Review

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A review of the use of giant reed (*Arundo donax* L.) in the biorefineries context

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Abstract: The massive availability of biomass generated by the common giant reed (*Arundo donax* L.) motivates the search for its possible industrial use for the generation of high added-value products through implementing a biorefinery approach. The literature demonstrates the potential of common cane to obtain different high-value compounds, such as levulinic acid, oligosaccharides, fermentable sugars, highly digestible fiber for animal feed, polyphenols, and natural fibers for composite materials, among others. The data shows the upward trend in Europe toward the generation of new green industries, grouped under the biorefinery concept. Therefore, this review summarizes the current knowledge on the use of *Arundo* to produce materials, fibers, and chemicals. Major environmental concerns related to this plant are also reviewed. Special attention has been paid to the potential use of *Arundo* to produce chemicals using green chemistry approaches, as a way to contribute to and advance the achievement of Sustainable Development Goals. Recommendations for future research are also outlined.

Keywords: *Arundo donax*; biomass; biorefinery; giant reed; green chemistry.

1 Introduction

Biorefineries are facilities aimed at transforming biomass into biobased products (Ministerio de Economía Industria y Competitividad 2017). A biorefinery integrates different processes, which can be chemical, physical, thermal, or biological, and allows the production of various high-value products. The variety of products is extensive, depending on the raw material used and the processes employed. These can range from energy products (biofuels such as biodiesel, bioethanol, or biogas) to fertilizers, animal feed, or bioplastics.

Certain plant species, such as *Arundo donax* L., also known as common cane, giant reed, or reed, have an impressive growth rate, are abundant around the globe during all year, and can be cultivated on marginal lands using low-quality waters (Licursi et al. 2018; Scordia and Cosentino 2019). These characteristics make these plants of high interest in the biorefineries sector, especially for producing ethanol and bioenergy products (Accardi et al. 2015; Jensen et al. 2018).

Reed has also gained attention in the production of some biomolecules, such as furfural or levulinic acid, among others (Antonetti et al. 2015; Di Fidio et al. 2020; Raspolli Galletti et al. 2013). Other uses of *Arundo* have been investigated, such as paper and pulp (Raposo Oliveira Garcez et al. 2022; Shatalov and Pereira 2006), biochar production (Ahmed 2016), or oil spill recovery (Fiore et al. 2019; Piperopoulos et al. 2021). Some other uses proposed for *Arundo* are found in the restoration of traditional architecture (Malheiro et al. 2021), also serving as insulation material (Barreca et al. 2019). Its cultivation is also a strategy for soil bioremediation (Alshaal et al. 2015; Fernando et al. 2016), with biomass's ulterior valorization for methane or biochar production.

The use of ground material or fibers from *Arundo* as filler or reinforcement in different matrices has also been studied in the literature, as these have similar properties to other widely studied vegetal fibers (Fiore et al. 2014b; Suárez et al. 2023). Most studies focus on particleboard production, using natural-derived binders or no binders (Andreu-Rodriguez et al. 2013; Barreca et al. 2019; Ferrández-García et al. 2012, 2019, 2020; Ferrández Villena et al. 2020; García-Ortuño et al. 2011). Other polymer composites studied consist of urea-formaldehyde, epoxy, or polyester (Dahmardeh

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Ghalehno et al. 2011), as well as polyethylene, polypropylene (Ortega et al. 2021; Suárez et al. 2021, 2022) or polylactic acid (Fiore et al. 2014a). Other authors also have proposed the production of composites for building applications, using concrete and plaster (Badagliacco et al. 2020; Manniello et al. 2022a,b; Martínez Gabarrón et al. 2014) or asphalt (Sargin Karahancer et al. 2016) as matrixes.

This paper aims to comprehensively review *Arundo*'s potential for its exploitation as biomass feedstock in a biorefinery context, including the potential benefits of its cultivation on the conservation and restoration of harmed riparian ecosystems. Special attention is paid to cascade processes to maximize the use of this lignocellulosic material.

Sustainable Development Goals (SDGs) are a set of 17 objectives, settled by the United Nations and adopted by most countries, to commit to the advancement of sustainable development, the reduction of inequalities, and the construction and consolidation of peaceful and fair societies. Some of these objectives relate to the sustainable production and consumption of goods, access to quality education, or the protection of earth and water ecosystems. There is a clear relationship between the bioeconomy, developed through the biorefineries, and SDGs, especially when it comes to the use (or reuse) of wastes or side-products form other processes. It is a clear way to make more efficient use of resources, reduce the amount of waste going to landfill, and produce valuable compounds under the principles of Green Chemistry (Leong et al. 2021; Solarte-Toro and Cardona Alzate 2021).

2 Methods

The literature review has assessed several papers related to *Arundo* and sustainable development. Although this paper focuses on evaluating the potential of this species for a biorefinery approach, different terms were used in the bibliographic search to have an idea of the potential applications of these plants in several contexts. The bibliographic search was performed in several databases (Scopus, Science Direct, Taylor & Francis, and Google Scholar), using the combination of the following keywords, plus the term "*Arundo*": *biorefinery, fiber, composite, ethanol, energy, invasive, environment, LCA (life cycle assessment), sustainable, renewable, value chain, green chemistry, fermentation, hydrolysis, valorization, polymer, profit, feed, soil, preservation, remediation*.

A remarkable number of papers have been published in the last decade (Figure 1); there has been an evident rise until 2019, with a decrease in the current year in the total number of published papers. Regarding the different topics, composites and invasive species are the least frequent. The trend in publications during this decade for the keywords used in the search is relatively stable.

From Scopus, the search performed using only "Arundo" led to 1475 publications, while 442 documents were downloaded using the list of keywords above. All papers were organized and compiled in the Mendeley software, classifying them by relevance for this paper and specific topic. To the authors' knowledge, only one review on *A. donax* L. and its potential in biorefinery has been found in the literature, dating back to 2014 (Corno et al. 2014).

From these 442 documents, considering the last 10 years and removing conference papers or sources not included in JCR, the list of documents decreased to 217. The next step was to analyze the authors' keywords from the retrieved articles, finding around 50 keywords repeated more than 5 times in the different works. These were reduced to 18 categories by grouping them by similarity; i.e., "toxic metals" includes "heavy metals" or "cadmium," "saccharification" includes "sugars," "oligosaccharides," "glucose," or "farming" also contains "crop" and "harvest"; the levels of appearance of these concepts are shown in Figure 2: (note that "*Arundo*," "*A. donax*," "reed," "giant reed," and "lignocellulosic biomass" were excluded from the list, as they appear in most documents).

