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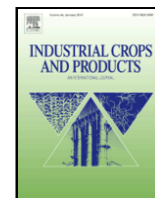


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## Tools for a multiproduct biorefinery of *Acacia dealbata* biomass

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### ABSTRACT

The forest wastes removed as a strategy to control the invasive shrub *Acacia dealbata* Link (silver wattle) can be regarded as a low cost renewable source of biomass for the production of biofuels, bioactives and chemicals. A number of studies have reported both conventional and novel processes for the utilization of different parts of the plant. This review presents an overview of the environmental problems associated to this shrub in invaded areas and a compilation of the technologies proposed for the extraction and production of commercially interesting compounds from silver wattle. Combination of such tools for the fractionated valorization of this resource following a zero waste biorefinery approach is discussed, with emphasis on the use of greener flexible technologies.

### 1. Introduction

Silver wattle or acacia (*Acacia dealbata* Link), a fast-growing species native to Southeastern Australia and introduced in other continents as ornamental trees or in forestry (Griffin et al., 2011), has become one of the most aggressive invasive plant worldwide (Fuentes-Ramírez et al., 2010; Richardson et al., 2015; Linhares and de Amorim, 2016; Nentwig et al., 2018). Studies on their impact, control and valorization in invaded areas can be found, including Southern Africa (De Neergaard et al., 2005; Coetzee et al., 2007; Henderson, 2007; Gouws and Shackleton, 2019; Hirsch et al., 2019), Chile (Albaugh et al., 2017; Langdon et al., 2019), and Southwest Europe (Carballeira and Reigosa, 1999; Sheppard et al., 2006; Carneiro et al., 2014; Nunes et al., 2020). In fact, this exotic specie causes severe problems in economic, social and environmental fields as recurrent rural fires in Iberian Peninsula (Raposo et al., 2020) so this non-native specie is officially classified as invasive plant (BOE, 2013; European Commission, 2014). Consequently, strategy plans for the purpose of controlling, eradicating and preventing the propagation of *A. dealbata* are mandatory (Abilleira et al., 2021). For this reason, live specimens cannot be subject to business so the crop of this wild widespread tree is not permitted in the affected zones (BOE, 2013; European Commission, 2014.) in order to preserve the native flora and relative animal life, especially in conservation areas (Hernández et al., 2014)."

The increase in wattle cover has led to changes in landscape, environment, species richness and availability of natural resources. This species affects the soil moisture due to the high water requirements, impacting on other biological parameters in mixed forests and shrublands, such as arthropods diversity (Coetzee et al., 2007), accelerated activities (Souza-Alonso et al., 2014b; and 2015), and production of nutrient-rich litter, and alteration of pH (except in very acidic soils) (Kuppers, 1996; Fernandes et al., 2020; Frederick et al., 1986; Albaugh et al., 2017). The allelopathic action is responsible for inhibition on the germination and radicle growth of different plants (Carballeira and Reigosa, 1999; Souza-Alonso et al., 2014b; Lorenzo et al., 2008), and soil microbes (Lorenzo et al., 2013). By changing soil properties and microbiota composition, *A. dealbata* seems to favour their own invasion and the proliferation of other secondary invaders, acting as "ecosystem transformers" (Vieites-Blanco and González-Prieto, 2020). The consequences related to the decreased biodiversity, altered ecosystem structure, new biotrophic relationships or alterations in water availability and fire regimes cannot be recovered even long periods after the invasion due to the resources aimed at their eradication are insufficient due to the magnitude of the large affected area (Souza-Alonso et al., 2017).

The invasive ability of this species is usually attributed to the high resprouting and seeding capacity, high investment in flower production, long fruiting period, native exclusion through allelopathic effects, high environmental plasticity, adaptation to burnt, cleared and low-resource environments, lack of enemies in the invaded area and to the

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tolerance to changing soil conditions (Lorenzo et al., 2010; Correia et al., 2014; Vieites-Blanco and González-Prieto, 2020). Human-mediated factors, such as soil disturbance, climate change and severe fires favored expansion (Lorenzo et al., 2010; Parepa et al., 2013; Rodríguez et al., 2017; Vieites-Blanco and González-Prieto, 2020).

The management of invasive plant populations has generated a complex debate and in the case of ecosystems dominated by acacias control is a challenging task, involving high cost of the long-term strategies and meticulous monitoring (Ferreira et al., 2011). A first stage would be prevention and early detection and the design and implementation of appropriate strategies (Souza-Alonso et al., 2017; Vicente et al., 2019) to reduce the population and mitigate its proliferation (Nunes et al., 2020), minimizing the impact on soil microbes and plant communities (Souza-Alonso et al., 2013).

Control and restoration of the soil-plant system has been addressed with physical and chemical tools. Cutting could contribute to the spread of the invasion and boost regrowth (Lorenzo et al., 2010), and physical removal or burning of acacia litter, affect soil properties and can enhance secondary invasions by increasing nitrogen concentration. A good approach consisted on the direct herbicide spraying after cutting (Souza-Alonso et al., 2013). Biological control is adequate, since the absence of specific predators requires the introduction of natural enemies (Vieites-Blanco and González-Prieto, 2020). Proactive ecosystem restoration may be needed, regenerating with native species after the eradication of *A. dealbata*. In order to prevent new introductions and to achieve sustainable control, the preventive approaches, novel integrative and cost-effective solutions including the collaboration of different agents and also transfrontier participation are preferred (Fernandes et al., 2019; Langdon et al., 2019; Lorenzo et al., 2019a).

Acacia stands may perform as biomass producers (Carneiro et al., 2016) and wood can be used as heat source, for furniture and building materials, medicinal use or green manure (De Neergaard et al., 2005), tannin and pulp production (Santos et al., 2006), gums and as cosmetic ingredients (Johnson, 2005). It has been considered a residue from pulp industry, when left in the forest, but the valorization for high value applications is encouraged (Oliveira et al., 2020; Borges et al., 2020). Furthermore, there is a growing interest on the valorisation or novel uses of this widely available and low cost biomass as a sustainable profitable strategy (Oliveira et al., 2020) according to the circular bio-economy (Souza-Alonso et al., 2017; Neiva et al., 2020a). In a recent review Correia et al. (2020) have proposed the biorefinery approach for the valorization of all parts of the plant into commercially interesting products. The plant waste resulting from management actions could be used for energy and/or bio-products (Carneiro et al., 2014), based on the large capacity for raw material supply. However, the attribution of a market value for this species could cause a pressure over the resource, which must be followed by control strategies (Nunes et al., 2020).

The present review aims at presenting a variety of potential uses and at compiling the validated processing schemes from literature to offer practical tools for alternative developments for the integral valorization of all parts of this resource. Emphasis is given to the utilization of greener, efficient and sustainable technologies.

## 2. Composition

The different parts of the tree of *Acacia dealbata* present a different composition, and characterization is required in order to propose a separate valorization of each fraction. Data in Fig. 1 show the bibliographic information on the proximal composition of *A. dealbata* wood, bark, leaves and flowers. In wood the major fraction is cellulose (accounting for 42–51 %), followed by hemicelluloses (up to 17–29 %). In the lipophilic extracts, sterols are the major components, other constituents being fatty acids, long-chain aliphatic alcohols, monoglycerides, and aromatic compounds (Oliveira et al., 2020).

