Tools for a multiproduct biorefinery of Acacia dealbata biomass

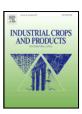
Article in Industrial Crops and Products · October 2021 DOI: 10.1016/j.indcrop.2021.113655 CITATIONS READS 146 13 6 authors, including: Ismael Rodriguez Gonzalez Lucía López-Hortas University of Vigo University of Vigo 15 PUBLICATIONS 227 CITATIONS 3 PUBLICATIONS 16 CITATIONS SEE PROFILE SEE PROFILE Beatriz Díaz Reinoso M. D. Torres University of Vigo University of Vigo 39 PUBLICATIONS 1,025 CITATIONS 125 PUBLICATIONS 3,019 CITATIONS SEE PROFILE SEE PROFILE

\$ \$\frac{1}{2} \rightarrow \frac{1}{2} \rightarrow \fr

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Tools for a multiproduct biorefinery of Acacia dealbata biomass

L. López-Hortas ^{a, *}, I. Rodríguez-González ^{a, b}, B. Díaz-Reinoso ^b, M.D. Torres ^a, A. Moure ^a, H. Domínguez ^a

^a CINBIO, Department of Chemical Engineering, Universidade de Vigo (Campus Ourense), Edificio Politécnico, As Lagoas, 32004 Ourense, Spain ^b CITI-University of Vigo, Parque Tecnolóxico de Galicia, Rúa Galicia nº 2, 32900 Ourense, Spain

ARTICLE INFO

Keywords:
Acacia dealbata
Bioactives
Biorefinery
Chemicals
Energy
Low cost biomass

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 chilling, eradicating and preventing the propagation of A. dealbata andatory (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 invasors, 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

E-mail address: luclopez@uvigo.es (L. López-Hortas).

Corresponding author.

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 ligning 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 β-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, dihydrospinasterol and stigmasterol and showed a high diversity of long-chain aliphatic alcohols, the most abundant being hexa cosan-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 palpimate 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 lipophylic extracts (Oliveira et al., 2020). Hydroxypipecolic and pipecolic 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-

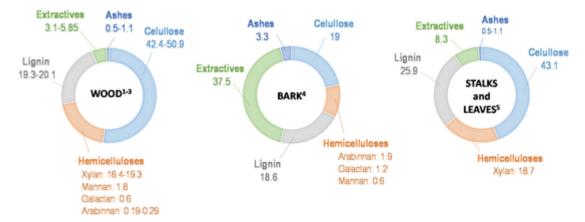


Fig. 1. Proximal composition reported for different parts of *Acacia dealbata* (wt % dry basis). References: ¹: Yáñez et al. (2009a); ²: Yáñez et al. (2009b); ³: Muñoz et al. (2007); ⁴: Neiva et al. (2020b); ⁵: Ferreira et al. (2001).

propanoids. Souza-Alonso et al. (2014a) have reported 27 compounds in the volatile fraction from flowers, hepta decadiene, n-nonadecane, n-tricosane, and octa decene, 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 scenary, 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 Pb²⁺ 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). Resorcinolictype 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 Acacia dealbata | Extraction (type: solid:liquid ratio, T, t) | lvent | 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 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 ^a , leaves and small branches ^b and litter ^c | 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/ a: Heptadecadiene, octadecene, n-nonadecane and n-tricosane; b: phytol; c: aromadendrene, globulol, heptadecadiene and n-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-hydroxylated benzoic 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-hydroxypipecolic acid, pipecolic 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- α gene expression/Phenolic profile (ellagic acid and isomer, procyanidin B1, rosmanol and saffeoyl 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 | | 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 | 99 % M, W 3-5% M | Antifungal activity, antioxidant capacity (FRAP), antimicrobial and antiquorum 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 Acacia dealbata | Extraction (type: solid:liquid ratio, T, t) | Solvent | Bioactive properties/target compounds | Reference |
|--|---|---|--|---|--|
| | Leaves, leaf litter, flowers litter, pods litter and seeds Leaf ^d , flowers ^e and pods ^f litter | 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/ d : Maculosin, moretenone and resorcinol; c : anisal, p -anisyl alcohol, methyl p -anisate and stigmasterol; f : d - a -tocopherol, quinone, lupanin and stigmasterol | Aguilera et al. (2015b) |
| | 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 | 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 palpimate and lupeol) | Pereira et al. (1996) |
| | Wood, bark and leaves | SE: 1:10, -, - SE: 1:10, -, 45 min | E, M, A 50 % E | • • | Luís et al. (2012) |
| | Flowers | SLE: -, -, 24 h | 80 % E, C, EA, W, EA:H (1:1, v/v) | - /Flavonoids compounds (isomyricitrin and isoquercitrin) | Movsumov et al. (2017) |
| | | SLE ^g : 1:20, 40 °C, 24 h Sc-CO ₂ ^h : -, 45 °C, 180 min at 30 MPa | | Antioxidant capacity (TEAC)/ [§] : Hydrocarbons (docosane, heptadecane, hexacosane, octacosane and tetracosane); ^h : 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: -, $110~^{\circ}\text{C}$, $100~\text{min}$ at $2\cdot 10^{-6}$ bar | Н, Е | - /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 (dihydrospinasteryl glucoside and spinasteryl glucoside), alcohols, caffeic acid esters (hexaconasyl caffeate), cinnamic acid esters (n -alkyl caffeates -hexadecanyl-, n -alkyl coumarates - hexacosanyl coumarate- and n -alkyl ferulates -octacosanyl ferulate-), fatty acids, free sterols, monoglycerides, steryl esters and steryl glucosides | Freire et al. (2007) |
| | Flowers | - | | - /Chalcone glucoside (4,2',4',6'-tetrahydroxy-3-methoxychalcone 2'-[O-rhamnosyl-(1 \rightarrow 4)-side]) - /Chalcone glucoside (4,2',4',6'-tetrahydroxy-3-methoxychalcone 2'-O- β -D-glucoside) and cernuoside (4, 6,3',4'-tetrahydroxyaurone 4-O- β -D- | Imperato (1982a) Imperato (1982b) |
| | Bark | SE: -, RT, 24 h | D, E, W | glucoside) - /Phenolics (resorcinol) and polysaccharides (glucose) | Neiva et al. (2020a,b) |