Biorefinery, bioenergy, and chemical synthesis account for over a third of the total author keywords. In contrast, the remaining keywords appeared less frequently, with a slight prevalence of "composites" and "thermal processing". These five keywords appear in half of the studied papers, so this review focuses on these terms. The first section of this document focuses on plant characteristics, abundance, cultivation, invasive character, and environmental applications, such as soil remediation. The paper then reviews *Arundo*'s use for obtaining chemicals in a biorefinery context, including thermal and biobased processes for producing chemicals (sugars, levulinic, succinic acid, etc.), bioenergy, and biobased composites, thus covering most of the categories mentioned above.

The online tool Inciteful XYZ (Literature connector) has been used to refine the search and reduce the number of papers from the over 400 retrieved. This open-source tool produces graphs with connections among different papers related to a specific field. A chart showing the relationships between various studies on the use of *Arundo* in biorefineries is obtained (Figure 3). The tool also provides the most important papers in the field, refining the search by the number of citations and closeness to the papers used as seeds, which in this case were the ones listed in Figure 3a. The interconnections in Figure 3b were obtained by refining the search to show papers on *Arundo*. With all this, 50 papers were selected as the most relevant to the topic. The list of references contains more bibliography apart from these 50 studies, as Inciteful has only been applied to the use of *Arundo* and not its cultivation or environmental behavior.

3 Giant reed (*A. donax* L.)

A. donax L. is a perennial grass from the *Gramineae* family, with an uncertain origin due to its small size and the high number of chromosomes, although many authors place its origin in East Asia (Jensen et al. 2018). Giant reed produces flowers, although its seeds are not usually viable, at least out of Asia (Jiménez-Ruiz et al. 2021); this plant reproduces through the rhizome or by producing roots on the nodes

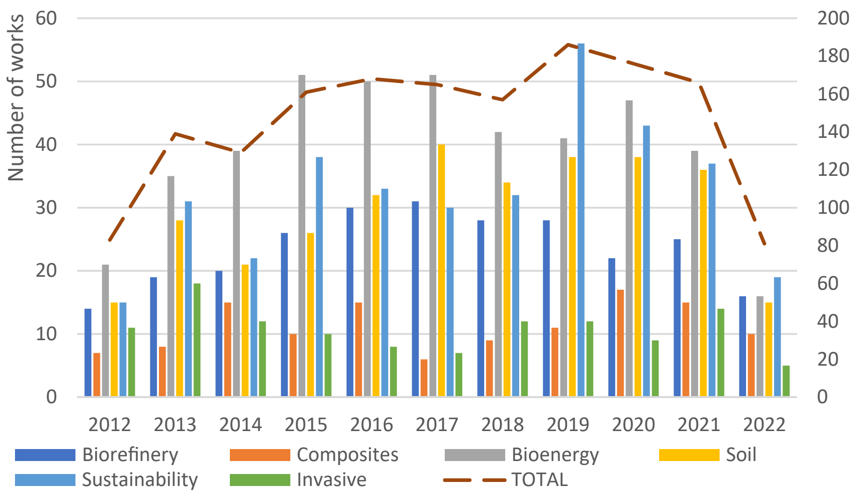

Figure 1: Evolution of publications in Scopus related to different keywords and *Arundo* in the last decade.

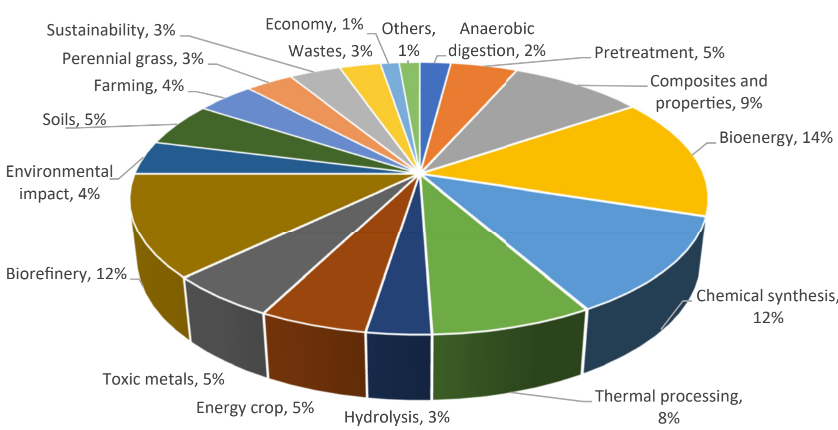

Figure 2: Frequencies of appearance of authors' keywords.

(Corno et al. 2014), which explains its rapid spread and poor genetic diversity (Pilu et al. 2014; Sicilia et al. 2020). When intended to be used as an energy crop, the clonal selection is needed to increase the characteristics of the plant, namely the number of culms and culm diameter and height (Amaducci and Perego 2015; Danelli et al. 2019, 2020; Fabbrini et al. 2019). Figure 4 shows two specimens of *Arundo* and the main parts of the plant: leaves, culm or stem, and rhizome.

Stems or culms are hollow and have diameters around 2–3 cm, reaching up to 6 m in height, with stem-clasping leaves along the entire stem (Csurhes 2016). Giant reed is generally recognized as an interesting source of biomass due to its high productivity and low requirements (Jensen et al. 2018), as it can be grown on almost any type of soil and with a minimal amount of water (Ahmed 2016), with high thermal and pathogens resistance (Accardi et al. 2015; Amaducci and Perego 2015; Lewandowski et al. 2003).

The rapid growth of this species and its quick adaption to a wide range of environmental conditions, even drought or high salinity (Romero-Munar et al. 2018a,b; Sánchez et al. 2015), which point them as a promising source of lignocellulosic feedstock, have contributed to its great spread and naturalization, especially in Mediterranean countries, where it has also become invasive (Lambertini 2019; Shtein et al. 2021). *Arundo* is considered one of the worst invasive plants in the world (Jiménez-Ruiz et al. 2021), and several actions take place periodically to try to control their spread in many parts of the world. Of particular concern is the distribution of *Arundo* in the Mediterranean or subtropical climate areas, such as Algeria, Morocco, Brazil, France, Portugal, Spain, Italy, and Australia, among others (Ministerio de Agricultura Alimentación y Medioambiente 2013). This is due to the rapid growth of this specie, of up to 10 cm per day (You et al. 2013), its pyrophyte nature, and its contribution to the spread of fires.