In bark, tannin content is higher (up to 74 %) than in other parts of the trunk and shows typical oligomeric structures, which are potential commercial sources of proanthocyanidin tannins (Reid et al., 2013), also the flavonoid content in *A. dealbata* is higher than in other genus (Yildiz et al., 2018). Bark lignins show a predominance of compounds derived from G, S and H lignin units (up to 57, 36 and 12 %), and high amounts of resorcinol and  $\beta$ -ether linkages, but lower content of condensed carbon-carbon linkages, such as phenylcoumarans, resinols, dibenzodioxocins and spirodienones (Neiva et al., 2020b). The bark is also rich in polysaccharides, contains free sterols, such as spinasterol, dihydropinasterol and stigmasterol and showed a high diversity of long-chain aliphatic alcohols, the most abundant being hexacosan-1-ol (Freire et al., 2005 and 2007; Oliveira et al., 2020). Terpenoids and monoglycerides were found among the major components of the lipophilic bark extracts (Neiva et al., 2020b; Oliveira et al., 2020) and saturated fatty acids accounted for 90 % of the total fatty acids content in bark.

Leaves have the highest diversity of compounds, many of them exclusive. The diterpene alcohol phytol (Souza-Alonso et al., 2014a), the lupene type triterpenes, lupenone, lupeol, lupenyl palmitate and lupenyl cinnamate being particularly abundant (Pereira et al., 1996). Fatty acids, long-chain aliphatic alcohols, monoglycerides, and aromatic compounds were also detected in the lipophilic extracts (Oliveira et al., 2020). Hydroxypipericolic and pipericolic acids and cyclic imino acids, present in aqueous extracts, were not exclusive of leaves and some of them could be synthesized as a defense against fungi, bacteria, and virus (Kunii et al., 1996).

Volatile organic compounds are found in the lipophilic extracts from flowers and are mainly derived from isoprenoid pathways, belonging to terpenoids, fatty acid derivatives, benzenoids and phenyl-

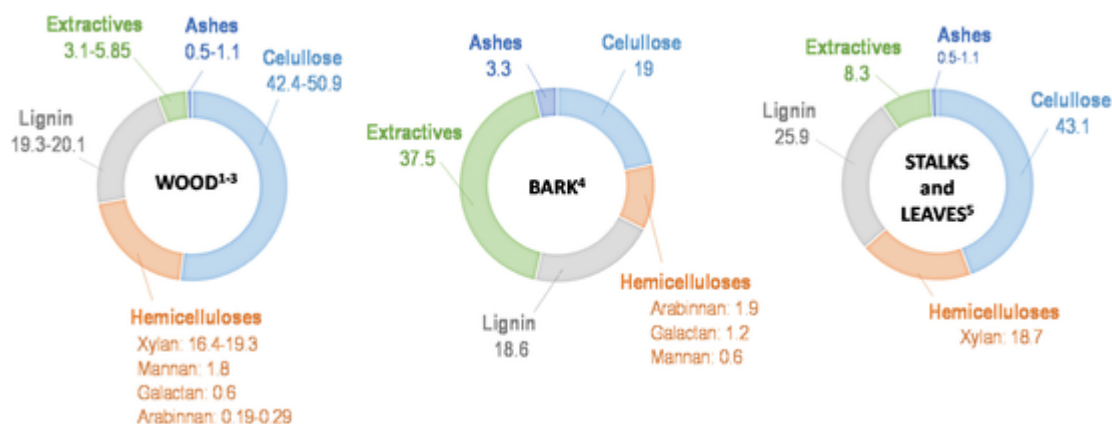


Fig. 1. Proximal composition reported for different parts of *Acacia dealbata* (wt % dry basis). References: <sup>1</sup>: Yáñez et al. (2009a); <sup>2</sup>: Yáñez et al. (2009b); <sup>3</sup>: Muñoz et al. (2007); <sup>4</sup>: Neiva et al. (2020b); <sup>5</sup>: Ferreira et al. (2001).

propanoids. Souza-Alonso et al. (2014a) have reported 27 compounds in the volatile fraction from flowers, heptadecadiene, n-nonadecane, n-tricosane, and octadecene, accounting for more than 60 % of the fraction (Perriot et al., 2010). The pollen grains contain a wide variety of compounds, the major ones being alkanes. Diethyl ether or aqueous extraction of *A. dealbata* pollen released benzoic acid and its 2-hydroxy and 4-hydroxy derivatives (Fountain et al., 1995), the first two may be implicated in plant hormone mediated processes in pollination.

### 3. Applications

*Acacia dealbata* biomass, either from forest exploitation or from the management of invasive species, can be a low cost source of high-value compounds (Oliveira et al., 2020), particularly in countries where the existing stands must be controlled through large scale eradication plans. In this scenario, the development cost-effective processing of the whole resource to obtain a range of bio-based products and integration into the existing infrastructure is desirable (Pinto et al., 2015).

#### 3.1. Whole biomass utilization

The simplest valorization routes are based on the use of the whole resource. Potential agricultural applications as green manure appear limited due to the high content of polyphenols (Freire et al., 2005). However, the use of alternative energy sources is increasingly important due to the necessity to minimize the consumption of fossil fuels and fight climate changes and the use of *A. dealbata* for energy may represent an opportunity to reduce the costs of eradication (Carneiro et al., 2014). There is a high potential for this species in the production of pellets for energy, particularly the joint use of all the biomass, trunks with bark, branches, and leaves. Ferreira et al. (2014) activated *A. dealbata* pellets in an industrial scale production plant, assessed the fuel efficiency for combustion in a biomass industrial boiler and in household equipment, and observed that acacia pellets were less efficient and the emissions were higher than for pine pellets.

Pyrolysis has good industrial perspectives for biomass conversion into fuels and chemicals, since three fractions: gas, bio-oil, and char can be obtained. Biomass flash pyrolysis offers advantages derived from its versatility, simplicity and low capital investment, since it can be performed at moderate temperatures in different reactor configurations (Ferreira et al., 2020), and leads to high bio-oil yields (Carneiro et al., 2014). In order to cut costs derived from separation and classification strategies, the joint valorization of the whole biomass from *A. dealbata* and from other forest shrub wastes could be beneficial and the economy of the process would be favored. Pyrolysis of the highly heterogeneous forest wastes was performed at 500 °C in a continuous reactor to obtain fuels and chemicals. This process yielded more than 75 % bio-oil, 20 % char and 5 % gas. Bio-oils are composed mainly of 30–40 % weight water, phenols, ketones, acids and furans, with lower contents of saccharides, aldehydes and alcohols whereas the gas fraction consists mainly of carbon dioxide and monoxide, and a lower amount of C1–C3 hydrocarbons (Amutio et al., 2013). Char formation is favored by a high lignin content, the higher concentration of extractives in bark and leaves also leads to higher reactivity and bark also produces a higher methane content in the gas fraction but lower bio-oil yields. Char is a by-product from pyrolysis is suitable for energetic valorization for its high carbon content, high heating value 27.5 (MJ/kg) and negligible sulfur content, but can also be used to produce activated carbons or for soil amendment to improve fertility. *A. dealbata* biochar obtained by pyrolysis (450 °C, 8 h) has been proposed for the formulation of amendments at the 3:97 mass ratio with solid waste material from sewage, chemical and food plants to restore a soil from a mine tailing (Forján et al., 2016).