The flowers are glomerulus globul processences. -: 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: Dichlorometane; DPPH 2-diphenyl-1-picrylhydrazyl free radical scavenging assay; E: Ethanol; EA: Ethyl acetate; FRAP: Ferric reducing antioxidant power; GPx: Glutathione pertoxidase 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-CO₂: 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-α:

■ Tumor necrosis factor α; 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 β -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 α -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- α (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 nonpolar 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 2Bioethanol production from *Acacia dealbata* wood.

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

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(3ethylbenzthiazoline-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 cytotoxity 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, α-amyrin, squalene, 22,23dihydrospinasterol, aromatic compounds, such as tyrosol, vanillic and p-coumaric acids and other compounds, such as glycerol and α 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 lever by the pod litter (Aguilera et al., 2015a; Lorenzo et al., 2016), but the use of pods is not recommened 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

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 progressivelyl 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 α-tocopherol. Alternatively, supercritical fluid extraction with CO_2 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 α -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 β -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.

Allelopatic 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_2O_2 levels, protein and malondial dehyde 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 succesful 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.

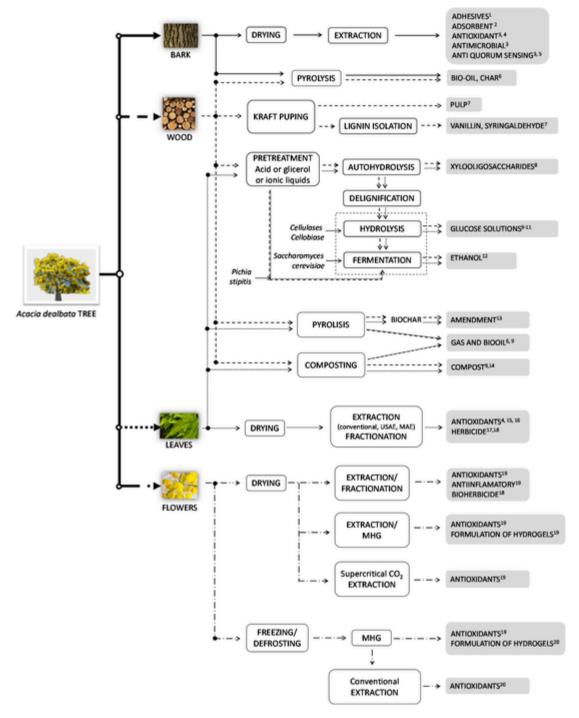


Fig. 2. Proposed biorefinery scheme based on reported studies of individual valorization of the different parts of *Acacia dealbata*. References: ¹: Berlin (2011a); ²: Okoli et al. (2018); ³: Yildiz et al. (2018); ⁴: Oliveira et al. (2020); ⁵: Neiva et al. (2020a); ⁶: Amutio et al. (2013); ¬: Pinto et al. (2015); ¬s. Yáñez et al. (2009a); ¬s. Yáñez et al. (2009b); ¹¹: Yáñez et al. (2014); ¹¹: Domínguez et al. (2014); ¹²: Ferreira et al. (2011); ¹³: Forján et al. (2016); ¹⁴: Tejada et al. (2014); ¹⁵: Luís et al. (2012); ¹⁵: Borges et al. (2020); ¹¹: Souza-Alonso et al. (2019); ¹³: Lorenzo et al. (2019a), ¹¹: Casas et al. (2020); ²¹: 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.

Acknowledgement

This research was funded by Spanish Ministry of Economy and Competitiveness, grant numbers BES-2016-076840 and RYC2018-024454-I and project CTM2015-68503-R.