However, this species is not included in Europe's list of invasive alien species of Union concern (European Union 2017), but instead has been pointed out as a promising source of lignocellulose materials and has been included as an energy crop in the European Union (EU) (Eurostat 2020). For example, in 2013, Italy accounted for around 4000 ha of *Arundo* cultivation lands (Mantziaris et al. 2017), being the

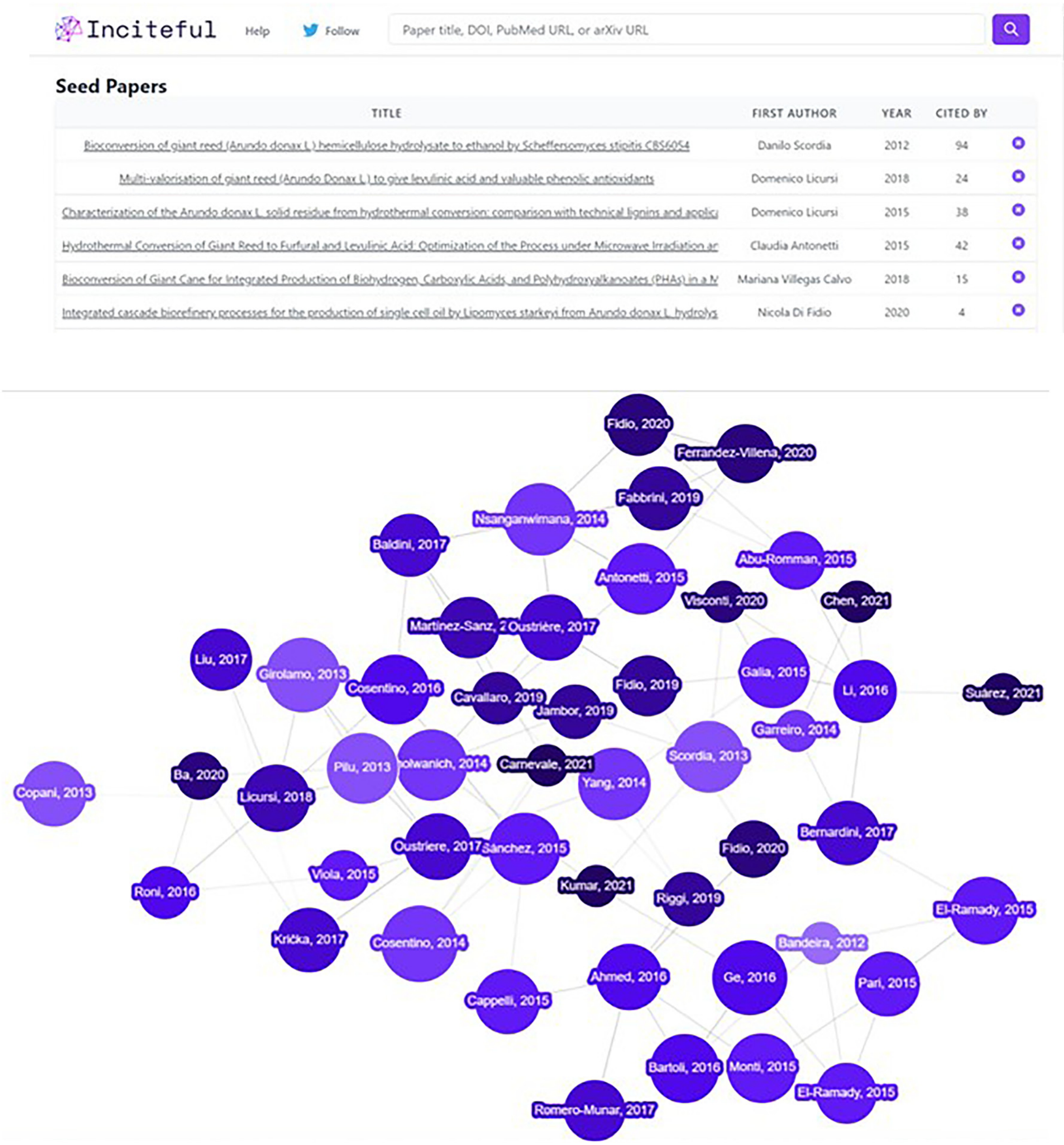

Figure 3: (a) Seed papers used at Inciteful XYZ and (b) graph showing the connections between the most important papers in the literature search.

most extensive area in Europe (no further data are published to date). Another example is found in Spain, where *Arundo* was considered an invasive plant in the 2013 catalogue (Ministerio de Agricultura Alimentación y Medioambiente 2013; Jiménez-Ruiz et al. 2021), being removed in a later revision of the document in 2019 (Ministerio para la Transición Ecológica 2019), after being included in a governmental document about biorefineries in Spain and interest crops (Ministerio de Economía Industria y Competitividad 2017), launched in 2017.

This change allows for the industrial use of *Arundo* in Spain, aligned with most countries worldwide. It then seems there is still a controversy between those authors considering *Arundo* as a resource to exploit and those concerned by the invasive character of the plant. In any case, most studies agree in stating that the invasive character of this plant should not be neglected, even if it is considered naturalized. It should not be forgotten that an uncontrolled spread can lead to biodiversity loss and increase fire events' periodicity and susceptibility (Jiménez-Ruiz et al. 2021). Issues associated with the end of the crop cycle should also be considered, as plants and rhizomes need to be removed (Corno et al. 2014). Corno et al. (2014) and Jiménez-Ruiz et al. (2021) suggest using

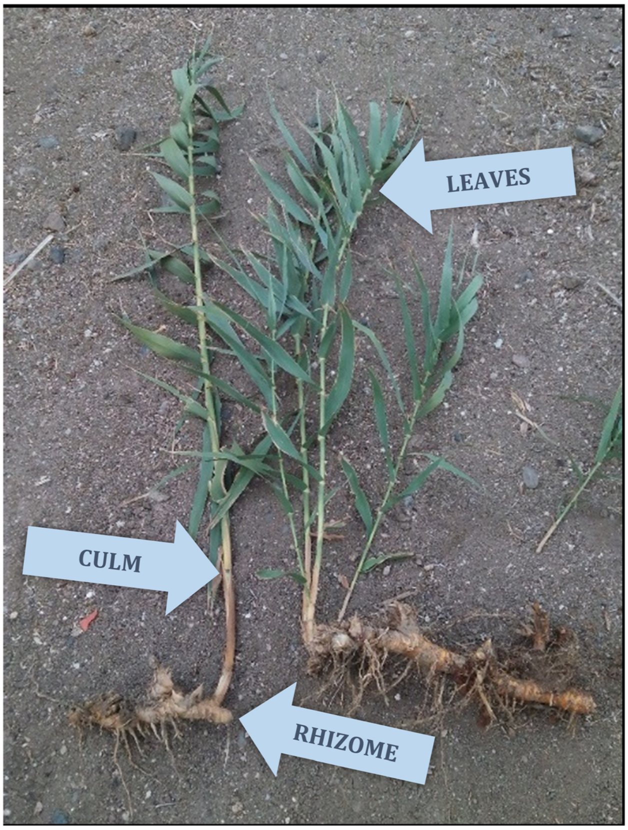

Figure 4: Different parts of *Arundo donax* L. plants.

glyphosate solution to damage new canes and inhibit the germination of new plants; this is apparently the most cost-effective solution for *Arundo* control.

