the H factor (Equation (1), T in kelvin and t in minutes) used in the microdigester. As the reactor system used in the scale-up cooking assays requires a non-negligible time to reach the cooking temperature, the time at reaction temperature was adjusted to obtain the same H factor as in the optimized point of the microdigester assays. The H factor was determined for each species through Equation (1). The H factors used for the optimum points were 607 for *A. dealbata* (Ad), 846 for *A. longifolia* (Al), 660 for *A. mearnsii* (Am), 1082 for *A. melanoxylon* (Amx), 1173 for *A. saligna* (As), 846 for *Acacia* mixture (Amix), and 846 for *E. globulus* (Eg).

$$H = \int_0^t e^{\left(43.2 - \frac{16{,}115}{T}\right)} dt \tag{1}$$

After pulping, the pulps were thoroughly washed, disintegrated, and screened for shives and uncooked material removal.

2.3.3. Kraft Pulp Characterization

Pulp yield was calculated as the ratio between the screened pulp weight (oven-dry) and the wood sample (oven-dry), expressed as a percentage. The Kappa number of the pulp was determined according to the Tappi Useful Test Method UM 246 [22]. The degree of polymerization of the pulps was determined using cupriethylenediamine (CED), as described in the SCAN-CM 15:88 test method [24]. Hexenuronic acid content (HexA, mmol/g) was determined through UV spectrophotometric detection at 245 nm and 480 nm after 2 h acid hydrolysis of 0.5 g of pulp with a buffer of sodium formate at 110 °C according to Equation (2), where ε is the molar absorption coefficient at 245 (8.7 $\mu M^{-1} cm^{-1}$), and m is the pulp oven-dry mass in kg. Each mmol of HexA corresponds to 0.086 Kappa number per gram of pulp [25]. The HexA were presented as Kappa number equivalents, representing their effect on this parameter.

$$\mathrm{HexA} = \frac{\left(\frac{A_{245} - A_{480}}{\varepsilon \times m}\right)}{4} \quad (2)$$

The specific wood consumption reported as m^3 of wood per ton of pulp was determined according to Equation (3) to ascertain the volume of wood required to produce one ton of unbleached kraft pulp. Pulp yield is expressed in ton of kraft pulp per ton of wood and basic density in ton of dry wood per m^3 of wood.

$$\mathrm{SWC}\ (\mathrm{m}^3_{\mathrm{wood}}/\mathrm{ton}_{\mathrm{pulp}}) = \frac{1}{(\text{Pulp Yield} \times \text{Basic Density})} \quad (3)$$

2.3.4. Bleaching

Pulps were bleached using an ECF (elemental chlorine-free) sequence of oxidation with chloride dioxide (D), followed by alkaline extraction (E) (D0-E1-D1-E2-D2). The D0 stage was conducted at 45 °C, for 30 min, with a chlorine dioxide charge (expressed as active chlorine) corresponding to a Kappa factor of 0.2 (charge % = Kappa number × 0.2). The chlorine dioxide charges (expressed as active chlorine) were 1.3% and 0.6% in D1 and D2. The D1 stage was conducted at 70 °C, during 120 min, and the D2 stage was carried out at 70 °C, during 180 min, with a consistency of 10%. The bleaching performance was evaluated by measuring the brightness and the intrinsic viscosity (SCAN-CM 15:88) [24].

2.4. Papermaking Potential

The bleached pulps were beaten at 500 and 2500 revolutions in a PFI mill under a refining intensity of 1.77 N·mm^{-1} (as defined in ISO 5264-2) [26]. The drainability of the pulp suspension (°SR) was determined by Schopper-Riegler methodology according to ISO 5267-1 [26]. The water retention value (WRV) of the pulp fibers was determined by centrifugation of the wet pulp samples for 15 min at 3000× *g*, according to SCAN-C 62:00 [24]. The morphological properties of the pulp fibers were measured using a Morfi® (LB-01) analyzer (Techpap, Grenoble, France), and slenderness ratio was calculated as the ratio of the fiber's length and their width. Handsheets were produced with a basis weight of 60 g·m^{-2} and conditioned according to ISO 5269-1 and ISO 187 [26]. The properties measured were as follows: bulk density, tensile and tear indexes (according to ISO 5270:2012), Bendtsen air permeability (according to ISO 5636-3:2013) [24], internal bond strength (Scott type, according to Tappi 569 pm-00) [22], and dry zero-span tensile (according to Tappi T231 cm-07) [22] and optical properties (brightness and opacity, according to ISO 2470 and 2471 [26], respectively).

3. Results and Discussion

3.1. Wood Chemical Composition

Table 1 shows the summative chemical composition analysis of the five *Acacia* species as well as the monosaccharides that compose the sugar polymers (cellulose and hemicelluloses). Since *Eucalyptus globulus* was chosen to be the comparison species regarding the pulp and paper characterization, its composition was also added to the table.

Table 1. Summative chemical composition as mass percentages regarding oven-dry wood of *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), and *A. saligna* (As) in comparison to *Eucalyptus globulus* (Eg) wood.