References

- Abilleira, F., Varela, P., Cancela, Á., Álvarez, X., Sánchez, Á., Valero, E., 2021. Tannins extraction from *Pinus pinaster* and *Acacia dealbata* bark with applications in the industry. Ind. Crops Prod. 164, 113394. https://doi.org/10.1016/j.indcrop.2021.113394.
- Aguilera, N., Becerra, J., Guedes, L.M., Villas eñor-Parada, C., González, L., Hernández, V., 2015a. Allelopathic effect of the invasive *Acacia dealbata* Link (Fabaceae) on two native plant species in south-central Chile. Gayana Bot. 72, 231–239. https://doi.org/10.4067/S0717-66432015000200007.
- Aguilera, N., Becerra, J., Villaseñor-Parada, C., Lorenzo, P., González, L., Hernández, V., 2015b. Effects and identification of chemical compounds released from the invasive Acacia dealbata Link. Chem. Ecol. 31, 479–493. https://doi.org/10.1080/02757540.2015.1050004.
- Albaugh, T.J., Rubilar, R.A., Maier, C.A., Acuña, E.A., Cook, R.L., 2017. Biomass and nutrient mass of Acacia dealbata and Eucalyptus globulus bioenergy plantations. Biomass Bioenerg. 97, 162–171. https://doi.org/10.1016/j.biombioe.2016.12.025.
- Amutio, M., Lopez, G., Alvarez, J., Moreira, R., Duarte, G., Nunes, J., Olazar, M., Bilbao, J., 2013. Pyrolysis kinetics of forestry residues from the Portuguese Central Inland Region. Chem. Eng. Res. Des. 91, 2682–2690. https://doi.org/10.1016/j.cherd.2013.05.031.
- Anjos, O., García-Gonzalo, E., Santos, A.J.A., Simões, R., Martínez-Torres, J., Pereira, H., García-Nieto, P.J., 2015. Using apparent density of paper from hardwood kraft pulps to predict sheet properties, based on unsupervised classification and multivariable regression techniques. BioResources 10, 5920-5931. https://doi.org/10.15376/biores.10.3.5920-5931.
- Berlin, A. 2011a. Adhesive Composition Containing Modified Lignin. Patent CN102959033B.
- Berlin, A., 2011b. Carbon Fibre Compositions Comprising Lignin Derivatives. Patent US10533030B2.
- Berlin, A., 2016. Resin Compositions Comprising Lignin Derivatives. Patent US20160185810A.
- BOE, 2013. Real Decreto 630/2013, de 2 de agosto, por el que se regula el Catálogo español de especies exóticas invasoras. Boletín Oficial del Estado 185, 56764–56786. https://www.boe.es/buscar/act.php?id=BOE-A-2013-8565.
- Borges, A., José, H., Homem, V., Simões, M., 2020. Comparison of techniques and solvents on the antimicrobial and antioxidant potential of extracts from *Acacia dealbata* and *Olea europaea*. Antibiotics 9, 48. https://doi.org/10.3390/antibiotics9020048.
- Carballeira, A., Reigosa, M.J., 1999. Effects of natural leachates of *Acacia dealbata* Link in Galicia (NW Spain). Bot. Bull. Acad. Sin. 40 (1), 87–92. https://ejournal.sinica.edu.tw/bbas/content/1999/1/bot41-10.pdf.
- Carneiro, M., Moreira, R., Gominho, J., Fabião, A., 2014. Could control of invasive acacias be a source of biomass for energy under mediterranean conditions?. Chem. Eng. Trans. 37, 187–192. https://doi.org/10.3303/ CET1437032.
- Carneiro, M., Moreira, R., Gominho, J., Abreu, F., Fabião, A., 2016. Early growth of invasive acacias as a potential biomass-for-energy source under Mediterranean conditions. Int. J. Agric. Resour. Gov. Ecol. 12, 155–169. https://doi.org/10.1504/IJARGE.2016.076901.
- Casas, M.P., Conde, E., Ribeiro, D., Fernandes, E., Domínguez, H., Torres, M.D., 2020. Bioactive properties of *Acacia dealbata* flowers extracts. Waste Biomass Valorization 11, 2549–2557. https://doi.org/10.1007/s12649-019-00639-4.
- Casas, M.P., López-Hortas, L., Díaz-Reinoso, B., Moure, A., Domínguez, H., 2021. Supercritical CO₂ extracts from Acacia dealbata flowers. J. Supercrit. Fluids 173, 105223. https://doi.org/10.1016/j.supflu.2021.105223.
- Coetzee, B.W.T., van Rensburg, B.J., Robertson, M.P., 2007. Invasion of grasslands by silver wattle, Acacia dealbata (Mimosaceae), alters beetle (Coleoptera) assemblage structure. Afr. Entomol. 15, 328–339. https://doi.