#### 3.2. Separate utilization

##### 3.2.1. Bark

**3.2.1.1. Bark tannins.** Condensed tannins can bind to proteins and difficult their degradation. The reduced methanogenesis and improved ruminant performances of purified condensed *A. dealbata* tannins was confirmed by decreased fermentation parameters (gas, methane, ammonia and volatile fatty acids) (Khelalfa et al., 2020). Alternative applications have been tried for bark tannins. They are potential plant biostimulants. Application of a bark methanol/distilled water (97:3, v:v) extract on onion plants growing in saline soils increased height, as well as leaf, root and total biomass, and increased the sugar content in the plant and the protein content in leaves (Lorenzo et al., 2019b). Another application is their use as adsorbents. Okoli et al. (2018) synthesized resins from tannin-rich *Acacia* sp as a low cost Pb<sup>2+</sup> adsorbent, with maximum monolayer coverage capacity of 190 mg/g.

Tannins extracted from *A. dealbata* bark with water at 90 °C, yielding 17 % solids with a Stiasny number of 82 %, were used as alternative environmentally safe adhesives once hardened with formaldehyde or hexamethylenetetramine as crosslinking agents (Lisperguer et al., 2016). Alternatively, these compounds can be recovered during or after pulping of *A. dealbata* wood (Berlin, 2011a; and 2016). Resorcinolic-type tannins from these species find applications as thermosetting binders for wood and their antimicrobial properties make this application in wood composites and adhesives very attractive (Neiva et al., 2020b). Berlin (2011b) claimed the use of native lignin with high alkoxy contents and/or carbon contents, for their acceptable spinnability for the production of carbon fibres with adequate tensile strengths and modulus of elasticity.

Textile industry is searching for non-toxic, biocompatible and cleaner natural dyes from renewable materials, to partially replace synthetic dyes or to diminish their environmental impact. Linhares and de Amorim (2017) prepared a medium color natural dye for cotton fabric, obtained from *A. dealbata* bark. Tannins, which are the best natural mordants for cotton and other cellulosic fibers, can replace some toxic metallic salts. Mordant agents, acting as a link between fiber and dyes, improves color-fastness against light and washing and increase color yield. Olive tree pruning wastes (extracted at 120 °C for 60 min), used as dyeing bath, and *A. dealbata* tree bark extracts, used as mordant, were successfully used to dye cellulosic fibres, with acceptable color-fastness properties (Linhares and de Amorim, 2016).

**3.2.1.2. Bioactives.** Barks from biomass collected from forest operations to control *A. dealbata*, can be valorized due to their high extractives content. Crude bark extracts contain compounds that might be interesting for cosmetic, pharmaceutical and food applications as cheap and natural antioxidants and bioactives (Neiva et al., 2020a), a potential known since its traditional use for the treatment of several diseases in ayurvedic medicine (Sowndhararajan et al., 2015). The large variation in extractives content and composition with species, age, edaphoclimatic conditions, season and tree health can be attenuated by homogenization (Neiva et al., 2020a). Bark has a high content of extractives, about 46 % of the dry weight, most of them being polar compounds. Among the valuable compounds are phenolics, their content in the bark is greater than in the sapwood (Yildiz et al., 2018).

The extraction yields are highly dependent on the solvent, those safer and operating under mild extraction conditions being preferable (Neiva et al., 2020a). Both water and ethanol extracts showed potent radical scavenging properties, which favor their use in some applications (Lawson et al., 2010). A summary of this potential is presented in Table 1. The phenolic content of the hexane extracts was very low whereas up to 70 % was found in the ethanolic extracts, with 44 % condensed tannins. However, water extracted more flavonoids than ethanol, which was more efficient than water to extract compounds

**Table 1**Potential applications, bioactive properties and composition of extracts from different parts of *Acacia dealbata*.

Potential applications	Part of <i>Acacia dealbata</i>	Extraction (type: solid:liquid ratio, T, t)	Solvent	Bioactive properties/target compounds	Reference
Antimicrobial and antioxidant agents against oxidative stress	Leaves	SLE: 1:10, 20 °C, 60 min UE: 1:10, -, - at 420 W SE: 1:60, -, 16 h MAE: 1:10, -, 5 min at 162 W	A, E, D, H, M, W A, E, D, H, M, W	Antioxidant capacity (DPPH, TEAC) and antimicrobial activity/ -	Borges et al. (2020)
Antioxidant agents against oxidative stress	Stem bark	SE: -, -, -	PE, A	Viability of human HepG2 cells and antioxidant enzymes (CAT, CuZnSOD, MnSOD and GPx) activities	Sowndhararajan et al. (2015)
Antioxidant agents against oxidative stress with applicability as cosmetic active ingredient	Flowers	MHG: -, -, 180 min at 75 W SD: 1:5, -, min SLE: 1:10, 40 °C, 24 h	- W 50 % E	Antioxidant capacity (DPPH, P, TEAC and TCC)/ -	López-Hortas et al. (2020)
Antioxidant agents against oxidative stress and phytotoxic agent	Seeds Flowers <sup>a</sup> , leaves and small branches <sup>b</sup> and litter <sup>c</sup>	SLE: 0.2:3, 4 °C, 15 min SLE-LN: -, -, 4 h	HEPES-KOH-EDTA W, P	Oxidative stress parameters (antioxidant SOD and POX enzymatic activities and MDA content) and phytotoxicity on the germination and growth processes/ <sup>a</sup> : Heptadecadiene, octadecene, <i>n</i> -nonadecane and <i>n</i> -tricosane; <sup>b</sup> : phytol; <sup>c</sup> : aromadendrene, globulol, heptadecadiene and <i>n</i> -nonadecane	Souza-Alonso et al. (2014a)
Medicinal uses as analgesic and antipyretic agents Foodstuffs preservation	Pollen	SLE: -, 4 °C, 16.5 h	PS	- /Benzoic acid and hydroxylated benzoic acids (2-hydroxybenzoic acid and 4-hydroxybenzoic acid)	Fountain et al. (1995)
Medicinal uses as anticarcinogenic and antitumorigenic activity, cytotoxic, inhibitor of Epstein-Barr virus, modulator of diabetic nephropathy and reductor of plasma and liver cholesterol levels potential agents	Bark and wood	SE: -, RT, 8 h	D	- /Lipophilic extracts (free sterols -dihydrospinasterol and spinasterol- and steryl glucosides-dihydrospinasteryl glucoside and spinasteryl glucoside-)	Freire et al. 2005
Medicinal as antibacterial, antifungal and antiviral activity and inhibition of IL-2 and HIV protease potential agents	Leaves, seeds, stalks and roots	SLE: 1:2, 100 °C, 15 min	W	- /Cyclic imino acids (4-hydroxypipelicolic acid, pipelicolic acid and proline)	Kunii et al. (1996)
Medicinal uses as antiinflammatory potential agents	Stem bark	SE: -, -, -	PE, A	Inhibitory activity on NO production in LPS-stimulated murine macrophage RAW 264.7 cells due to the suppression of INOS, COX-2 and TNF- $\alpha$ gene expression/Phenolic profile (ellagic acid and isomer, procyanidin B1, rosmanol and saffeoil glucose)	Sowndhararajan et al. (2016)
Medicinal uses with applicability as pharmaceutical agent integrated in bioactive hydrogel matrices	Flowers	SLE: 1:20, 40 °C, 24 h SE: -, -, 12 h SLE: 1:15, RT, 12 h SLE: 1:15, RT, 12 h MHG: -, -, - at 400 W	96 % E H, D, EA, B W AW -	Antioxidant capacity (TEAC) antibrowning activity, antilipogenic and anti-inflammatory activities, cytotoxicity against tumoral cells and TPC/ -	Casas et al. (2020)
Protection against fungal agents	Bark and wood (heartwood and sapwood)	SLE: 5:50, RT, 24 h SLE: -, 80 °C, 2 h SLE: -, RT, 2 h	99 % M, W 3–5% M	Antifungal activity, antioxidant capacity (FRAP), antimicrobial and anti-quorum sensing activities, CTC, TFC and TPC/ -	Yildiz et al. (2018)
Phytotoxic agent	Flowers, leaf litter and pods	SLE: ~ 20:1, 10 °C, 72 h	W	Phytotoxicity on the germination and growth processes/ -	Aguilera et al. (2015a)