	Ad	**Al**	**Am**	**Amx**	**As**	**Eg [23]**
Ashes	**0.4 ± 0.03**	**0.4 ± 0.01**	**0.3 ± 0.01**	**0.3 ± 0.01**	**1.1 ± 0.22**	**0.8**
Extractives	**5.0 ± 0.1**	**5.0 ± 0.1**	**6.6 ± 0.2**	**8.0 ± 0.2**	**4.0 ± 0.1**	**4.4**
n-Hexane	0.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3
EtOH	3.2 ± 0.1	3.8 ± 0.0	4.6 ± 0.1	7.1 ± 0.2	2.4 ± 0.0	1.4

Water	1.6 ± 0.1	1.1 ± 0.0	1.8 ± 0.2	0.7 ± 0.1	1.4 ± 0.1	2.7
Lignin	**23.0 ± 0.1**	**23.7 ± 0.2**	**20.8 ± 0.1**	**20.8 ± 0.1**	**23.5 ± 0.1**	**24.3**
Klason	19.7 ± 0.1	20.6 ± 0.2	18.3 ± 0.1	18.1 ± 0.0	20.6 ± 0.1	19.9
Soluble	3.2 ± 0.1	3.2 ± 0.0	2.5 ± 0.0	2.7 ± 0.1	2.9 ± 0.1	4.4
Polysaccharides	**71.1 ± 0.9**	**67.5 ± 2.6**	**71.6 ± 0.8**	**68.7 ± 1.5**	**68.7 ± 0.6**	**63.3**
Cellulose	41.8 ± 1.1	44.2 ± 2.3	45.0 ± 0.4	43.1 ± 1.1	41.0 ± 0.6	40.0
Hemicelluloses	29.3 ± 2.0	23.3 ± 0.3	26.6 ± 0.5	25.6 ± 0.8	27.7 ± 0.9	23.3
Monosaccharides and acetyl groups	**79.7 ± 1.0**	**75.5 ± 2.8**	**80.2 ± 0.8**	**77.0 ± 1.7**	**77.1 ± 0.7**	**70.8**
Ramnose	0.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3
Arabinose	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.6
Galactose	0.2 ± 0.0	0.1 ± 0.0	0.3 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	1.6
Glucose	46.4 ± 1.2	49.1 ± 2.6	50.1 ± 0.4	47.8 ± 1.2	45.6 ± 0.6	44.4
Xylose	23.6 ± 0.5	19.1 ± 1.6	23.5 ± 0.4	20.9 ± 0.7	22.0 ± 0.1	18.0
Mannose	*	*	*	*	*	0.9
Galacturonic acid	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.5 ± 0.0	0.9
Glucuronic acid	0.0	0.0	0.0	0.0	0.0	0.1
Acetates	8.8 ± 2.7	6.7 ± 1.4	5.8 ± 0.2	7.6 ± 0.8	8.5 ± 0.9	4.0

*- not measured (accounted within Xylose).

The five *Acacia* species are similar in composition, although with some considerable differences. *A. saligna* showed three-times the ash content of all other *Acacia* species, although not much higher than *E. globulus*. Although the inorganic content might negatively affect both the equipment and final product [27], the values found here were too low to impact the possible use of these species for pulping purposes. The extractive contents were higher than those of *E. globulus* for all but *A. saligna*, with *A. melanoxylon* presenting significantly higher values (8%), as previously reported for *A. melanoxylon* heartwood [19]. The higher extractive contents are typically associated with higher chemical consumption in cooking; nevertheless, the apolar fraction (n-hexane) of the extracts, which is the most problematic one regarding end products and equipment issues [28,29], was found to be relatively low.

The lignin content varied between 21 and 24%, slightly lower for all Acacia species compared to that of *E. globulus*. On the other hand, the soluble lignin (less recalcitrant and more easily degraded) represented around 13% of the total for all *Acacia* species, while for *E. globulus*, it was considerably higher (18%).

Regarding the polysaccharide fraction, the main end-product target of the pulping process, the *Acacia* species showed higher content than *E. globulus*, with *A. mearnsii* presenting the highest cellulose (indirectly determined from glucose) and lowest acetate contents (acetyl group from hemicelluloses). Lignocellulosic biomass with high acetyl groups (determined here as acetates) will lead to higher consumption of reagents upon their hydrolyzation in an alkaline medium [30].

The high glucose and xylose (the latter two-times higher than previously observed) [31] and low lignin contents (with low Klason lignin 18.3%) show good perspectives for the pulping of *A. mearnsii*. *A. longifolia*, on the other end, showed the exact opposite, with higher lignin and lower polysaccharide contents than the remaining *Acacia* species. *A. saligna* and *A. dealbata* presented lower cellulose, significant lignin, and the highest acetate contents, which point to harsher delignification conditions and lower expected theoretical pulp yields.

Overall, the wood from the *Acacia* species studied showed typical hardwood chemical composition values, apparently compatible with pulping and paper production.

3.2. Kraft Pulping Experimental Design and Optimization

To understand the influence of temperature (T) and active alkali (AA) on the *Acacia* kraft pulping process, a central composite design was established with a domain of temperatures between 151 and 179 °C and active alkali between 16 and 24% as Na_2O. The values were chosen to accommodate the typical values for these variables at the mill scale, using hardwood as the raw material. The experimental points (temperature and active alkali pairs) and respective response variables, pulp yield, and Kappa number are displayed in Table 2 for each *Acacia* species.