Figure 5 summarizes the main environmental drawbacks and potential benefits of *Arundo* as raw material for industrial purposes, as discussed in Sections 3.1 and 3.2.

3.1 Cultivation

The cultivation of *Arundo* has been proven attractive as a lignocellulosic feedstock material (Amaducci and Perego 2015; Bonfante et al. 2017; D'Imporzano et al. 2018; Lewandowski et al. 2003). It is considered a promising crop for the biorefineries sector, with good environmental behavior (due to the low need for water and fertilizer) and resistance to salinity and polluted soils. It is generally recognized that this crop is highly water-demanding, although some authors point out that low-quality water can be used (Amaducci and Perego 2015). Other authors also state that other energy crops, such as *Miscanthus giganteus* or *Cynara cardunculus* provide lower yields in dry mass with higher water requirements, which also gives a positive point to *Arundo* (Fazio and Barbanti 2014; Ge et al. 2016; Monti et al. 2009; Singh et al. 2018). In this sense, Angelini et al. (2009) compared *Arundo* and *Miscanthus* over a 10-year period and found a higher yield in dry biomass for *Arundo* as well as a higher calorific value and energy yields. On the other hand, the work by Krička et al. (2017) reveals that, due to its higher lignin and ash content, *Arundo* has better performance than *Miscanthus* as solid fuel, while *Miscanthus* can also be used for obtaining liquid fuel. Other studies have also shown that *Arundo* is less affected by harvesting time or weather conditions compared to *Miscanthus* or switchgrass, which is a further advantage for reed cultivation (Alexopoulou et al. 2015; Monti et al. 2015; Nassi o Di Nasso et al. 2011).

Despite its invasive potential, several papers dealing with its cultivation and crop optimization can be found in the literature (Cosentino et al. 2006; Dragoni et al. 2015a). Some studies have assessed the storage of *Arundo* to avoid energy losses or material degradation prior to its use

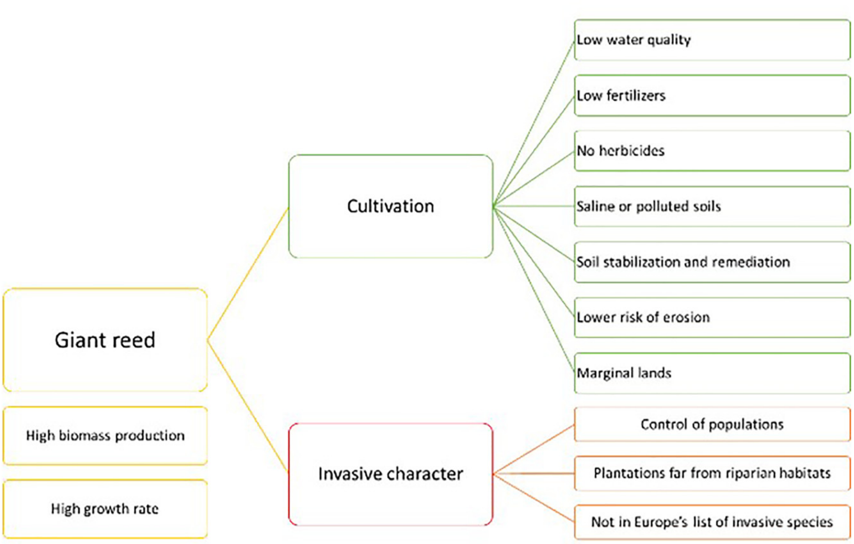

Figure 5: Potential environmental benefits and drawbacks of *Arundo donax* L. use in an industrial context.

(Pari et al. 2015, 2021). Besides, some authors consider its cultivation of interest in the Mediterranean basin and other arid regions with possible soil losses due to its growth potential in unfavorable conditions (Forte et al. 2015).

Regarding cultivation, the crucial step is the first year, the planting (Corno et al. 2014; Romero-Munar et al. 2018a,b). Corno et al. (2014) indicate that 5000 to 10,000 plants/ha, or 10,000–20,000 in warm climates, are required to obtain good production in years 1–2, and the overall duration of the plantation is around 15 years. Once the plants are settled, they usually don't require watering, fertilization, or herbicide treatment, as *Arundo* suppresses weeds (Curt et al. 2017; Gazoulis et al. 2021). However, using fertilizers generally results in higher biomass yields; especially when using nitrogen, better development of rhizomes and new sprouts are obtained, thus increasing the yields. Biomass yields are highly variable and dependent on climate, year of cultivation, and crop management and vary from 1.3 to 45.2 t/ha (Corno et al. 2014), with a more common yield of 30 t/ha (Corno et al. 2014; Dragoni et al. 2015b; Siri-Prieto et al. 2021). Some studies have also indicated that lower plantation densities could lead to higher biomass yields due to lower resource competition (Corno et al. 2014; Lewandowski et al. 2003). The studies performed by Christou in the framework of the EuroBioRef project (from the 7th EU framework) arrived at similar conclusions, that is, similar dry mass yields for *Arundo* cultivation versus *Miscanthus* (15–35 t/ha vs. 10–30, respectively), with similar needs of nitrogen fertilization, although reed cultivation was limited to the Mediterranean area (Christou 2011). The potential economic benefits for these cultivations were also assessed in such project, concluding that *Miscanthus* cultivation could produce around 250 €/ha, while *Arundo* could reach up to 400 €/ha, considering a plantation for 20-year period in both cases.

Although most studies on the crop optimization are performed in the Mediterranean basin, the Giant Reed Network project (FAIR-CT-96-2028) performed in the European Union (Bacher et al. 2001) studied the cultivation of giant reed in Germany, finding that it is possible to produce giant reed in cold climatic conditions, although at lower yields, with a maximum of 25 t/ha, which was, in any case, a similar yield to *Miscanthus* grown in similar conditions.

The excessive pressure on soils and the lack of regulation on their recovery and preservation have brought about huge areas of degraded or polluted soils, where cultivation of food or plant species sensitive to metals or high salinity levels is not possible. The lack of vegetation contributes to further erosion and soil loss, with negative consequences for the environment. In Europe, over 400,000 km^2 are in high risk of desertification and soil lose, especially in the Mediterranean basin (Ferreira et al. 2022). The cultivation of plant species, such as *Arundo*, might help reduce the effects of the unsustainable management practices performed decades ago. The soils restoring would reduce the negative impacts associated with such degradation, which lead to the loss of ecosystems service and affects biodiversity. Besides, the cultivation of such species, with high biomass rate production, would provide a second benefit: the stable availability of biomass useful as raw material for green chemical industries, which is one of the main factors affecting the biorefinery growth, without any displacement in food production.