(continued on next page)

Table 1 (continued)

Potential applications	Part of <i>Acacia dealbata</i>	Extraction (type: solid:liquid ratio, T, t)	Solvent	Bioactive properties/target compounds	Reference
	Leaves, leaf litter, flowers, litter, pods, litter and seeds	SLE: ~ 20:1, 10 °C, 72 h SLE: -, 22 °C, 240 h	W 96 % M, H, EA, W	Phytotoxicity on the germination and growth processes/ <sup>d</sup> : Maculosin, moretenone and resorcinol; <sup>e</sup> : anisal, <i>p</i> -anisyl alcohol, methyl <i>p</i> -anisate and stigmasterol; <sup>f</sup> : <i>d</i> - $\alpha$ -tocopherol, quinone, lupanin and stigmasterol	Aguilera et al. (2015b)
	Leaf <sup>d</sup> , flowers <sup>e</sup> and pods <sup>f</sup> litter				
	Flowers, leaves and bark	SLE: -, RT, 9 weeks	97 % M, M:W (2:1, v/v), H, EA, W	Phytotoxicity on the germination and growth processes/ -	Lorenzo et al. (2016)
	Flowers	SLE: -, RT, 9 weeks	97 % M, M:W (2:1, v/v), H, EA, W	Phytotoxicity on the germination and growth processes/Methyl anisate and methyl cinnamate	Lorenzo et al. 2019a
Valorization as biologically active compounds resource	Leaves, flowers and seeds	SE: -, -, -	H, M	- /Lupene type triterpenes (lupenone, lupenyl cinnamate and lupenyl palmitate and lupeol)	Pereira et al. (1996)
	Wood, bark and leaves	SE: 1:10, -, - SE: 1:10, -, 45 min SLE: -, -, 24 h	E, M, A 50 % E 80 % E, C, EA, W, EA:H (1:1, v/v)	Alkaloids, antioxidant activity ( $\beta$ -carotene bleaching test and DPPH*), TFC and TPC/Phenolic compounds (caffeic, chlorogenic, <i>p</i> -coumaric, ellagic, ferulic and syringic acids and quercetin)	Luís et al. (2012)
	Flowers	SLE <sup>g</sup> : 1:20, 40 °C, 24 h Sc-CO <sub>2</sub> <sup>h</sup> : -, 45 °C, 180 min at 30 MPa	96 % E 10 % E	- /Flavonoids compounds (isomycitrin and isoquercitrin)	Movsumov et al. (2017)
		SLE <sup>g</sup> : 1:20, 40 °C, 24 h Sc-CO <sub>2</sub> <sup>h</sup> : -, 45 °C, 180 min at 30 MPa	96 % E 10 % E	Antioxidant capacity (TEAC)/ <sup>g</sup> : Hydrocarbons (docosane, heptadecane, hexacosane, octacosane and tetracosane); <sup>h</sup> : alcohols (lupeol) and hydrocarbons (docosane, hexacosane, octacosane and tetracosane)	Casas et al. (Casas et al., 2021)
Valorization as flavor and perfume ingredients	Flowers, leaves and small branches	SLE-MD: -, 110 °C, 100 min at 2 · 10 <sup>-6</sup> bar	H, E	- /2-Phenethyl alcohol, (Z)-heptadec-8-ene, ethyl palmitate, heptadecane, lupenone, lupeol, methyl anisate, nonadecane and palmitic acid	Perriot et al. (2010)
Valorization as phenolic compounds resource	Bark	SE: -, RT, 8 h	D	- / $\Delta^7$ -steryl glucosides (dihydrospinastryl glucoside and spinastryl glucoside), alcohols, caffeic acid esters (hexacosanyl caffeate), cinnamic acid esters ( <i>n</i> -alkyl caffeates -hexadecanyl-, <i>n</i> -alkyl coumarates - hexacosanyl coumarate- and <i>n</i> -alkyl ferulates -octacosanyl ferulate-), fatty acids, free sterols, monoglycerides, steryl esters and steryl glucosides	Freire et al. (2007)
	Flowers	-	95 % E	- /Chalcone glucoside (4,2',4',6'-tetrahydroxy-3-methoxychalcone 2'-[O-rhamnosyl-(1→4)-side])	Imperato (1982a)
		-	95 % E	- /Chalcone glucoside (4,2',4',6'-tetrahydroxy-3-methoxychalcone 2'-O- $\beta$ -D-glucoside) and cernuoside (4, 6,3',4'-tetrahydroxyaurone 4-O- $\beta$ -D-glucoside)	Imperato (1982b)
	Bark	SE: -, RT, 24 h	D, E, W	- /Phenolics (resorcinol) and polysaccharides (glucose)	Neiva et al. (2020a,b)

The flowers are **glomerulus globulus** in inflorescences. -: Data not specified; A: Acetone; AW: Acidified water (1.2 M HCl); B: *n*-Butanol; C: Chloroform; CAT: Catalase enzyme activity; COX-2: Cyclooxygenase-2; CTC: Condensed tannins content; CuZnSOD: Copper-zinc superoxide dismutase enzyme activity; D: Dichloromethane; DPPH: 2,2-diphenyl-1-picrylhydrazyl free radical scavenging assay; E: Ethanol; EA: Ethyl acetate; FRAP: Ferric reducing antioxidant power; GPx: Glutathione peroxidase enzyme activity; H: *n*-Hexane; HEPES-KOH-EDTA: N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid)-KOH solution buffer (50 mM, pH 7.8) with ethylenediaminetetraacetic acid solution (0.1 mM); INOS: Inducible nitric oxide synthase; LPS: Lipopolysaccharide; M: Methanol; MAE: Microwave assisted extraction; MDA: Malondialdehyde; MHG: Microwave hydrodiffusion and gravity extraction; MnSOD: Manganese superoxide dismutase enzyme activity; P: *n*-Pentane; PE: Petroleum ether; POX: Peroxidase enzymatic activity; PS: Physiological saline solution (0.9 % w/v NaCl); RT: room temperature; Sc-CO<sub>2</sub>: Supercritical fluid extraction with carbon dioxide; SD: Steam distillation; SE: Soxhlet extraction; SLE: Solid-liquid extraction; SLE-LN: Solid-liquid extraction using Likens-Nickerson apparatus; SLE-MD: Solid-liquid extraction in combination with molecular distillation system; SOD: Dismutase peroxidase enzymatic activity; TCC: Total carotenoid content; TEAC: Trolox equivalent antioxidant capacity; TFC: Total flavonoid content; TNF- $\alpha$ :



◀ Tumor necrosis factor  $\alpha$ ; TPC: Total phenolic content; UE: Ultrasound extraction; W: Water. The superscripts listed in the second column correspond to the "Target Compounds" in the fifth column.

with antioxidant activity, measured as reducing power, radical scavenging and  $\beta$ -carotene bleaching inhibition (Yildiz et al., 2018).