The variability within species was not pronounced, with screened pulp yield (g of pulp per 100 g of wood) varying between 46 and 58% and Kappa number (representing residual lignin and hexenuronic acids) between 6 and 60. As expected, harsher conditions (higher temperatures and/or chemical charges) lead to lower pulp yield and Kappa number since the reaction is further extended with higher degradation and solubilization of both lignin and carbohydrate polymers (especially hemicelluloses).

Nevertheless, some differences could be seen, with *Acacia saligna* recurrently showing higher Kappa number values and lower pulp yields for almost all experimental runs than the remaining species. The delignification of *Acacia melanoxylon* appeared to be easier at softer conditions, with the Kappa number varying solely from 9 to 38 within the domain of the experiment, even though it could not reach values as low as some other species. Other species, such as *Acacia mangium* and *Acacia auriculiforms*, were also tested for pulping with temperatures and active alkali in the range of this work but resulted in yields lower than the ones obtained here (39%–45% and 37%–45%, respectively). Kappa numbers for both species are within the domain of the present work [32,33].

Table 2. Response surface methodology (process variables: temperature—T and active alkali—AA) and experimental design results regarding pulp yield (Y) and Kappa number (K) of *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), and *A. saligna* (As). The process variables studied were temperature (T) and active alkali (AA).

T (°C)	AA (%)	Ad		Al		Am		Amx		As	
		Y (%)	K	Y (%)	K	Y (%)	K	Y (%)	K	Y (%)	K
155	17	57	45	58	46	58	43	58	38	57	57
155	23	52	22	52	26	53	22	53	20	51	39
175	17	52	10	52	13	53	12	52	14	51	14
175	23	47	7	48	8	49	8	48	10	46	11
151	20	56	46	56	49	57	43	56	36	57	60
179	20	49	7	49	6	49	9	49	9	48	10
165	16	56	13	56	24	57	23	55	25	56	31
165	24	49	9	50	12	51	11	50	12	48	18
165	20	51	13	51	13	53	14	52	14	51	20
165	20	52	13	52	13	52	14	52	14	51	21

These data were used to produce models that correlated reaction temperature and chemical charge with pulp yield and Kappa number, presented for each species in Supplementary Material. Using the combination of both pulp yield and Kappa number models, a theoretical optimization was achieved for each species that would retrieve the reaction temperature and active alkali pair that would give the highest yield at a Kappa number of 17 (typical setpoint value used in the *Eucalyptus globulus* kraft pulping industry for bleached kraft pulp production). Using those restraints with the models, the optimal reaction temperatures and active alkali conditions were determined (Table 3).

To determine the proximity of each model to reality, pulps were produced using those optimized factors. Overall results showed that both the experimental yield and Kappa number were quite close to the expected theoretical values, except for the Kappa number of *Acacia melanoxylon*, which achieved a lower Kappa number than expected (14.7

instead of 17.5). In the optimized points, we also determined the hexenuronic acids (expressed as Kappa number equivalents) and the degree of polymerization of the pulp. The permanganate consumption by the hexenuronic acids in the Kappa number procedure represents between 3.8 and 4.6 Kappa number units, meaning that 21%–28% of the Kappa number could be traced to the hexenuronic acids and not the lignin polymer. Hexenuronic acids consume reagents in the bleaching process and are detrimental to the optical properties and their stability [34].

The degree of polymerization of the unbleached pulps was high, showing a low degradation of the cellulose polymer. *Acacia melanoxylon* presented the highest DP value, 4850, with *A. saligna* showing the lowest.

A pulping scale-up was achieved using the optimized conditions for each wood species. Since heating up would require a ramp in this case, the time at temperature was adjusted for each batch to obtain the same overall H factor as in the smaller experiments.

An equitable mixture of all *Acacia* species was tested to determine the possibility and characteristics of pulps produced without discriminating the *Acacia* species. This experiment would better approach a real situation where the raw material is not totally discriminated, and the *Acacia* wood source and type are unknown. In this case, we used average pulping conditions of reaction temperature (170 °C) and active alkali (17% as Na_2O). We also produced *Eucalyptus globulus* pulp under the same conditions to serve as the standard pulp for comparison reasons, since this is the most common hardwood species used in the Iberian Peninsula for bleached kraft pulp production. Each pulp was bleached following a typical ECF sequence, and the results of unbleached and bleached pulps obtained for each species are presented in Table 3.

The yields obtained were tendentially lower than theoretical and those obtained with the small digesters, with pulp produced, having lower hexenuronic acids and a lower degree of polymerization. This seems to show that the scale-up operation leads to higher polysaccharide degradation, higher solubilization, and removal of hexenuronic acids.

Acacia species achieved higher pulp yields (52.3%–53.5%) than *E. globulus* (51.4%) under optimized conditions, reaching the proposed 17 Kappa number for all except *A. longifolia*, which only reached 19 Kappa number. Similar results were presented previously for *A dealbata* and *A. melanoxylon* wood [13,18,19], with pulp yields above 50% and Kappa numbers below 17. Being widely planted in Brazil, mostly for bark tannin production, the wood of *A. mearnsii* has also been tested for pulp production, with pulp yields (57%–47%) and Kappa numbers (all below 17%) presented for a vast active alkali range [31]. To the best of our knowledge, no previous pulping study for *A. saligna* and *A. longifolia* woods was found.