3.2 Potential environmental benefits of *Arundo* cultivation

The invasive potential of this species and the controversy about its cultivation and use have already been mentioned. However, there are also some studies on the potential environmental benefits of giant reed cultivation, which goes beyond its use to produce bio-chemicals or bio-energy products. Several studies have shown the potential of energy crops for the remediation of polluted soils. For example, Bernal et al. (2021) reported soil phytostabilization as a result of cultivating *Arundo* and other perennial grass on soils with mining trace elements (Cd, Cu, Zn, As, etc.). Similarly, Garau et al. (2021) achieved soil stabilization and increased metals uptake with municipal solid waste compost. Zeng et al. (2022) also achieved high levels of Cu removal (over 75 %) in *Arundo* plantations, with higher efficiencies when alternated with other species cultivated together. Furthermore, Cristaldi et al. (2020) found a high bioaccumulation ratio of several metals in the giant reed, especially for Ad, Hg, and As, apart from Cu.

Besides soil remediation, reed can also be used to treat industrial wastes, such as red mud from alumina production (Zhang et al. 2021). According to Buss and collaborators, the biomass obtained from plants growing in polluted soils cannot be used as raw material for any application. They found that biochar produced in heavily polluted soils led to high concentrations of such metals, which exceed the permitted values (Buss et al. 2016). However, a good yield in methane production could still be obtained from such biomass (Bernal et al. 2021). Giant reed can also be used to set up wetlands for wastewater purification in isolated regions with good performance (Liu et al. 2019, 2021a; Otter et al. 2020). Other authors highlight the benefits of this plant for the soil, as organic carbon content in the soil is increased while total nitrogen is kept stable (Fagnano et al. 2015; Siri-

Prieto et al. 2021). These authors also emphasize the potential of *Arundo* to reduce soil erosion; Hong and Lee (2016) reached a similar conclusion regarding soil erosion in coastal environments.

Several authors have studied the sustainability of growing cane as a resource for the implementation of biorefineries, concluding that the fertilization stages are essential to the life cycle and the impact generated by this crop (Bosco et al. 2016; Fagnano et al. 2015; Forte et al. 2015). Some authors point out that the use of wild plants supports a better state of conservation of natural spaces due to the control of its excessive growth; this, together with the non-fertilization or irrigation of the plants, also results in better environmental performance. Most of the studies on the environmental performance of *Arundo* crops found in the literature do not provide, clear results. For example, Forte et al. (2015) concluded that the ecological load related to nitrogen fertilization and the harvesting operations provide the highest environmental impacts. Despite pointing out that further studies are required, the study seems to arrive at a positive environmental behavior of such crops, as also found by Zucaro et al. (2018), stating that giant reed crops can act as greenhouse gases sink.

Monti et al. (2009) performed a life cycle assessment (LCA) to compare the environmental and yield performance of reed cultivation versus rotation of maize-wheat, finding reductions over 50 % in environmental impact for reed, as also concluded by Dragoni et al. (2015b). However, Schmidt et al. (2015) indicate that giant reed cultivation should only occur in marginal lands, avoiding watering and fertilization and adapting the processing chain to the plant properties. Abreu et al. (2022) make the same recommendation and signal the potential benefits of *Arundo* and other perennial grasses cultivations on marginal lands, especially for biofuel production. These authors highlight the low research performed to date in transforming reed biomass into biofuels, anticipating a high rise in the interest of this plant for this purpose.

Furthermore, Solinas et al. (2019) have calculated that reed cultivation provides a 20 % reduction of the environmental impact caused by sorghum, as water and nitrogen inputs are the factors with the highest weights, and these could have been optimized. In this sense, sludge from wastewaters can be used as fertilizer, achieving similar yields to N-fertilized crops (Cano-Ruiz et al. 2021). Other authors proposed the irrigation of these crops with wastewaters; for example, Costa et al. (2016) have determined no changes in the dry mass production when using piggery wastewaters, while Shilpi et al. have obtained higher yields in dry biomass and methane production when the crop is irrigated with municipal or abattoir wastewaters (Shilpi et al. 2019). Besides, *Arundo* crops have been proposed to treat wastewaters (Zhang et al. 2021), reducing the risk of nitrate pollution, thus increasing the options to use cattle slurry as fertilizer (Ceotto et al. 2018).

Other authors propose using indigenous plants as an alternative to these invasive species. For example, *Arundo micrantha*, native to the Mediterranean region, has been compared in terms of yield to *A. donax*, leading to the obtaining of dry matter in high proportions, while also being able to grow on marginal lands with wastewater use (Tomàs et al. 2020).

All studies on LCA of giant reed crops agree on the lack of a tool measuring environmental impacts capable of considering the case and site-specific analysis and the difficulty in considering watering needs in that tool, and that further efforts are needed to get a more realistic and defined picture. In any case, *Arundo* has been considered to meet the sustainability criteria to produce biomass suitable for biofuels or other compounds production (Cappelli et al. 2015; Gazoulis et al. 2021). Furthermore, some studies highlight the potential of *Arundo* as an industrial crop in polluted soils as a strategy to increase the sustainability of the industry by increasing the amount of soil cultivated without any displacement in food production (Nsanganwimana et al. 2014).

Even if there is no absolute consensus on the use of *Arundo* as feedstock and its environmental benefits, most authors agree on the benefits of using this species, based on its rapid growth, good yields on dry matter, and low-quality water use, although measures should be taken to avoid its dispersion in the natural environment, especially in riparian habitats.

The availability of marginal and degraded soils, especially with high salinity in the Mediterranean area, and the ability of *Arundo* to grow in such conditions make it interesting to conduct long-term studies on the production of biomass and evolution of soils quality using no fertilizers and low-quality waters, as this is also a scarce resource in this area. The studies performed to date do not take place over a long period, enough to assess the associated changes that occur in the ground (organic matter, nitrogen content, permeability, etc.). Even if the production of biomass is not maximized by optimized cultivation conditions (watering and fertilization), the potential benefits on soil remediation and preservation with low inputs, together with the production of bioproducts of high-added value through a biorefinery scheme, would favorably tip the balance through the exploitation of such degraded soils, both at economic and environmental levels.

The LCA tools and the biorefineries are relatively recent, and there are not still appropriate methods to consider the huge number of factors involved in determining the environmental impact of such industries, especially when the raw material is not obtained from conventional agricultural processes. Even if the need of inorganic fertilizers, which pose adverse impacts, was demonstrated as necessary, the influence on the potential soil recovery would need to also be introduced in the analysis. Soils are still rather unknown and there is a lack of accurate systematic and comparable data about their environmental, societal, and economic implications, especially when they are degraded (Ferreira et al. 2022). Hence, there is still massive work to undertake before such data can be accurately introduced into environmental assessments to determine the potential effects of *Arundo* (or any other species) cultivation for biorefinery use.