Methanol and acetone extracts are potent *in vitro* antioxidants (Sowndhararajan et al., 2013). The later exhibited higher contents of phenolics and flavonoids and also higher antiradical activity, reducing capacity, metal chelation and peroxidation inhibition than methanol extracts and were also superior to butylated hydroxyanisole and  $\alpha$ -tocopherol (Sowndhararajan et al., 2013 and 2015). Moreover, the stem bark acetone extracts up-regulated the expression of antioxidant enzymes (superoxide dismutase, glutathione peroxidase and catalase) in hydrogen peroxide-induced human hepatoma cells (Sowndhararajan et al., 2015) and showed antiinflammatory properties, by decreasing the nitric oxide production by macrophages as well as the expression of inducible nitric oxide synthase, cyclooxygenase-2 and tumor necrosis factor- $\alpha$  (Sowndhararajan et al., 2016). They have identified caffeoyl glucose, procyanidin B1, ellagic acid, ellagic acid isomer and rosmanol in the extracts.

Both water and ethanol showed similar extraction yields, with more sugars on the water extracts and more phenolics on the ethanolic ones. Polar extracts were active against bacteria and yeast strains and non-polar ones were good against *Candida* sp. The bark methanolic extracts were potent antimicrobials, whereas hexane extracts only inhibited the growth of *Staphylococcus aureus* (Yildiz et al., 2018). *A. dealbata* tannins were incorporated in the formulation of disinfection or prevention agents acting against non-enveloped viruses (Tadashi et al., 2013). The tannins, flavonoids, lignans, stilbenes, terpenes and terpenoids present in *A. dealbata* bark extracts show anti-quorum sensing activity. Methanol extracts (5 %) from *A. dealbata* bark were more active those from sapwood and heartwood for protecting Scots pine wood against the decay resistance due to the brown rot fungus, *Coniophora puteana* (Yildiz et al., 2018).

### 3.2.2. Wood

The hardwood from *A. dealbata* has been proposed as a promising energy crop, with low requirements and high productivity and its pulping and papermaking potential is also well known. The kraft process performance of *A. dealbata* is comparable to that of *Eucalyptus globulus*, and is favored by the higher pulp yield and the lower residual lignin content after cooking. Due to the characteristics of the fibres, length, coarseness, width and flexibility the resulting *A. dealbata* paper is denser and exhibits higher tensile and burst strength, but lower tear resistance (Santos et al., 2006; Anjos et al., 2015).

**3.2.2.1. Fermentable sugars for the production of chemicals and bioethanol.** The high content of cellulose in *A. dealbata* suggest that this material could be a potential feedstock for bioethanol production. This aspect is showed in Table 2. A pretreatment step is required in order to enhance the cellulose accessibility. Ferreira et al. (2011) proposed an acid treatment (0.8 % sulfuric acid at 180 °C for 15 min), which recovered 62 % cellulose and after bioconversion with *Pichia stipitis* the ethanol yield was 0.36 and 0.37 g/g for both the water soluble fraction and for the residual solids after an enzymatic treatment with cellulase and cellobiase.

Green solvents show potential advantages and ionic liquid pretreatment enhanced the susceptibility to hydrolysis by increasing the accessibility of enzymes to cellulose, disrupting the structure, breaking lignin, causing swelling and reducing the cellulose crystallinity. Yáñez et al. (2014) pretreated *A. dealbata* wood with 1-ethyl-3-methylimidazolium acetate and the resulting solids were treated at 130 °C for 180 min or at 150 °C for 30 min, to attain cellulose and xy-

**Table 2**

Bioethanol production from *Acacia dealbata* wood.

Pretreatment (P) /Hydrolysis (H) Fermentation (Conditions and yield)	References
P: Air-drying, milling (< 8 mm screen) AH: up to 215 °C, LSR 8 g/g Alcaline washing: 4.5 % NaOH, 130 °C, 3 h EH: Commercial cellulase and $\beta$ -glucosidase, LSR 30 g/g, pH 4.85, 48.5 °C, 48 h, 20 FPU/g Fermentable sugars yield: 47.3 g glucose/100 g solids from AH	Yáñez et al. (2009b)
P: Debarking, chipping, milling, sieving (< 250 $\mu$ m), ionic liquid 1-ethyl-3-methylimidazolium acetate, 150 °C, 30 min EH: Commercial cellulase and $\beta$ -glucosidase, LSR 26 g/g, pH 4.85, 48.5 °C, 48 h, 20 FPU/g Fermentable sugars yield: 100 % glucose conversion	Yáñez et al. (2014)
P: Debarked, chipped, air-dried, sieved (1–250 mm) Autocatalytic glycerol-water media, 80 wt %, LSR 6 g/g, 230 °C, 1 h	Domínguez et al. (2014)
h Alkaline/ neutral washing: 1 % NaOH, 20 °C/ water, 60 °C/ water, 20 °C EH: Commercial cellulase and $\beta$ -glucosidase, LSR 26 g/g, pH 4.85, 48.5 °C, 48 h, 20 FPU/g Fermentable sugars: 85.4 g glucose/L	
P: <i>Ganoderma australis</i> , 27 °C, 30 days, 55 % MC Delignification: 60 % E, 200 °C, 1 h Cold alkaline washing: 1 % NaOH Saccharification: 100 % yield EH: Commercial cellulase and $\beta$ -glucosidase, LSR 30 g/g, pH 4.8, 50 °C, 72 h, 20 FPU/g SHF: <i>Saccharomyces cerevisiae</i> , 30 °C, 48 h, 45 g hydrolyzates, 62 % ethanol SSF: Commercial enzymes, <i>Saccharomyces cerevisiae</i> , 37 °C, 48 h, 30 g liquor/ g solid, 69 % ethanol	Muñoz et al. (2007)
P: Air-dried, milled (< 1 mm) Acid treatment: 0.8 % H <sub>2</sub> SO <sub>4</sub> , 180 °C, 15 min EH: Commercial cellulase and $\beta$ -glucosidase, 5 % (w/v) of dry biomass, pH 4.8, 50 °C, 72 h, 25 FPU/g SHF: <i>Saccharomyces cerevisiae</i> , 30 °C, 24 h, 10.31 g ethanol/L SSF: Commercial enzymes, <i>Saccharomyces cerevisiae</i> , 30 °C, 48 h, 7.53 g ethanol/L	Ferreira et al., 2007)

AH: Autohydrolysis; E: Ethanol; EH: Enzymatic hydrolysis; F: Fermentation; FPU: Filter paper units; H: Hydrolysis; LSR: Liquid to solid ratio; MC: Moisture content; P: Pretreatment; T: Temperature; t: Time; SHF: Separate enzymatic hydrolysis and fermentation; SSF: Simultaneous enzymatic saccharification and fermentation.

lan recoveries of almost 90 and 70 %, respectively. Further enzymatic hydrolysis led to high fermentable glucose yields with almost quantitative cellulose hydrolysis. The use of water as an antisolvent favored recycling and direct reusability of the ionic liquid in successive pretreatment cycles allowing lower pretreatment costs.