The bleaching process showed 4%–5% mass losses and eliminated almost all hexenuronic acids (93%–96% for *Acacia* species and 97% for *E. globulus*). There was a decrease in the pulp degree of polymerization of roughly 9%–13% with bleaching, indicating some degradation of the cellulose polymer. Nevertheless, the pulps' DP were considerably high, with all *Acacia* species presenting higher DP than *E. globulus.*

Considering solely the delignification variables determined and expressed here, it is possible to verify that the *Acacia* species appear to be interesting raw materials with comparable yields and delignification patterns to *E. globulus*.

Table 3. Optimum pulping values of temperature (T) and active alkali (AA), pulp yield (Y), Kappa number (K), hexenuronic acid component in Kappa number (HexA), and pulp degree of polymerization (DP), for response surface methodology theoretical and experimental optimal points and scale-up unbleached and bleached pulps.

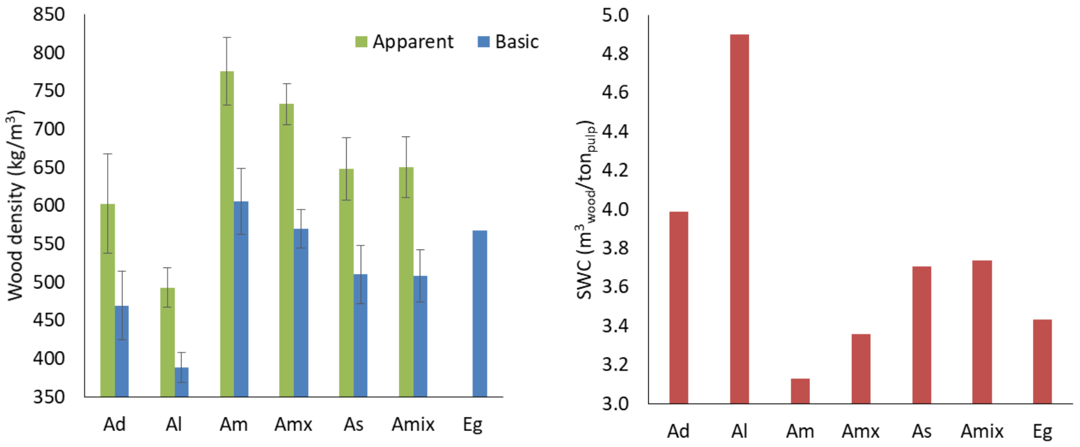
	Optimum		**Optimum Point RSM (Small Digesters)**						**Optimum Point Scale-Up**						
	Factor Values		**Theoretic**		**Experimental**				**Unbleached**				**Bleached**		
	T (°C)	**AA (%)**	**Y (%)**	**K**	**Y (%)**	**K**	**HexA**	**DP**	**Y (%)**	**K**	**HexA**	**DP**	**Y (%)**	**HexA**	**DP**
Ad	165	17	54.5	16.8	55.0	18.3	3.8	4402	53.5	16.4	3.6	3514	95.9	0.2	3203
Al	169	16	54.2	16.6	54.3	17.4	4.6	4152	52.6	19.1	4.3	3490	95.6	0.2	3086

Am	166	18	54.1	16.8	53.2	17.1	3.8	3811	52.8	15.4	3.4	3305	94.9	0.2	2956
Amx	172	16	53.3	17.5	53.6	14.7	4.1	4850	52.3	17.4	3.8	4215	95.6	0.2	3690
As	173	16	52.9	16.8	52.5	16.6	4.3	3728	52.9	17.5	4.1	3211	95.1	0.2	2867
Amix	170	17							52.6	17.0	3.7	3526	95.3	0.2	3085
Eg	170	17							51.4	15.5	4.1	3242	95.8	0.1	2835

Specific wood consumption (SWC) is a very important variable considering the wood volume required to produce a specific amount of pulp. This variable combines the wood basic density and the pulp yields, providing helpful and necessary information related to the reactor and process equipment size required for a specific pulp output. Figure 1 presents the wood's apparent and basic densities (left plot) and the specific wood consumption (SWC, right plot) for *Acacia* species and *E. globulus. Acacia mearnsii* and *A. melanoxylon* showed higher densities, leading to lower SWC (3.1 and 3.3 m^3 of wood to produce one ton of bleached pulp, respectively) than that of *E. globulus* (3.4 m^3_{wood}/ton_{pulp}). In the opposite direction, *A. longifolia*, with a very low wood density (<400 kg/m^3), obtained a very high SWC (4.9 m^3_{wood}/ton_{pulp}). Although not typically presented, this parameter correlates to the equipment, material transportation, and handling and storage costs, giving a better idea of the viability of a certain raw material. From the data collected, *A. mearnsii*, *A. melanoxylon*, *A. saligna*, and the *Acacia* mixture have approximate SWC values to the *E. globulus*, while *A. dealbata* and, more noticeably, *A. longifolia* show higher and therefore more costly SWC. This parameter is severely influenced by wood density, which can be highly variable within species, as demonstrated by Santos [20] for *A. melanoxylon* that presented basic wood densities from 449 to 649 kg/m^3 for different provenances and trunk height levels.