- org/10.4001/1021-3589-15.2.328.
- Conde, E., Moure, A., Domínguez, H., Parajó, J.C., 2008. Fractionation of antioxidants from autohydrolysis of barley husks. J. Agric. Food Chem. 56, 10651–10659. https://doi.org/10.1021/jf801710a.
- Correia, M., Castro, S., Ferrero, V., Crisóstomo, J.A., Rodríguez-Echeverría, S., 2014. Reproductive biology and success of invasive Australian acacias in Portugal. Bot. J. Linn. Soc. 174, 574–588. https://doi.org/10.1111/boj.12155.
- Correia, R., Quintela, J.C., Duarte, M.P., Gonçalves, M., 2020. Insights for the valorization of biomass from portuguese ilnvasive *Acacia* spp. In a biorefinery perspective. Forest 11 (12), 1342. https://doi.org/10.3390/f11121342.
- De Neergaard, A., Saarnak, C., Hill, T., Khanyile, M., Berzosa, A.M., Birch-Thomsen, T., 2005. Australian wattle species in the Drakensberg region of South Africa an invasive alien or a natural resource?. Agric. Syst. 85 (3), 216–233. https://doi.org/10.1016/j.agsy.2005.06.009.
- Domínguez, E., Romaní, A., Alonso, J.L., Parajó, J.C., Yáñez, R., 2014. A biorefinery approach based on fractionation with a cheap industrial byproduct for getting value from an invasive woody species. Bioresour. Technol. 173, 301–308. https://doi.org/10.1016/j.biortech.2014.09.104.
- European Commission, 2014. Regulation (EU) No 1143/2014. of the European Parliament and of the Council of 22 October 2014 on the prevention and management of the introduction and spread of invasive alien species. Off. J. Europ. Un. 317, 35-55. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri = celex% 3A32014R1143.
- Fernandes, R.F., Honrado, J.P., Guisan, A., Roxo, A., Alves, P., Martins, J., Vicente, J.R., 2019. Species distribution models support the need of international cooperation towards successful management of plant invasions. J. Nat. Conserv. 49, 85–94. https://doi.org/10.1016/j.jnc.2019.04.001.
- Fernandes, M.R., Aguiar, F.C., Martins, M.J., Rico, N., Ferreira, M.T., Correia, A. C., 2020. Carbon stock estimations in a mediterranean riparian forest: a case study combining field data and UAV imagery. Forests 11, 376. https://doi.org/10.3390/F11040376.
- Ferreira, C., Mendonça, R., Baeza, J., Berlin, A., Saddler, J., Freer, J., 2007. Bioethanol production from bio-organosolv pulps of *Pinus radiata* and *Acacia dealbata*. J. Chem. Technol. Biotechnol. 82, 767–774. https://doi.org/10.1002/jctb.1737.
- Ferreira, S., Gil, N., Queiroz, J.A., Duarte, A.P., Domingues, F.C., 2011. An evaluation of the potential of *Acacia dealbata* as raw material for bioethanol production. Bioresour. Technol. 102, 4766–4773. https://doi.org/10.1016/j.biortech.2011.01.051.
- Ferreira, T., Paiva, J.M., Pinho, C., 2014. Performance assessment of invasive *Acacia dealbata* as a fuel for a domestic pellet boiler. Chem. Eng. Trans. 42, 73–78. https://doi.org/10.3303/CET1442013.
- Ferreira, T., Paiva, J.M., Pinho, C., 2020. Comparative analysis of fluidized and fixed beds to obtain data on the Char Pellet's combustion regime. Int. J. Energy Clean Environ. 21, 237–268. https://doi.org/10.1615/INTERJENERCLEANENV. 2020034608
- Forján, R., Asensio, V., Rodríguez-Vila, A., Covelo, E.F., 2016. Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing. Catena 137, 120–125. https://doi.org/10.1016/j.catena.2015.09.010.
- Fountain, D.W., Cornford, C.A., Shaw, G.J., 1995. Benzoic acid and hydroxylated benzoic acids in pollen. Grana 34, 213–216. https://doi.org/10.1080/ 00173139509429046.
- Frederick, D.J., Madgwick, H.A.I., Jurgensen, M.F., Oliver, G.R., 1986. Dry matter, energy, and nutrient contents of 8-year-old stands of *Eucalyptus regnans*, *Acacia dealbata*, and *Pinus radiata* in New Zealand. N. Z. J. For. Sci. 15 (2), 142–157. https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.723. 8026&rep=rep1&type=pdf.
- Freire, C. S. R., Coelho, D. S. C., Santos, N.M., Silvestre, A. J.D., Neto, C. P., 2005. Identification of Δ7 phytosterols and phytosteryl glucosides in the wood and bark of several *Acacia* species. Lipids 40, 317–322. https://doi.org/10.1007/s11745-005-1388-v.
- Freire, C. S. R., Silvestre, A. J. D., Neto, C. P., 2007. Demonstration of long-chainnal kyl caffeates and $\Delta 7$ -steryl glucosides in the bark of *Acacia* species by gas chromatography-mass spectrometry. Phytochem. Anal. 18, 151–156. https://doi.org/10.1002/pca.964.
- Fuentes-Ramírez, A., Pauchard, A., Marticorena, A., Sánchez, P., 2010. Relación entre la invasión de *Acacia dealbata* Link (Fabaceae: Mimosoideae) y la riqueza de especies vegetales en el centro-sur de Chile. Gayana Bot. 67, 188–197. https://doi.org/10.4067/S0717-66432010000200004.
- Garrote, G., Cruz, J.M., Domínguez, H., Parajó, J.C., 2008. Non-isothermal autohydrolysis of barley husks: product distribution and antioxidant activity of ethyl acetate soluble fractions. J. Food Eng. 84, 544–552. https://doi.org/ 10.1016/j.jfoodeng.2007.06.021.
- Gouws, A.J., Shackleton, C.M., 2019. A spatio-temporal, landscape perspective on *Acacia dealbata* invasions and broader land use and cover changes in the northern Eastern Cape, South Africa. Environ. Monit. Assess. 191, 1–20. https://doi.org/10.1007/s10661-019-7204-y.
- Griffin, A.R., Midgley, S.J., Bush, D., Cunningham, P.J., Rinaudo, A.T., 2011. Global uses of Australian acacias - Recent trends and future prospects. Divers. Distrib. 17, 837–847. https://doi.org/10.1111/j.1472-4642.2011.00814.x.
- Henderson, L., 2007. Invasive, naturalized and casual alien plants in southern Africa: A summary based on the Southern African plant invaders Atlas (SAPIA). Bothalia 37, 215–248. https://doi.org/10.4102/abc.v37i2.322.
- Hernández, L., Martínez-Fernández, J., Cañellas, I., de la Cueva, A.V., 2014. Assessing spatio-temporal rates, patterns and determinants of biological invasions in forest ecosystems. The case of *Acacia* species in NW Spain. For.