Domínguez et al. (2014) proposed the fractionation of *A. dealbata* wood with glycerol-water media at 230 °C for 1 h and further alkaline and neutral washing stages. The solid phase was extensively delignified (almost 80 %), preserving more than 90 % cellulose in the solid phase and enhancing the susceptibility to enzymatic hydrolysis. The chemical changes, the lowered xylan content and the structural modifications of the substrate improved the accessibility of enzymes to cellulose, but may also be responsible for the enhanced saccharification susceptibility.

In addition, the production of antimicrobial extracts has been considered from *A. dealbata* wood. The phenolic, flavonoid and condensed tannin contents of heartwood was ten times lower than in bark, in sapwood was even lower, and the reducing properties showing a similar trend. However, the methanolic extracts from the sapwood and heartwood are growth inhibitors of *S. aureus*, *Klebsiella pneumoniae* and *Listeria monocytogenes* (Yildiz et al., 2018).

### 3.2.3. Leaves

The shrub can be used as forage based on the composition, 40 % dry matter, with 4 % minerals, 15 % crude protein, 50 % neutral detergent fiber and 39 % acid detergent fiber and the metabolizable energy being 3.55 MJ/kg dry basis. In a study on the *in vitro* digestibility of shrubs using rumen fluid, *A. dealbata* produced the lowest volume of gas and methane, probably due to the highest phenols (36 g tannic acid eq/kg) and saponins (25 g diosgenin eq/kg) contents (Mebirouk-Boudechiche et al., 2015).

The most studied application of leaves is in relation to their specific composition and extractives content. Not only the type of extraction method had a significant effect on the bioactivity of the extracted compounds but can also influence the results of some test, i.e. on the germination and seedling growth. Lorenzo et al. (2016) observed that the compounds fractionated with hexane and ethyl acetate were more phytotoxic in dimethyl sulfoxide-buffer than in water bioassays whereas the opposite trend was found for compound from water fractions. The antioxidant properties of *A. dealbata* leaves can be attributed to the presence of phenolic compounds (chlorogenic acid, syringic acid, p-coumaric acid, ferulic acid, and ellagic acid), which are different for each *Acacia* species (Luís et al., 2012). Different solvents (water, methanol, ethanol, acetone, dichloromethane, and hexane) have been used for the extraction of bioactives from *A. dealbata* leaves. The highest total phenolic was attained with hydroalcoholic extracts (0.3 g GAE/g extract) and the total flavonoids and alkaloids were higher in acetone extracts. Quercetin was not found in acetone extracts and caffeic acid only in the hydroalcoholic extracts. Ethanol (Luís et al., 2012) and acetone provided the most active extracts regarding antioxidant and antimicrobial action against bacteria and yeasts (Borges et al., 2020). The adequate selection of the solvent and the application of intensification strategies (ultrasound, microwave) can enhance the process performance. Ultrasound extraction improved efficiency, reduced extraction time, and lowered solvent consumption. In a comparative study, ultrasound water extraction of leaves provided the highest yields but acetone extracts were the most active regarding antiradical properties against 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH•) and acetone, dichloromethane and ethanol against 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid (ABTS). Soxhlet and microwave assisted water extraction provided the most efficient extraction of antimicrobial compounds (Borges et al., 2020). Lipophilic extracts, accounting for only 6 % of the leaves, were higher than for other parts of the plant, were non cytotoxicity in liver, epidermis and dermis cell lines. Among the components in this fraction, saturated fatty acids accounted for 80 % of the total fatty acids, triacontan-1-ol was the major long-chain aliphatic alcohol, lupenone,  $\alpha$ -amyrin, squalene, 22,23-dihydrospinasterol, aromatic compounds, such as tyrosol, vanillic and p-coumaric acids and other compounds, such as glycerol and  $\alpha$ -tocopherol, have been reported (Oliveira et al., 2020).

One promising application of the bioactives from leaves could be their use as bioherbicides (Souza-Alonso et al., 2018). Their potential activity is in relation to the fact that invasive plants may compete with native flora by releasing compounds, which could be considered as a natural source of allelochemicals or phytotoxins for weed control. Although natural molecules have some limitations for this application, they are expected to be less toxic and more environmentally friendly than synthetic herbicides (Narwal, 2010; Lorenzo et al., 2016). Bioherbicide action of *A. dealbata* is well known. Both polar and non polar compounds from *A. dealbata* leaves, obtained after fractionation with solvents of increasing polarity (hexane, ethyl acetate, and water), inhibited the radicle length of *Lactuca sativa* (Lorenzo et al., 2016), decomposition of *A. dealbata* flowers alone or combined with leaves reduced the germination and radicle length of *L. sativa* (Carballeira and Reigosa, 1999; Souza-Alonso et al., 2014a; Reigosa and Carballeira, 2017), *Zea mays*, *Dicranum* sp., *Hedera hibernica*, *Leucobryum* sp. and *Dactylis glomerata* (Lorenzo et al., 2008), *Trifolium repens* and *Lolium*

*perenne* (Reigosa and Carballeira, 2017). The leaves exert the strongest allelopathic effect, followed by the flowers and at lower level by the pod litter (Aguilera et al., 2015a; Lorenzo et al., 2016), but the use of pods is not recommended because seeds can accidentally propagate invasion.

The need to develop new valorisation routes and new applications for the non-woody fractions has arisen considering their availability and the application of both leaf and branches could be an alternative (Freire et al., 2005). Yáñez et al. (2009a) proposed the use of *A. dealbata* trimming residues as bulking agents during co-composting with sewage sludge to improve the process, allowing adequate gas exchange and preventing excessive compaction of the substrate. The optimal conditions, leading to the highest temperature profile were attained with the acacia:sludge 1/2 (w/w) mixture. The compost prepared with acacia trimming:sewage sludge ratios (1:1) showed the greatest water-soluble carbohydrates and polyphenols content in soil, the lowest heavy metals contents and an increase of soil biochemical properties (Tejada et al., 2014).

### 3.2.4. Flowers

Mimosa absolute oil is prepared from flowers and twig ends and has woody, sweet, honey-like, floral, rich and exotic scent. It is non toxic or irritant and is used in the flavor and perfumery industry, conferring a natural note to the formulations (Perriot et al., 2010). Due to the low yield attained by steam-distillation, volatile nonpolar solvents are preferred, petroleum ether yields 0.7 % of concrete and hexane yields about 1 % of concrete, which after ethanol treatment produces up to 25 % of absolute oil (Perriot et al., 2010). Among the constituents, fatty acids, hydrocarbons, esters, aldehydes, diethyl acetals, alcohols, and ketones were identified in the volatile fraction. The most abundant being (2)-heptadec-8-ene, heptadecane, nonadecane, and palmitic acid. In the heavier fraction the major constituents were triterpenoids such as lupenone and lupeol (Pereira et al., 1996; Perriot et al., 2010).

Conventional solvent extraction has been usually applied. The presence of flavonoids has been reported in ethanolic extracts, naringenin, naringenin diglucoside, robinetin, rutin, quercetin, isoquercitrin and isomyricitrin (Imperato, 1982a; Movsumov et al., 2017), as well as anthochlor pigments, with phloroglucinol-type structures, which contribute to flower colors (Imperato, 1982b).