Previous works reported lower wood basic density for *A. dealbata* (351 kg/m^3) and *A. melanoxylon* (387 kg/m^3) but similar for *E. globulus* (536 kg/m^3) [10]. Searl [35] presented wood basic densities for *A. mearnsii* and *A. melanoxylon* on the same level as those found here but with higher values for *A. dealbata* (525–585 kg/m^3). Mmolotsi [36] reported for *A. saligna* basic density values between 470 and 730 kg/m^3, corroborating those found here.

Cremonez [37] and Magaton [38] presented values of SWC for *Eucalyptus grandis* and *Eucalyptus urophylla* between 3.6 and 4.6 m^3_{wood}/ton_{pulp}, which are tendentially higher than the values observed here with the exception of that of *A. longifolia*.



(**A**) (**B**)

Figure 1. Wood apparent (moisture content 11%–13%) and basic densities (**A**) and unbleached SWC (specific wood consumption) (**B**) for *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), *A. saligna* (As), and an equitable mixture of all *Acacia* woods (Amix) in comparison to *Eucalyptus globulus* (Eg) wood (basic density from [23]).

3.3. Papermaking Potential

To evaluate the papermaking potential of the *Acacia* bleached pulps produced, two refining levels (500 and 2500 revolutions) in addition to the unrefined pulps were obtained. This information enables a critical assertion on the mechanical, drainability, and optical performances of the fibers and paper obtained.

3.3.1. Fiber Properties

Table 4 shows the biometric characteristics and morphology of the *Acacia* fibers obtained and their variation upon beating. *Acacia mearnsii* and *A. saligna* presented the lowest fiber widths (15.6 µm and 15.9 µm) of all *Acacia* species, quite similar to the ones observed for *E. globulus* (15.6 µm), while *A. longifolia* showed a considerably higher average fiber width, roughly 22 µm for unbeaten pulp.

The average fiber length (weight in length) was found to be lower than that of *E. globulus* (849 µm) for all species except *A. melanoxylon* (918 µm). These lengths put *Acacia* species in the low range of the "short" fiber category. The same behavior, but in the opposite direction, was observed regarding fines, with only *A. melanoxylon* presenting lower amounts than *E. globulus. A. dealbata* and *A. longifolia* presented significantly higher fine elements than the other species. The fiber length values found here were substantially higher than those observed by Santos [13] for *Acacia melanoxylon* (650 µm) but similar to those presented for *A. dealbata* (660 µm). *A. mearnsii* showed lower fiber length and width than previously reported by Chan [16].

The lower coarseness of *A. dealbata* and *A. saligna* indicates that these fibers have thinner walls compared to *E. globulus* (the fiber width are of the same magnitude), leading to fibers with high collapsibility and flexibility. *A. longifolia* presents the highest coarseness but this does not lead necessarily to low collapsibility due to the highest fiber width. The slenderness ratio of *A. longifolia* was the lowest, 28, with *A. dealbata* also showing relatively low values, 35. Nevertheless, all species showed values below those of *E. globulus*. Higher slenderness values tend to improve forming and bonding paper properties [39]. According to Xu [40], slenderness ratio above 33 is one of the essential morphological parameters for good pulping and papermaking. *A. longifolia*'s lower value and *A. dealbata*'s very close slenderness ratio seem to indicate lower pulping potential.

The influence of beating was expected and typically registered for short fibers such as *Acacia* and *E. globulus*, with fiber length slightly decreasing and fines increasing as the beating was extended. This is due to the severance of the fiber extremities upon beating, which shortens the average fiber length and, with those extremities, cuts portions adding to the fines. This is most noticeable upon a higher beating as the first 500 revolutions straightens the fibers along the movement axis within the equipment, while the true beating mainly occurs after that. The increase in width comes from two factors: higher surface fiber microfibrillation that bulges the fibers outwards and reduction of the fibers extremities that are thinner, increasing the overall fiber average width.

Table 4. Morphological properties of pulp fibers produced from *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), *A. saligna* (As), and an equitable mixture of all *Acacia* (Amix) in comparison to *Eucalyptus globulus* (Eg).

	Rev	Fibers (millions/g)	Width (µm)	Length (µm)	Coarseness (mg/100 m)	Fine Elements % in Area
Ad	0	34	17.3	650	5.8	4.4
	500	36	17.5	640	5.6	4.7
	2500	37	18.3	631	5.5	5.5
Al	0	24	21.9	662	7.9	4.2
	500	25	22.2	661	7.8	4.5
	2500	25	22.8	650	7.8	4.7

Am	0	28	15.6	731	6.3	3.4
	500	30	16.1	731	6.1	3.3
	2500	29	17.1	720	6.2	4.1
Amx	0	22	17.5	918	6.7	2.3
	500	22	18.3	916	6.7	2.5
	2500	23	19.6	904	6.7	2.6
As	0	29	15.9	794	5.6	3.4
	500	30	16.3	794	5.5	3.5
	2500	32	17.0	775	5.4	3.7
Amix	0	27	17.5	753	6.4	3.4
	500	29	18.0	759	6.2	3.4
	2500	30	18.9	743	6.1	3.6
Eg	0	24	15.6	849	6.4	2.7
	500	26	16.2	851	6.2	2.8
	2500	26	17.3	835	6.4	3.4

3.3.2. Pulp and Handsheet Properties

The pulp and handsheet physical, strength, and optical properties for the unbeaten and beaten pulps of the five *Acacia* species plus the mixture and *E. globulus* can be seen in Figure 2. The properties studied here provide the necessary tools to assess the papermaking potential of the *Acacia* species wood.