4 Use of giant reed as raw material in biorefineries

Giant reed has been investigated for producing different bio-based products: chemicals, fibers for composite materials, polymers, or bioenergy products. This section is divided into three, discussing the application of *A. donax* L. in chemicals and bioenergy production. The first section gives an overview of the major components of giant reed. The production of chemicals such as bioethanol, levulinic, lactic, or succinic acid is covered in the second section, while the production of biogas and hydrogen as well as direct pyrolysis of the lignocellulosic material is discussed in the third section.

4.1 Composition of giant reed

Table 1 summarizes the composition of different parts of *Arundo* obtained from various references. Ash content is higher in the leaves than in the stems: 12 % versus about 3 %, respectively; the value for the entire plant is around 4 %, closer to the ash content in the culms, as most of the weight of the plant is due to the stem. As observed, the three major constituents of plant species (lignin, hemicellulose, and cellulose) are in similar proportions, with slightly higher values for hemicellulose (up to 42 %).

The chemical composition of this plant would allow a cascade approach for the solubilization and valorization of these three fractions. Other crops or residues widely studied in the biorefineries sector have similar compositional values to giant reed. For example, sugarcane bagasse has about 40 % cellulose, 24 % hemicellulose, and 24 % lignin (Chen et al. 2021; Jeon et al. 2010), wheat straw about 24 % cellulose and 25 % hemicellulose (Jeon et al. 2010), giant *miscanthus* about 35 % cellulose and 28 % hemicellulose (Baldini et al. 2017; Ge et al. 2011). These are widely studied raw materials for sugars or energy production, which shows the potential of *Arundo* to become raw materials for such products.

The higher lignin content of reed compared to other materials such as maize or *Miscanthus* might imply a higher recalcitrance of the material, and so that pre-treatment is probably needed to allow its further processing. However, as discussed later, these are performed in order to obtain a more selective fractioning of its components. The relatively mild conditions used for *Arundo* hydrolysis are indicative of the low recalcitrance of this biomass, which eases its processing. Such pre-treatments have been explored in literature and allow the release of sugars, mainly xylans, coming from the degradation of hemicellulose, but also the production of phenolic compounds with antioxidant activity, as discussed later in this paper.

On the other hand, the rhizome has the lowest content of structural carbohydrates due to its high concentration of free sugars and starch, around 30 % (Proietti et al. 2017). The variation in lignin has been attributed to the age of the plant, with more mature plants having a higher lignin content (Neto et al. 1997); Klason lignin contents reported for stems vary from 18 to 26 %, with lower values (10–15 %) for leaves. In any case, it is worth noting that the characterization method used can influence the results obtained and may lead to the over-quantification of some components. The use of wild or cultivated biomass, the climate, or the soil conditions, do not seem to provide any significant trend regarding the composition. As observed in Table 1, the plant composition data reported by the different papers are not always fully comparable, although the values provided might indicate that the vegetal material is quite stable, in terms of composition, which poses an indubitable advantage for its exploitation, as the processes followed wouldn't need to be adapted for different origins or growth conditions on the plant, or season of harvesting.

4.2 Giant reed for chemical synthesis

Levulinic acid, succinic acid, furfural, or xylitol are essential precursors in chemical synthesis and are considered some of the most important renewable molecules today, among others. These molecules, known as building blocks, are widely used in various industries to produce bioplastics, biofuels, phytosanitary products, or fertilizers (Antonetti et al. 2016). These are some of the main compounds obtained in biorefineries, and hence, the focus of this review.

Table 1: Composition (in % of dry mass) of different fractions of *Arundo donax* L.

Material	Origin	Lignin (%)			Holocellulose (%)		Extractives			Ashes (%)	References
		Klason (%)	Acid soluble (%)	Total (%)	Cellulose (%)	Hemicellulose (%)	Water	Ethanol	Total		
Stems	Spain; wild	21.1 ± 0.9	–	–	38.0 ± 4.6	34.0 ± 1.5	–	–	–	–	(Suárez et al. 2021)
	China; crop	18.4	1.24	19.7	42.2	30.5	–	–	–	3.0	(You et al. 2013)
	Portugal; wild	24.3	1.8	–	–	–	–	4.4	–	3.4	(Pinto et al. 2015)
	China; crop	20.2 ± 0.8	1.3 ± 0.0	21.5 ± 0.8	35.6 ± 1.6	24.0 ± 1.4	–	–	–	–	(You et al. 2018)
Leaves	Spain; wild	15.5 ± 2.0	–	–	27.7 ± 3.5	34.1 ± 3.3	–	–	–	–	(Suárez et al. 2021)
	China; crop	10.1	2.3	12.5	24.4	20.4	–	–	–	12.9	(You et al. 2013)
Plant	Spain; wild	24.9 ± 0.3	8.2 ± 1.0	32.4 ± 2.7	38.0 ± 3.7	42.4 ± 1.3	1.2 ± 0.3	1.8 ± 1.8	3.0 ± 2.2	4.9 ± 1.1	(Suárez et al. 2022)
	Italy; crop	24.3	1.8	26.1	39.5	25.8	–	–	4.2	4.4	(Licursi et al. 2015)
	Italy; crop	22.0 ± 0.0	0.9 ± 1.0	22.9 ± 1.0	36.3 ± 0.4	23.4 ± 0.4	–	–	15.4 ± 0.8	2.0 ± 0.0	(Di Fidio et al. 2019)
	Italy; crop	–	–	29.9	65.4		–	–	–	4.7	(Barana et al. 2016)
Rhizome	Spain; wild	19.1 ± 2.1	–	–	21.0 ± 1.0	29.6 ± 2.9	–	–	–	–	(Suárez et al. 2021)
	Italy; crop	19.1 ± 0.3	1.2 ± 0.0	20.3 ± 0.3	28.0 ± 0.7	13.9 ± 0.2	29.0 ± 1.8	3.6 ± 0.2	32.6 ± 2.0	7.4 ± 0.1	(Proietti et al. 2017)
	Italy; crop	17.8 ± 0.3	1.4 ± 0.3	19.2 ± 0.3	23.5 ± 0.3	11.9 ± 0.3	33.5 ± 1.8	3.2 ± 0.3	36.6 ± 1.7	5.9 ± 0.2	(Proietti et al. 2017)
	Italy; crop	17.1 ± 0.7	1.6 ± 0.0	18.7 ± 0.7	22.4 ± 0.3	11.1 ± 0.4	31.6 ± 0.6	3.0 ± 0.2	34.6 ± 0.4	5.0 ± 0.2	(Proietti et al. 2017)

Different parts of the plant have been used as raw material in hydrolysis reactions to break down the lignocellulosic material into fractions of interest. Table 2 summarizes the main pre-treatments applied to *Arundo* to increase digestibility and to obtain valuable products directly from this first step.