*A. dealbata* flower extracts can be used in perfumes, but the possibility of using such extracts or fractions as coloring or bioactive agents is yet to be explored. The ethanolic extracts, with more than 25 % phenolic content and 85 % of the ABTS radical scavenging potency of trolox, were proposed for cosmetic and pharmaceutical applications (Soto et al., 2018; Casas et al., 2020). Further fractionation of the 96 % ethanolic extracts with organic solvents (hexane, dichloromethane, ethyl acetate and n-butanol) led to extracts with protective action against neutrophils oxidative burst and moderately cytotoxic against colon carcinoma HCT-116 and lung adenocarcinoma A549 cells. The most active were the lipophilic fractions, whereas the antioxidant potency was higher for extracts with more phenolic content (Casas et al., 2020). Therefore, ethanolic extracts of *A. dealbata* flowers were incorporated in personal-care products and the sensory attributes confirmed their good acceptability by consumers (Soto et al., 2018). Moreover, the subsequent extraction of the residual solids in a sequence of ethanol, water, acid and microwave assisted extraction was proposed to obtain extracts useful as solvents in bioactive hydrogels, which were softer when the extracts contained more bioactive compounds (Casas et al., 2020).

Conventional solvent extraction may lead to thermal degradation, oxidative transformations of the target compounds and production of undesirable residues or solvent traces in the products. Alternative extraction techniques using greener solvents are progressively demanded based on safety and environmental issues. Microwave hydrodiffusion and gravity is a novel solvent free extraction technique consisting on



the irradiation of material and separation of the extract by gravity. The defrosted flowers provided very low extraction yields draining but the extracts obtained after 180 min at 75 W, recovered 0.15 mg phenolic/g dry flower, a 75 % of the value attained in distillation in more prolonged times, and the product showed 60 % of the trolox equivalent antioxidant capacity value of extracts obtained by distillation (López-Hortas et al., 2020). The remaining residual solids were obtained in dry form and the extractability of bioactives in a further solvent extraction stage with ethanol was markedly enhanced. The drained extracts were incorporated to an oil-in-water emulsion made with thermal spring waters and conferred similar protection against oxidation as butylated hydroxytoluene and  $\alpha$ -tocopherol. Alternatively, supercritical fluid extraction with CO<sub>2</sub> can be proposed to avoid the decomposition of labile compounds due to operation at low temperatures in the absence of light and oxygen. Casas et al. (2021) reported on the extraction of *A. dealbata* flowers at 30 MPa, 45 °C during 3 h using 10 % ethanol as modifier, to yield 15 % of the ethanol extractables and the product showed 20 % of the ABTS radical scavenging activity of trolox. The supercritical extract contained more compounds than conventional ethanolic extracts, and oxygenated triterpenes were the most abundant whereas aliphatic compounds were the main constituents in the product obtained by ethanol conventional extraction.

Bioherbicide utilization of flower bioactives has been reported. Lorenzo et al. (2019a) confirmed the potential phytotoxicity of non-volatile compounds found in *A. dealbata* flowers on the germination, seedling and plant growth of lettuce, wheat, and rigid ryegrass. Methyl cinnamate reduced enzyme activities in rigid ryegrass and lettuce and  $\alpha$ -amylase in rigid ryegrass. This compound also inhibited early stem and radicle growth of rigid ryegrass, but wheat plants, with larger seed size, were not affected.

### 3.2.5. Mixed aerial parts

Mixed aerial parts (wood, bark and leaves) have also been used for the production of antioxidant extracts (Luís et al., 2012). Hydroalcoholic (ethanol, methanol) provided higher values than acetone regarding phenolic concentration and antioxidant properties, measured as DPPH• radical scavenging and as inhibition of  $\beta$ -carotene and linoleic acid oxidation. The total amount of phenolic compounds reached 30 % of the extract and contained hydroxycinnamic acids (caffeic, chlorogenic, p-coumaric and ferulic) and gallic acid. Acetone and methanol favored the extraction of alkaloids.

Acacia residues have been proposed for weed control and crop protection. The incorporation of green manures with phytotoxic properties is being increasingly proposed to reduce the use of synthetic herbicides in agriculture. Souza-Alonso et al. (2020) reported the herbicide potential of *Acacia* sp residues for dicots at sites with low-weed density in the seed bank. Due to the absence of phytotoxic effects on maize and the minor modification in the physiological profile of the soil bacterial community, these residues could be proposed to complement other practices and to reduce the reliance on synthetic herbicides in maize-based cropping systems.

Allelopathic effects of soil and root extracts from *A. dealbata* were more potent than extracts from flowers (Souza-Alonso et al., 2019), dichloromethane and acetone fractions affected germination and radicle length of *L. sativa*, *D. glomerata* and *Cytisus scoparius*, and non polar fractions (from a sequential extraction process) affected the H<sub>2</sub>O<sub>2</sub> levels, protein and malondialdehyde content but not the enzymatic activities from the oxidative metabolism.

## 3.3. Biorefinery approaches

### 3.3.1. Pulp and bioactives

The polysaccharide content of this material has drawn attention as source of sugars for biobased products, but an exploitation route for lignin would contribute to the valorization of the streams generated in

biorefining processes. Pinto et al. (2015) optimized the kraft process to produce pulps from wood, reaching 46.5 % pulp yield and kappa number 14 at 160 °C and 210 min, with active alkali. The lignin in the waste stream or black liquor, which mainly contained inorganics, lignin and a small fraction of polysaccharides, was achieved by acid precipitation, centrifugation and washings, with a yield of 24 %. Despite the main fraction of inorganics could be eliminated, a part of carbohydrates was co-precipitated with lignins, particularly xylose. The lignin isolated from black liquors by acidification contained lower proportion of condensed structures, an advantage if the production of low molecular weight phenolics (vanillin and syringaldehyde) by oxidation. In a comparative study with other energy crops mimosa lignin presented low yield and the contamination of isolated lignin are weaknesses of this species.

### 3.3.2. Pulp and ethanol production

Muñoz et al. (2007) proposed an alternative pulping stage, consisting on pretreating wood with *Ganoderma australe* for 30 days at 27 °C and 55 % relative humidity, followed by an organosolv delignification steps with 60 % ethanol at 200 °C for 1 h. This treatment caused low cellulose losses, almost 10 % lignin removal, favored the further organosolv delignification, which yielded 51 % of a pulp with up to 95 % glucan and only 2 % lignin, and also facilitated the enzymatic process. These authors proposed the production of ethanol both in a separate enzymatic hydrolysis and fermentation or in a simultaneous enzymatic saccharification and fermentation, this later yielded a maximum ethanol conversion of 65 % referred to the initial wood.