The drainability resistance of pulp suspensions, evaluated by the Schopper-Riegler degree (°SR), showed a substantial variation within species (between 15 and 19 °SR for unbeaten and 30 and 43 °SR for 2500 rev). This variable is of extreme importance as it gives an idea of the energy required to increase the superficial fibrillation of the pulp and the subsequent increase in the strength of the paper properties. On the downside, it increases the resistance to water drainage from the pulp suspension in the papermaking process. Unbeaten short fiber pulp such as *Eucalyptus* should fall between 16 and 24 °SR [41], which was also the case for the *Acacia* species. At 2500 revolutions, the °SR increased above 30 for all pulps reaching over 40 for *A. dealbata* and *A. longifolia*, which might partly be a result of the higher fine element content (Table 4). *A. mearnsii* presented the lowest initial (15 °SR) and final (30 °SR) drainability resistance with beating behavior almost identical to that of *E. globulus.*

As expected, the paper density increased with beating, with all *Acacia* species presenting higher values than *E. globulus.* The relative high coarseness in a fiber with low width (low collapsibility) conjugated with a relative long fiber provides the morphological fiber properties for a relatively open fiber structure, which is a key characteristic of the Portuguese *E. globulus* pulp. Paper density tends to correlate positively with paper smoothness and inversely with brightness, light scattering, opacity, and air permeability, which was observed here. *A. dealbata* and *A. longifolia* presented the highest increases and absolute values for density with beating while presenting the lowest values for air permeability, brightness, opacity, and scattering coefficient.

The water retention value (WRV) increased with beating for all species but less profoundly for *A. mearnsii*, *E. globulus*, and the *Acacia* mixture. This behavior mimics, as expected, the °SR, where increasing fibrillation and fines by beating improves the pulps affinity to take up water and swell, even when opposed by higher gravity pulls. The only discrepancy was for the *Acacia* mixture, whose WRV was found to be similar to that of *E. globulus*, which did not happen regarding °SR. By combining different fibers from several species, the pulp obtained is not necessarily imprinted with the average values of the original raw materials.