4.2.1 Pre-treatments: hemicellulose solubilization

As summarized in Table 1, hemicellulose accounts for 20–40 % of the aerial part of the reed. So, most studies focus on the solubilization of this fraction to produce xylose, xylo-oligomers, furfural, and levulinic acid. Besides, hemicellulose is the most accessible compound to break. In addition, the digestibility and accessibility of cellulose for enzymatic digestion are increased during pre-treatment and consequently higher product yields.

In this sense, Shatalov and Pereira (2012) recovered 94 % of the xylose present in *Arundo* through acid hydrolysis, using a low concentration of sulfuric acid (1.27 %) and temperatures of 140 °C; the liquor obtained had a low content of glucose and degradation products, and the digestibility of the material increased from 9 to 70 % due to the treatment. This conversion means that 22 g of xylose/100 g of dry biomass was obtained and transformed to 0.54 g of xylitol/g of xylose (Shatalov et al. 2013). Other studies agree that the acid hydrolysis of common cane, under mild conditions, allows selective hydrolysis of hemicellulose, so liquors with more than 90 % xylose content are obtained (Torrado et al. 2014).

The particle size does not seem to significantly affect the yields obtained nor the selectivity of the hydrolysis reaction, which is an advantage when processing the material (Torrado et al. 2014). Di Fidio et al. (2019) conducted a similar study, using ferric chloride instead of acid and heating by microwaves. They achieved a xylose production yield of 98.2 % in the first stage. These authors proposed a cascade process so that the resulting solid after the first hydrolysis stage was used in a second hydrolysis stage (under similar

Table 2: Most common pre-treatments applied to giant reed.

Material	Pre-treatment	Conditions	Results	Objective	References
Plant	Autohydrolysis	200 °C 20 min SLR: 50 g/l water Semi-continuous system	Complete hemicellulose degradation: 4.6 % xylose + 24 % xylo-oligomers	Sugars	(Galia et al. 2015)
Plant	Autohydrolysis	185 °C Non-isothermal SLR: 1/8	Partial degradation of hemicellulose: 2.4–3.0 % xylo-oligomers, 0.6–0.7 % xylose, 0.9–1.1 % glucose Organosolv process to the solid	Cellulose pulp	(Caparrós et al. 2006; López et al. 2010)
Plant	Autohydrolysis	150 °C; 10 min SLR: 1/5	Increased solid digestibility: CH_4 yield 10 % higher than for untreated material (300 ml/g VS)	Methane	(di Girolamo et al. 2013)
Plant	Catalyzed hydrolysis	Amberlyst70 20 %	Hemicellulose hydrolysis: 18.9 g xylose/100 g biomass + 4.1 g glucose/100 g biomass	Sugars	(Di Fidio et al. 2020)
		100 g biomass/500 g solution 160 °C, 20 min	Solid further enzymatic hydrolyzation: 18.9 g/glucose/100 g biomass + lignin-rich solid		
Plant	Catalyst hydrolysis	HCl 0.4 M 100 °C, 2 h 5 % Ru/C 70 °C; 2 h	Direct obtaining of valerolactone: 16.3 g/100 g biomass	Chemicals: γ-valerolactone	(Raspolli Galletti et al. 2013)
Plant	Acid hydrolysis	5 % H_2SO_4 SLR: 1/10 121 °C, 20 min	Hemicellulose and cellulose degradation: 80 g/l sugars Hydrolysate fermentations: up to 180 g lipids/l	Lipids (biofuel)	(Pirozzi et al. 2015)
Plant	Acid hydrolysis	Autoclave 150–190 °C 15 min 1.68 % wt HCl 0.35 g biomass/5 g solution	Low temperature: high yield in furfural and moderate in levulinic acid: 8–9 % wt each High temperature: only traces of furfural and up to 22 % levulinic acid	Chemicals: levulinic acid, furfural	(Antonetti et al. 2015)
Plant	Acid hydrolysis	HCl 0.4 M	Complete conversion of hemicellulose and cellulose: 23.3 g levulinic acid/100 g biomass	Chemicals: levulinic acid	(Raspolli Galletti et al. 2013)
		100 °C, 2 h 9 % biomass	Partial depolymerization of lignin		
Stems	Acid hydrolysis	1.27 % H_2SO_4	Complete hemicellulose conversion: 94 % xylose recovery	Chemicals: xylose, sugars	(Shatalov and Pereira 2012)
		5 g biomass/75 ml solution 141.6 °C, 36.4 min	Increased solid digestibility (70 %): fermentation for sugars production		
Plant	Acid hydrolysis	40.7 g biomass/605 ml solution	Hemicellulose fractionation	Chemicals: levulinic acid, polyol for PU	(Bernardini et al. 2017)
		1.7 % HCl 190 °C, 1 h	Solid liquified with glycerol and PEG: 50 °C for 2 min and used as polyol for PU obtaining		
Plant	Acid hydrolysis	1 kg biomass/30 l solution	Liquid fraction: converted to furaldehyde with Amberlyst 15: 33.5 % furfural (10 min, 157 °C)	Ethanol	(De Bari et al. 2020)
		H_2SO_4 1.4 % wt 200 °C, 5 min	Solid fraction suitable for enzymatic hydrolysis and fermentation: 43–51 g ethanol/l		
Plant	Acid + alkaline hydrolysis (plus precipitation)	HCl 0.1 M, 2 h, 100 °C	48 % Lignin recovery, with high purity (98 %)	Lignin	(Barana et al. 2016)
		NaOH 0.1 M, 2 h, 100 °C Acidification and precipitation	A further step of bleaching with H_2O_2 and acid hydrolysis allows obtaining cellulose nanocrystals		

Table 2: (continued)