- Ecol. Manage. 329, 206-213. https://doi.org/10.1016/j.foreco.2014.05.058.
- Hirsch, H., Castillo, M.L., Impson, F.A.C., Kleinjan, C., Richardson, D.M., Le Roux, J.J., 2019. Ghosts from the past: even comprehensive sampling of the native range may not be enough to unravel the introduction history of invasive species - the case of Acacia dealbata invasions in South Africa. Am. J. Bot. 106, 352–362. https://doi.org/10.1002/ajb2.1244.
- Imperato, F., 1982a. A new chalcone glucoside and cernuoside from the flowers of Acacia dealbata. Experientia 38, 67–68. https://doi.org/10.1007/BF01944531.
- Imperato, F., 1982b. A chalcone glycoside from Acacia dealbata. Phytochemistry 21, 480-481. https://doi.org/10.1016/S0031-9422(00)95301-9.
- Johnson, W., 2005. Final report of the safety assessment of Acacia catechu gum, Acacia concinna fruit extract, Acacia dealbata leaf extract, Acacia dealbata leaf wax, Acacia decurrens extract, Acacia farnesiana extract, Acacia farnesiana flower wax, Acacia farnesiana gum, Acacia senegal extract, Acacia senegal gum, and Acacia senegal gum extract. Int. J. Toxicol. 24, 75–118. https://doi.org/10. 1080/10915810500257170.
- Khelalfa, K., Arhab, R., Martín-García, A.I., Zaabat, N., Belanche, A., 2020. Effect of Acacia purified tannins extract and polyethylene glycol treatment on in vitro ruminal fermentation pattern and methane production. Effect of Acacia tannins on fermentation and methane production. AsPac J. Mol. Biol. Biotechnol. 28 (2), 50-62. https://doi.org/10.35118/apjmbb.2020.028.2.06.
- Kunii, Y., Otsuka, M., Kashino, S., Takeuchi, H., Ohmori, S., 1996. 4-Hydroxypipecolic acid and pipecolic acid in *Acacia* species: their determination by high-performance liquid chromatography, its application to leguminous plants, and configuration of 4-hydroxypipecolic acid. J. Agric. Food Chem. 44, 483-487. https://doi.org/10.1021/jf950214d.
- Kuppers, B.I.L., 1996. Nitrogen and Rubisco contents in eucalypt canopies as affected by Acacia neighbourhood. Plant Physiol. Biochem. 34 (5), 753–760.
- Langdon, B., Pauchard, A., Bustamante, R.O., 2019. Acacia dealbata invasion in Chile: surprises from climatic niche and species distribution models. Ecol. Evol. 9, 7562–7573. https://doi.org/10.1002/ece3.5295.
- Lawson, F., Livia Y.T., Nakamoto S., Ono K., Tsunoda T., Uhlherr, P.H.T., Yazaki Y., 2010. Active Oxygen Scavenger. Patent JP2011051992A.
- Linhares, T., de Amorim, M.T.P., 2016. Cotton dyeing with extract from renewable agro industrial bio-resources: a step towards sustainability. In: Fangueir, R., Rana, S. (Eds.), Natural Fibres: Advances in Science and Technology Towards Industrial Applications. RILEM Bookseries. Kluwer Academic Publishers, pp. 441–453. https://doi.org/10.1007/978-94-017-7515-1_35.
- Linhares, T., de Amorim, M.T.P., 2017. LCA of textile dyeing with *Acacia dealbata* tree bark: a case study research. Procedia Eng. 200, 365–369. https://doi.org/10.1016/j.proeng.2017.07.051.
- Lisperguer, J., Saravia, Y., Vergara, E., 2016. Structure and thermal behavior of tannins from Acacia dealbata bark and their reactivity toward form aldehyde. J. Chil. Chem. Soc. 61 (4), 3188–3190. https://doi.org/10.4067/S0717-97072016000400007.
- López-Hortas, L., Falqué, E., Domínguez, H., Torres, M.D., 2020. Microwave hydrodiffusion and gravity versus conventional distillation for Acacia dealbata flowers. Recovery of bioactive extracts for cosmetic purposes. J. Clean. Prod. 274, 123143. https://doi.org/10.1016/j.jclepro.2020.123143.
- Lorenzo, P., Pazos-Malvido, E., González, L., Reigosa, M.J., 2008. Allelopathic interference of invasive Acacia dealbata: physiological effects. Allelopathy J. 22 (2), 452–461. https://doi.org/10.1007/s11258-010-9831-9.
- Lorenzo, P., González, L., Reigosa, M.J., 2010. The genus Acacia as invader: the characteristic case of Acacia dealbata link in Europe. Ann. For. Sci. 67, 101. https://doi.org/10.1051/forest/2009082.
- Lorenzo, P., Pereira, C.S., Rodríguez-Echeverría, S., 2013. Differential impact on soil microbes of allelopathic compounds released by the invasive *Acacia de albata* Link. Soil Biol. Biochem. 57, 156–163. https://doi.org/10.1016/j. soilbio.2012.08.018.
- Lorenzo, P., Reboredo-Durán, J., Múñoz, L., González, L., Freitas, H., Rodríguez-Echeverría, S., 2016. Inconsistency in the detection of phytotoxic effects: a test with *Acacia dealbata* extracts using two different methods. Phytochem. Lett. 15, 190–198. https://doi.org/10.1016/j.phytol.2015.11.001.
- Lorenzo, P., Reboredo-Durán, J., Muñoz, L., Freitas, H., González, L., 2019a. Herbicidal properties of the commercial formulation of methyl cinnamate, a natural compound in the invasive silver wattle (*Acacia dealbata*). Weed Sci. 68, 69–78. https://doi.org/10.1017/wsc.2019.68.
- Lorenzo, P., Souza-Alonso, P., Guisande-Collazo, A., Freitas, H., 2019b. Influence of Acacia dealbata Link bark extracts on the growth of Allium cepa L. plants under high salinity conditions. J. Sci. Food Agric. 99, 4072–4081. https://doi. org/10.1002/jsfa.9637.
- Luís, A., Gil, N., Amaral, M.E., Duarte, A.P., 2012. Antioxidant activities of extracts from Acacia melanoxylon, Acacia dealbata and Olea europaea and alkaloids estimation. Int. J. Pharm. Pharm. Sci. 4 (1), 225–231.
- Mebirouk-Boudechiche, L., Abidi, S., Cherif, M., Bouzouraa, I., 2015. In vitro digestibility and fermentation kinetics of five fodder shrubs leaves in northern of Algeria. Rev. Med. Vet. 166 (11–12), 350–359.
- Movsumov, I.S., Garaev, E.E., Herbette, G., Baghdikian, B., Ollivier, E., Elias, R., Suleimanov, T.A., Garaev, E.A., 2017. Flavonoids of *Acacia dealbata* and *Filipendula vulgaris* growing in Azerbaijan. Chem. Nat. Compd. 53, 754–755. https://doi.org/10.1007/s10600-017-2111-3.
- Muñoz, C., Mendonça, R., Baeza, J., Berlin, A., Saddler, J., Freer, J., 2007. Bioethanol production from bio-organosolv pulps of *Pinus radiata* and *Acacia dealbata*. J. Chem. Technol. Biotechnol. 82 (8), 767–774. https://doi.org/10.1002/jctb.1737.
- Narwal, S.S., 2010. Allelopathy in ecological sustainable organic agriculture. In:

- Reigosa, M.J., Pedrol, N., González, L. (Eds.), Allelopathy. A Physiological Process With Ecological Implications. pp. 537–564. https://doi.org/10.1007/1-4020-4280-9 24.
- Neiva, D.M., Luís, Â., Gominho, J., Domingues, F., Duarte, A.P., Pereira, H., 2020a. Bark residues valorization potential regarding antioxidant and antimicrobial extracts. Wood Sci. Technol. 54, 559–585. https://doi.org/10.1007/s00226-020-01168-3.
- Neiva, D.M., Rencoret, J., Marques, G., Gutiérrez, A., Gominho, J., Pereira, H., Río, J.C., 2020b. Lignin from tree barks: chemical structure and valorization. Chem. Sus. Chem. 13, 4537–4547. https://doi.org/10.1002/cssc.202000431.
- Nentwig, W., Bacher, S., Kumschick, S., Pyšek, P., Vilà, M., 2018. More than "100 worst" alien species in Europe. Biol. Invasions 20, 1611–1621. https://doi.org/10.1007/s10530-017-1651-6.
- Nunes, L.J.R., Raposo, M.A.M., Meireles, C.I.R., Pinto Gomes, C.J., Ribeiro, N.M. C.A., 2020. Control of invasive forest Species through the creation of a value chain: acacia dealbata biomass recovery. Environments 7, 39. https://doi.org/10.3390/environments7050039.
- Okoli, B., Shilowa, P., Anyanwu, G., Modise, J., 2018. Removal of Pb²⁺ from water by synthesized tannin resins from invasive South African trees. Water 10, 648. https://doi.org/10.3390/w10050648.
- Oliveira, C.S.D., Moreira, P., Resende, J., Cruz, M.T., Pereira, C.M.F., Silva, A.M. S., Santos, S.A.O., Silvestre, A.J.D., 2020. Characterization and cytotoxicity assessment of the lipophilic fractions of different morphological parts of *Acacia dealbata*. Int. J. Mol. Sci. 21, 1814. https://doi.org/10.3390/iims21051814.
- Parepa, M., Fischer, M., Bossdorf, O., 2013. Environmental variability promotes plant invasion. Nat. Commun. 4, 1604. https://doi.org/10.1038/ ncomms 2632.
- Pereira, F.B.M., Domingues, F.M.J., Silva, A.M.S., 1996. Triterpenes from Acacia dealbata. Nat. Prod. Lett. 8, 97–103. https://doi.org/10.1080/ 10575639608043247.
- Perriot, R., Breme, K., Meierhenrich, U.J., Carenini, E., Ferrando, G., Baldovini, N., 2010. Chemical composition of French mimosa absolute oil. J. Agric. Food Chem. 58, 1844–1849. https://doi.org/10.1021/jf903264n.
- Pinto, P.C. R., Oliveira, C., Costa, C.A., Gaspar, A., Faria, T., Ataíde, J., Rodrigues, A.E., 2015. Kraft delignification of energy crops in view of pulp production and lignin valorization. Ind. Crops Prod. 71, 153–162. https://doi. org/10.1016/j.indcrop.2015.03.069.
- Raposo, M.A.M., Pinto-Gomes, C.J., Nunes, L.J.R., 2020. Selective shrub management to preserve Mediterranean forests and reduce the risk of fire: the case of mainland Portugal. Fire 3 (4), 65. https://doi.org/10.3390/fire30.40065
- Reid, D.G., Bonnet, S.L., Kemp, G., Van Der Westhuizen, J.H., 2013. Analysis of commercial proanthocyanidins. Part 4: solid state 13C NMR as a tool for in situ analysis of proanthocyanidin tannins, in heartwood and bark of quebracho and acacia, and related species. Phytochemistry 94, 243–248. https://doi.org/10.1016/j.phytochem.2013.06.007.
- Reigosa, M. J., Carballeira Ocaña, A., 2017. Phytotoxicity in topsoils collected under Acacia dealbata Link in Galicia (NW Spain). J. Allelochem. Interact. 3, 15–21. http://j_allel_inter.webs.uvigo.es/images/issues/volume3-1/JAI_Volume3-1 article2.pdf.
- Richardson, D.M., Le Roux, J.J., Wilson, J.R.U., 2015. Australian acacias as invasive species: lessons to be learn from regions with long planting histories. South. For. 77, 31–39. https://doi.org/10.2989/20702620.2014.999305.
- Rodríguez, J., Lorenzo, P., González, L., 2017. Different growth strategies to invade undisturbed plant communities by Acacia dealbata Link. For. Ecol. Manage. 399, 47–53. https://doi.org/10.1016/j.foreco.2017.05.007.
- Santos, A.J.A., Anjos, O.M.S., Simões, R.M.S., 2006. Papermaking potential of Acacia dealbata and Acacia melanoxylon. Appita J. 59 (1), 58–64. https://ubibliorum.ubi.pt/bitstream/10400.6/643/1/APPITA1.pdf.
- Sheppard, A.W., Shaw, R.H., Sforza, R., 2006. Top 20 environmental weeds for classical biological control in Europe: a review of opportunities, regulations and other barriers to adoption. Weed Res. 46, 93–117. https://doi.org/10. 1111/j.1365-3180.2006.00497.x.
- Soto, M., Parada, M., Falqué, E., Domínguez, H., 2018. Personal-care products formulated with natural antioxidant extracts. Cosmetics 5, 13. https://doi. org/10.3390/cosmetics5010013.
- Souza-Alonso, P., Lorenzo, P., Rubido-Bará, M., González, L., 2013. Effectiveness of management strategies in *Acacia dealbata* link invasion, native vegetation and soil microbial community responses. For. Ecol. Manag. 304 (5), 464–472. https://doi.org/10.1016/j.foreco.2013.05.053.
- Souza-Alonso, P., González, L., Cavaleiro, C., 2014a. Ambient has become strained. Identification of *Acacia dealbata* link volatiles interfering with germination and early growth of native species. J. Chem. Ecol. 40, 1051–1061. https://doi.org/10.1007/s10886-014-0498-x.
- Souza-Alonso, P., Novoa, A., González, L., 2014b. Soil biochemical alterations and microbial community responses under *Acacia dealbata* Link invasion. Soil Biol. Biochem. 79, 100–108. https://doi.org/10.1016/j.soilbio.2014.09.008.
- Souza-Alonso, P., Guisande-Collazo, A., González, L., 2015. Gradualism in Acacia dealbata Link invasion: impact on soil chemistry and microbial community over a chronological sequence. Soil Biol. Biochem. 80, 315–323. https://doi.org/10.1016/j.soilbio.2014.10.022.
- Souza-Alonso, P., Rodríguez, J., González, L., Lorenzo, P., 2017. Here to stay. Recent advances and perspectives about *Acacia* invasion in Mediterranean areas. Ann. For. Sci. 74, 55. https://doi.org/10.1007/s13595-017-0651-0.
- Souza-Alonso, P., Puig, C.G., Pedrol, N., Freitas, H., Rodríguez-Echeverriá, S.,