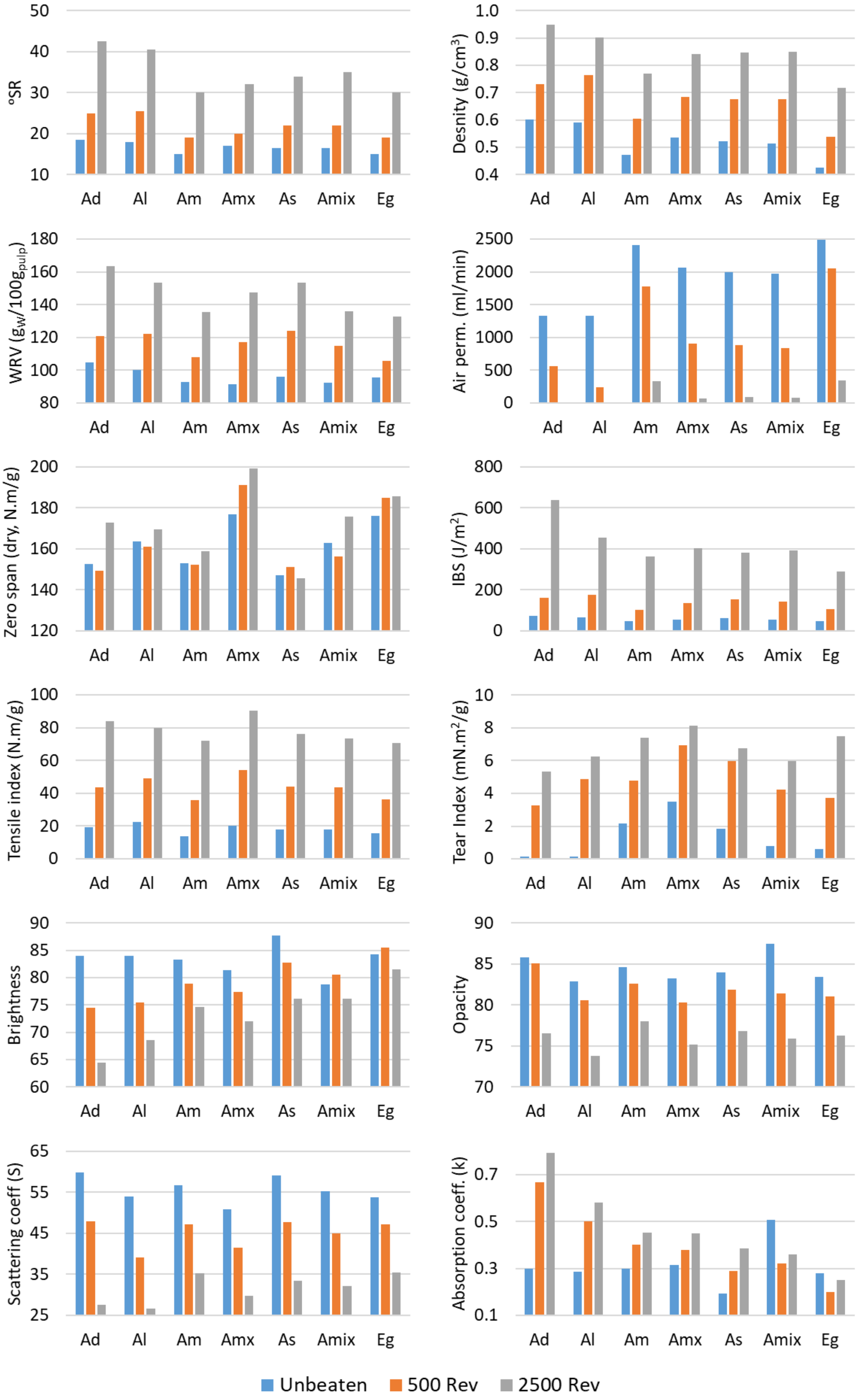


Figure 2. Physical (Schopper-Riegler degree—°SR, bulk, water retention value—WRV, and air permeability), strength (dry zero span, internal bond strength—IBS, tensile index, and tear index) and optical properties (brightness, opacity, scattering coefficient, and absorption coefficient) of unbeaten, 500 Rev., and 2500 Rev. of *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), *A. saligna* (As), and an equitable mixture of all *Acacia* (Amix) pulps in comparison to *Eucalyptus globulus* (Eg) pulp.

Regarding fiber strength, measured through the zero span, we could observe that only *A. melanoxylon* surpassed the *E. globulus*, although the mixture also came close. This parameter represents the intrinsic strength of the fiber (indicative of the maximum strength that the pulp could theoretically obtain). Nevertheless, the interfiber bonds are the prevalent factor in paper strength, which explains the discrepancy between fiber strength (much higher) and the paper tensile strength. *A. saligna* presented the lowest zero strength, which might be derived from its fibers being probably thin-walled (low coarseness and fiber width allied to high fiber length).

Regarding tensile index (indicative of fiber strength, fiber bonding, and fiber length), we observed that there was a slight variation within different pulps and that the beating behavior was somewhat similar with unbeaten pulps showing values between 16 and 23 N·m/g that increased to 71–90 N·m/g for the 2500 rev pulps. *E. globulus* reached the lowest tensile strength of all pulps at the maximum beating tested, which is in accordance with its lowest paper density. In fact, when density (or its inverse, bulk) is taken into account, the *E. globulus* pulp exhibits superior performance (Figure 3), with higher tensile index for the same paper density than of all *Acacia*. This tendency had also been found previously when comparing *Acacia* species and *E. globulus* [13].

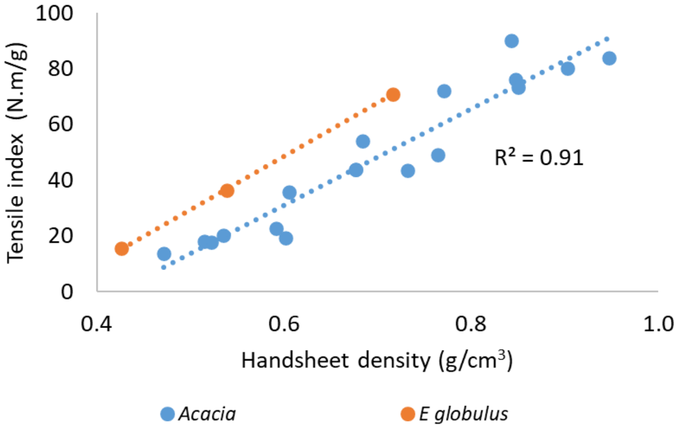


Figure 3. Handsheet density correlation with tensile index for all *Acacia* species and comparison with *E. globulus* pulps.

The tear index (strength required to withstand a tearing force) was low for unbeaten pulps, especially for *A. dealbata* and *A. longifolia* species, but reached values after beating between 5 and 8 mN·m^2/g. Santos [13] presented higher values for tensile strength for both *A. dealbata* and *A. melanoxylon* at 2500 rev beating point (90–100 N·m/g) but similar values of tear index (6–8 mN·m^2/g); although in that case, *A. dealbata* showed better overall strength results than *A. melanoxylon*, opposite to the findings here. Both tensile index and tear index obtained in this work were considerably lower that those described for *Acacia mangium* unbeaten [32] and beaten pulps [42]; although in those cases, the pulps were never dried, which typically lead to higher strength property values.

The internal bond strength (IBS, ability to resist splitting when a tensile load is applied through the paper's thickness, in the Z direction) followed the same patterns as the paper density, with *A. dealbata* and *A. longifolia* presenting the highest values. Xenografic or offset paper typical values of IBS are within 220–400 J/m^2, which was the gamma of the values obtained for all pulps studied here after beating at 2500 rev.