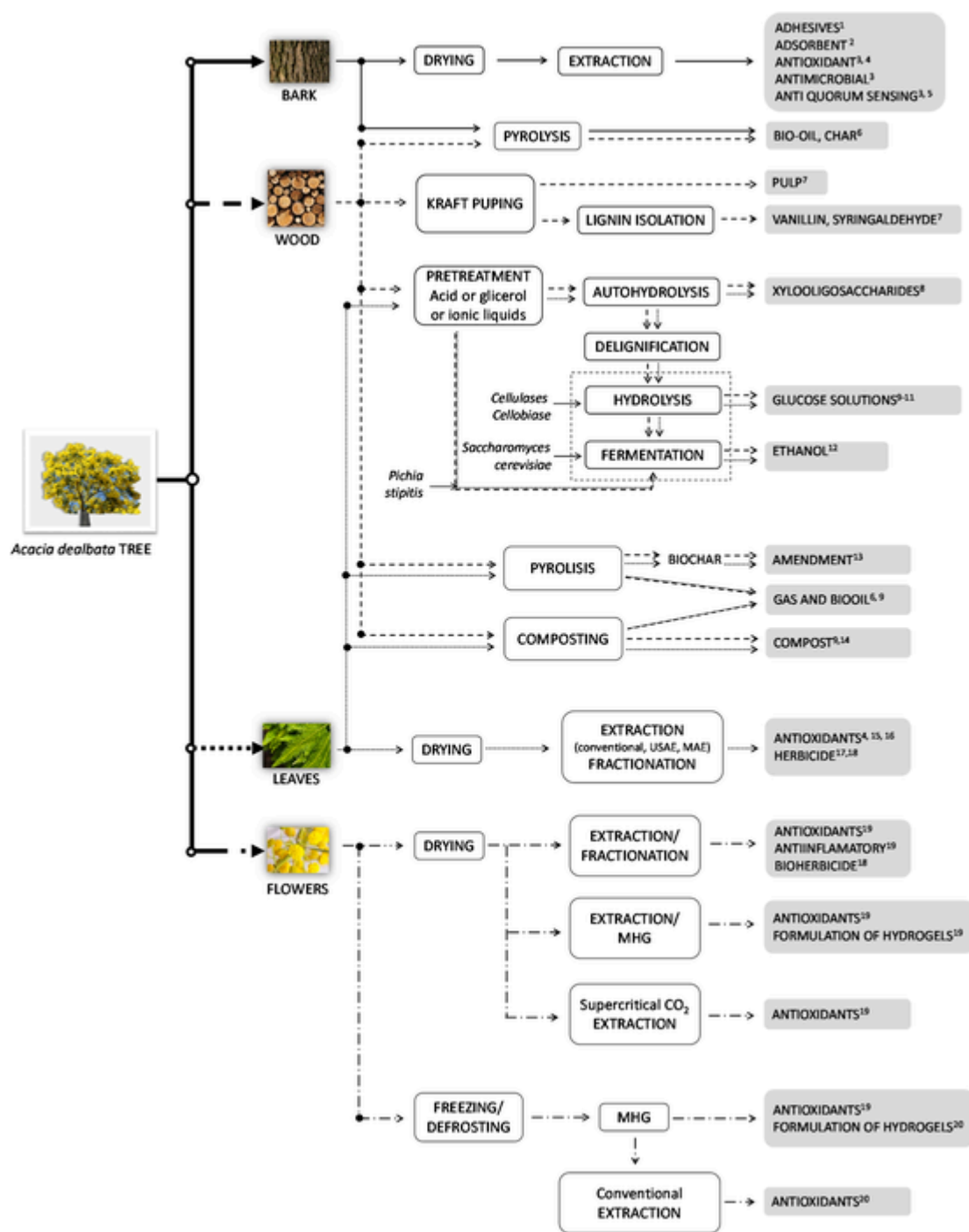
### 3.3.3. Xylooligosaccharides and fermentation media for ethanol production

Aqueous processing with pressurized hot water or autohydrolysis has been proposed as the first stage for the fractionation of this material. The liquid phase generated in the hydrolytic process contains saccharides, both mono- and oligosaccharides, suitable as a carbon source for bioconversion processes and suitable as prebiotic ingredients, respectively. Other minor compounds, such as sugar-degradation compounds, acetic acid and phenolic compounds should be selectively removed. This scheme has been successful for other lignocellulosics for the valorization of oligosaccharides and phenolics (Garrote et al., 2008), which could be further refined (Vegas et al., 2006; Conde et al., 2008).

Yáñez et al. (2009c) proposed autohydrolysis as a first biorefinery stage for *A. dealbata* wood operating under non isothermal heating up to 215 °C. Under these conditions, up to 70 % conversion of xylan into xylooligosaccharides was achieved and both cellulose and lignin remained almost unaltered in solid phase. The spent solids from treatments, containing 65 % cellulose, 8 % hemicelluloses, and 27 % lignin, can be further delignified and hydrolyzed with cellulolytic enzymes for the production of sugar solutions used as carbon source for the bioconversion to ethanol. The treatment of the solid phase remaining after autohydrolysis has been proposed using 4.5 % sodium hydroxide at 130 °C during 3 h to enhance cellulose susceptibility towards enzymatic hydrolysis, yielding 47 g glucose/100 g autohydrolysis solids in 48 h (Yáñez et al., 2009c).

### 3.3.4. Total utilization in a biorefinery scheme

A compilation of the literature information of the previous sections is summarized in Fig. 2, showing a wide variety of possibilities for the integral valorization of *A. dealbata* biomass. Multistage and multiproduct processes are preferred with the aim of using all fractions and to provide several commercially interesting final products, following the scheme of biorefineries. Decisions on the raw materials and final products could be taken based on the availability and demands, respectively.



**Fig. 2.** Proposed biorefinery scheme based on reported studies of individual valorization of the different parts of *Acacia dealbata*. References: <sup>1</sup>: Berlin (2011a); <sup>2</sup>: Okoli et al. (2018); <sup>3</sup>: Yildiz et al. (2018); <sup>4</sup>: Oliveira et al. (2020); <sup>5</sup>: Neiva et al. (2020a); <sup>6</sup>: Amutio et al. (2013); <sup>7</sup>: Pinto et al. (2015); <sup>8</sup>: Yáñez et al (2009a); <sup>9</sup>: Yáñez et al. (2009b); <sup>10</sup>: Yáñez et al. (2014); <sup>11</sup>: Domínguez et al. (2014); <sup>12</sup>: Ferreira et al. (2011); <sup>13</sup>: Forján et al. (2016); <sup>14</sup>: Tejada et al. (2014); <sup>15</sup>: Lufs et al. (2012); <sup>16</sup>: Borges et al. (2020); <sup>17</sup>: Souza-Alonso et al. (2019); <sup>18</sup>: Lorenzo et al. (2019a); <sup>19</sup>: Casas et al. (2020); <sup>20</sup>: López-Hortas et al. (2020).

#### 4. Conclusions and perspectives

*Acacia dealbata* Link is an invasive species that requires control measures to avoid undesirable effects on the invaded ecosystems. Due to the costly and underoptimal efficiency of the available strategies, the search for potential uses for this low cost resource is attracting increasing research interest. From the data of different processing schemes for the extraction or for the production of commercially valuable compounds described in literature, a flexible multistage multiprod-

uct process could be defined according to the demands and economic considerations. In the design of such process, the utilization of greener solvents, especially water and ethanol, and efficient extraction processes, based on intensification with high pressure, ultrasounds or microwave is encouraged. Additional studies characterizing the products obtained are required if their food, cosmetic or pharmaceutical use is proposed, including the identification of the chemical constituents, the presence of undesirable compounds, such as contaminants or pesticide residues and their activity and stability. In order to fulfill the re-

quirements of sustainability and zero waste processes a biorefinery approach should be considered for each of the plant parts.

## Uncited reference

Ferreira et al. (2007).

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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