- Lorenzo, P., 2018. Exploring the use of residues from the invasive *Acacia* sp. For weed control. Renew. Agric. Food Syst. 35 (1), 26–37. https://doi.org/10.1017/51742170518000170.
- Souza-Alonso, P., Puig, C.G., González, L., 2019. Plant responses to wide-range polarity extracts from invasive Acacia dealbata link. Allelopathy J. 47 (2), 267–282. https://doi.org/10.26651/allelo.j/2019-47-2-1237.
- Sowndhar ar aj an, K., Joseph, J.M., Manian, S., 2013. Antioxidant and free radical scavenging activities of Indian Acacias: Acacia leucophloea (Roxb.) Willd., Acacia ferruginea Dc., Acacia dealbata Link. and Acacia pennata (L.) Willd. Int. J. Food Prop. 16, 1717–1729. https://doi.org/10.1080/10942912.2011. 604895.
- Sowndhar ar aj an, K., Hong, S., Jhoo, J.W., Kim, S., Chin, N.L., 2015. Effect of acetone extract from stem bark of Acacia species (A. dealbata, A. ferruginea and A. leucophloea) on antioxidant enzymes status in hydrogen peroxide-induced HepG2 cells. Saudi J. Biol. Sci. 22, 685–691. https://doi.org/10.1016/j.sjbs. 2015.03.010.
- Sowndhararajan, K., Santhanam, R., Hong, S., Jhoo, J.W., Kim, S., 2016. Suppressive effects of acetone extract from the stem bark of three *Acacia* species on nitric oxide production in lipopolysa ccharide-stimulated RAW 264.7 macrophage cells. Asian Pac. J. Trop. Biomed. 6, 658–664. https://doi.org/10.1016/j.apjtb.2016.06.005.
- Tadashi S., Yasushi, O., Takemasa, S., Toru, T., Yoshiaki N., 2013. Method for disinfection or infection control against a non-enveloped virus. Patent US20130302453A1.
- Tejada, M., Gómez, I., Fernández-Boy, E., Díaz, M.J., 2014. Effects of sewage sludge and Acacia dealbata composts on soil biochemical and chemical properties. Commun. Soil Sci. Plant Anal. 45, 570–580. https://doi.org/10. 1080/00103624.2013.874017.
- Vegas, R., Luque, S., Alvarez, J.R., Alonso, J.L., Domínguez, H., Parajó, J.C., 2006. Membrane-assisted processing of xylooligosaccharide-containing liquors. J. Agric. Food Chem. 54, 5430–5436. https://doi.org/10.1021/