One of the biggest shortcomings of the *Acacia* pulps compared to *E. globulus* was the optical characteristics of the pulps produced, especially after beating. It is known that the brightness decreases with beating, but in the present case, the fall was pronounced. The biggest fall occurred for *A. dealbata*, with brightness dropping from 84% for unbeaten pulp to 64% at 2500 rev. This behavior was similar (although to a lesser degree) to all other

Acacia species, except for the *Acacia* mixture, which showed a brightness variation behavior closest to the *E. globulus.* The highest light absorption increase, lowest scattering coefficients, and low opacity observed after *A. dealbata* and *A. longifolia* beating led to their sharpest brightness decrease, probably associated with thinner fiber walls with a higher tendency to collapse.

3.3.3. Handsheet at 30 °SR

To better compare the characteristics of the pulps obtained from the different *Acacia* species, we interpolated all parameters for a °SR value typically used by the pulping industry for printing and writing paper (30 °SR), with results presented in Table 5.

Table 5. Physical (bulk, water retention value—WRV, and air permeability), strength (dry zero span, internal bond strength—IBS, tensile index, and tear index), and optical properties (brightness, opacity, scattering coefficient, and absorption coefficient) for *A. dealbata* (Ad), *A. longifolia* (Al), *A. mearnsii* (Am), *A. melanoxylon* (Amx), *A. saligna* (As), and an equitable mixture of all *Acacia* (Amix) in comparison to *Eucalyptus globulus* (Eg) at 30 °SR.

	Ad	**Al**	**Am**	**Amx**	**As**	**Amix**	**Eg**
Rev required	1070	1100	2500	2167	1835	1730	2500
Density (g/cm^3)	0.78	0.80	0.77	0.81	0.78	0.78	0.73
WRV (g$_W$/100 g$_{pulp}$)	133	132	136	142	144	128	133
Air permeability (mL/min)	410	170	330	210	350	370	350
Internal bond strength (J/m^2)	298	260	362	360	306	296	290
Zero span (N·m/g)	156	164	159	198	147	168	185
Tensile index (N·m/g)	55	58	72	84	65	62	70
Tear index (mN·m^2/g)	3.8	5.3	7.4	7.9	6.5	5.3	7.5
Brightness (%)	71.5	73.5	74.5	73	78.5	78.0	81.5
Opacity (%)	82.5	78.5	78	76	78.5	78	81.5
Transparency (%)	27.5	31	31	33	29.5	30	31
Scattering coefficient (S)	42	35.5	35.5	32	38	37	35.5
Absorption coefficient (k)	0.73	0.54	0.45	0.43	0.34	0.34	0.25

The beating energy required to achieve the drainability was lowest for *A. dealbata* and *A. longifolia*, while *A. mearnsii* and *E. globulus* would need over twice as much energy to reach 30 °SR. This will impact the energy requirements and refining costs. On the other hand, the handsheet strength properties of *A. dealbata* and *A. longifolia* were quite low at this drainage resistance, which decrease their pulping suitability.

A. mearnsii showed the highest similarity to *E. globulus* regarding fiber morphological characteristics (Table 4: width, length, coarseness), leading to similar handsheet characteristics except for the optical properties, which are slightly lower, due to the higher handsheet density (0.77 vs. 0.73 g/cm^3). With the highest wood density and respective lowest specific wood consumption (SWC), this species seems to be very interesting for this end-use.

Acacia melanoxylon showed the highest handsheet strength properties presenting very good pulping potential, allying very good wood density (and subsequent low specific wood consumption) and fiber/paper characteristics.

With the highest water retention value and considerable handsheet strength levels but needing only 73% of the energy required to achieve this °SR (compared to *E. globulus*), *A. saligna* might be an interesting candidate for tissue paper production, whose process tends to aim at lower drainage resistance.

The equitable mixture of all *Acacia* species theoretically presents the lowest value of WRV of all pulps studied and lower strength values, although achieving the second highest pulp brightness, close to that of *E. globulus*, and only surpassed by *A. saligna*.

4. Conclusions

The invasive *Acacia* species studied here presented close chemical composition to that of *E. globulus* that is most typically used for kraft pulp production in the Iberian Peninsula, although with higher polysaccharide and lower lignin contents. The optimized pulping process (to achieve Kappa number 17) produced pulps with slightly higher yields and polysaccharide degree of polymerization than those obtained for *E. globulus. Acacia dealbata* and especially *Acacia longifolia* presented low wood basic density resulting in high specific wood consumption (SWC), making them less attractive as raw materials for pulp and paper production on account of the expected higher transportation, production, and equipment costs. The opposite can be said regarding *A. mearnsii* and *A. melanoxylon*, which showed lower SWC than *E. globulus*. These two species' higher handsheet strength characteristics make them interesting materials for pulping production. The biggest drawback was that all *Acacia* species lost substantial optical properties upon refining.

Nevertheless, most of the species studied here seem adequate enough for pulping and paper end-use, adding to the always-in-need pulpwood supply chain, either alone or as an addition to the *E. globulus* pulp production. The mixture of all *Acacia* species simultaneous pulping tested here proved effective in producing pulp with acceptable characteristics, thus enabling the indiscriminate use of *Acacia* wood regardless of the species, bypassing the expected difficulty of having to identify the species of the waste wood collected upon invasive control actions. By valorizing and giving purpose to the wood wastes from invasive control actions, we can help promote them and increase their effectiveness in achieving a more sustainable and balanced ecosystem or use these species as crops for pulp production in those countries where they are not considered invasive.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/f15050822/s1, Supplementary File S1—Response surface methodology models for pulping.

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