- if060525w.
- Vicente, J.R., Kueffer, C., Richardson, D.M., Vaz, A.S., Cabral, J.A., Hui, C., Araújo, M.B., Kühn, I., Kull, C.A., Verburg, P.H., Marchante, E., Honrado, J. P., 2019. Different environmental drivers of alien tree invasion affect different life-stages and operate at different spatial scales. For. Ecol. Manage. 433, 263–275. https://doi.org/10.1016/j.foreco.2018.10.065.
- Vieites-Blanco, C., González-Prieto, S.J., 2020. Invasiveness, ecological impacts and control of acacias in southwestern Europe a review. Web Ecol. 20 (2), 33–51. https://doi.org/10.5194/we-20-33-2020.
- Yáñez, R., Alonso, J.L., Díaz, M.J., 2009a. Influence of bulking agent on sewage sludge composting process. Bioresour. Technol. 100, 5827–5833. https://doi. org/10.1016/j.biortech.2009.05.073.
- Yáñez, R., Romaní, A., Garrote, G., Alonso, J.L., Parajó, J.C., 2009b. Experimental evaluation of alkaline treatment as a method for enhancing the enzymatic digestibility of autohydrolysed *Acacia dealbata*. J. Chem. Technol. Biotechnol. 84, 1070–1077. https://doi.org/10.1002/jctb.2136.
- Yáñez, R., Romaní, A., Garrote, G., Luis Alonso, J., Parajó, J.C., 2009c. Processing of Acacia dealbata in aqueous media: first step of a wood biorefinery. Ind. Eng. Chem. Res. 48, 6618–6626. https://doi.org/10.1021/ ice002333
- Yáñez, R., Gómez, B., Martínez, M., Gullón, B., Alonso, J.L., 2014. Valorization of an invasive woody species, Acacia dealbata by means of ionic liquid pretreatment and enzymatic hydrolysis. J. Chem. Technol. Biotechnol. 89, 1337–1343. https://doi.org/10.1002/jctb.4207.
- Yildiz, S., Gürgen, A., Can, Z., Tabbouche, S.A., Kiliç, A.O., 2018. Some bioactive properties of *Acacia dealbata* extracts and their potential utilization in wood protection. Drewno 61 (202), 81–97. https://doi.org/10.12841/wood.1644-3985.255.03.