Material	Pre-treatment	Conditions	Results	Objective	References
Plant	Alkaline pulping (plus precipitation)	18 % alkali SLR: 1:4 160 °C, 210 min	0.5 kg pulp/kg biomass + 128 lignin/kg biomass	Cellulose pulp Chemicals: polyphenols from lignin	(Pinto et al. 2015)
Plant	Autohydrolysis assisted with microwaves	200 °C 20 min SLR: 50 g/l water	55 % hemicellulose + 16 % cellulose degradation: 9.8 % xylose + 4.5 % xylo-oligomers + 1.8 % glucose	Chemicals: xylose	(Galia et al. 2015)
Plant	Alkaline assisted with microwaves	0.5 % w/v NaOH Liquid to solid ratio: 15:1 (ml/g biomass) 120 °C, 5 min	Maximum sugars yield: 4.5 g sugars/100 g biomass	Sugars	(Komolwanich et al. 2014)
Plant	Acid assisted with microwaves	Autoclave 190 °C 1 h 0.1 % HCl 41 g biomass/580 g solution	20–23 % levulinic acid 30 % lignin: reactive hydrochar	Chemicals: levulinic acid	(Licursi et al. 2015)
Plant	Acid assisted with microwaves	1.66 % HCl LSR: 15 g/g 190 °C, 20 min	21.3 % levulinic acid 28.9 % hydrochar	Chemicals: levulinic acid	(Licursi et al. 2018)
Plant	Catalyzed hydrolysis assisted with microwaves	1.6 wt % $FeCl_3$ 9 % biomass 150 °C, 2.5 min	Hemicellulose solubilization: 98.2 % xylose obtained 14.1 % glucose also obtained	Chemicals: xylose	(Di Fidio et al. 2019)
Plant	Acid+catalyst hydrolysis assisted with microwaves	2.8 wt% $FeCl_3$ 9 % biomass 150 °C, 2.5 min	Hemicellulose solubilization: 19.4 g xylose/l, 5.6 g glucose/l Enzymatic digestion of the solid: 12.6 g glucose/l Glucose fermentation: 7.8 g single cell oil/l (15–25 % lipids)	Lipids (biofuel)	(Di Fidio et al. 2021)
Plant	Catalyzed hydrolysis assisted with microwaves	2.4 wt % $FeCl_3$ 9 % biomass 190 °C, 30 min	Levulinic acid yield: 57.6 % Formic acid: 65 %	Chemicals: levulinic acid, formic acid	(Di Fidio et al. 2019)
Plant	Two steps assisted with microwaves: alkaline + acid hydrolysis	0.5 % NaOH + 0.5 % w/v H_2SO_4 Liquid to solid ratio: 15:1 (ml/g biomass) 180 °C, 30 min	Final sugars yield: 31.9 g/100 g biomass	Sugars	(Komolwanich et al. 2014)
Plant	Ionic liquid	[C4mim]Cl + AmberlystTM 35DRY 5 g biomass/95 g solvent 160 °C, 1.5 h	Hemicellulose content reduction Higher digestibility of the solid: higher glucose yields (10.4 g vs. 1.2 glucose/l)	Sugars	(You et al. 2016)
Plant	Ionic liquid	[C2C1im][OAc] 160 °C, 3 h	Solids with increased digestibility: glucan conversion to glucose: 40.8–76.2 %	Sugars	(Corno et al. 2016)
Plant	Ionic liquid	[Bmim]HSO_4 16 g/l SLR: 20 g biomass/200 ml 80 °C, 3 h	Higher digestibility of solids: 7.9 g glucose/L Photofermentation of liquors: 101.6 ml H_2/g TS (35 % higher than for untreated biomass)	Hydrogen	(Chen et al. 2022)
Plant	Ionic liquid	[C2C1im][OAc] 160 °C, 3 h	Increased solids digestibility: 71 % cellulose converted to glucose Dark fermentation: 70.5 N ml/g biomass + 100 mg/l organic acids Fermentation of OA: 100g PHA/kg biomass	Chemicals: ethanol, PHA	(Villegas Calvo et al. 2018)
Plant	Switchable ionic liquid	DBU/MEA/SO_2	67 % lignin extraction		(Gavilà et al. 2018)

Table 2: (continued)

Material	Pre-treatment	Conditions	Results	Objective	References
		2 g biomass/10 g SIL + 6 ml water	Digestible solid: 5.7 g glucose/l, fully transformed in 5.6 g lactic acid/l by fermentation	Chemicals: lactic acid	
		120 °C, 2 h	High D-lactic acid purity (>97 %)		
Plant	White rot fungi	Pleurotus ostreatus 30 % solid loading in water 26 °C, 30 days	30 % lignin degradation: increased anaerobic digestion: 130.9 N mL/g VS	Methane	(Piccitto et al. 2022)
Plant	Mechanical	Hammer + pin mill	Reduction in lignin content: 137 % increase in CH_4 production versus untreated biomass (212 N ml/g VS)	Methane	(Dell'Omo and Spena 2020)

conditions). In addition to the lignin-rich solid obtained after the second hydrolysis stage, levulinic acid (with a yield of 57.6 %) and formic acid (up to 65 % yields) were also produced.

The milder conditions favored furfural production, while more severe conditions generated levulinic acid (Antonetti et al. 2015). These authors also used an acid catalyzer (Amberlyst-70), obtaining similar xylose yields (about 96 %) with high selectivity. The cellulose-rich solid was further hydrolyzed using the same catalyzer, resulting in glucose yields of over 30 %, although enzymatic hydrolysis provided higher conversion values, higher than 55 %. In this study, Di Fidio et al. (2020) successfully recovered xylose and glucose without the pre-treatment of the *Arundo*. Komolwanich et al. (2014) hydrolyzed *Arundo* with microwave heating in an alkali solution followed by dilute acid hydrolysis; this two-step process increased the sugar release, reaching up to 31.9 g glucose/100 g.

Likewise, Galia et al. (2015) performed the hydrolysis of reed biomass (stalks and leaves) in pure water under microwave irradiation in batches and compared it with continuous processing by hot water. The work proposed this strategy to ease the scaling-up of the autohydrolysis process and also as an approach to Green Chemistry principles, as no reagents were used. Authors found that, although hemicellulose degradation was similar, microwaves are most effective in depolymerizing cellulose, which increases the possibilities for the later use of the solid fraction. Given the high amount of biochar produced, its exploitation must be considered; this by-product is a valuable source of simple phenolic compounds with good antioxidant properties (Licursi et al. 2015, 2018).

Raspolli-Galleti et al. (2013) reported for the first time the production of levulinic acid with yields above 23 %, which corresponds to almost 83 % of the theoretical yield, using HCl as a catalyzer and working at 190 °C. These authors also used a ruthenium-based catalyst to directly obtain γ-valerolactone, a compound of great interest for biofuel production, at 70 °C, getting yields close to 17 %, with almost complete conversion of the levulinic acid. Under similar conditions to those used for xylose production, Licursi et al. (2018) proposed using microwaves and very diluted hydrochloric acid (1.66 %), reaching temperatures of 190 °C, and the use of an autoclave (under the same conditions) as possible treatments for plant material. They reported similar yields of levulinic acid and carbon, 22 % and 30 % respectively (Licursi et al. 2015, 2018).

In a different work, Licursi et al. (2015) obtained yields of around 8–10 % furfural and 23–25 % levulinic acid under these mild conditions and low concentrations of HCl; these conditions also allow for the recycling of most water and acid. In a one-step process, levulinic acid is the only product obtained, with similar yields. It then appears that a two-step mild process could be more advantageous than a single step, in terms of yields, although a lifecycle assessment would be needed to balance obtained yields, with regard to the inputs and their respective impacts. The solid fraction obtained in both cases is rich in lignin and shows higher thermal stability than commercial lignin, with some reactivity due to the presence of free carbonyl and hydroxyl groups, which makes them classified as reactive hydrochar, with low solubility, similar to Brown coal.

Most studies emphasize the need for pre-treatment for producing sugars (or directly to obtain interesting final products) and for improving the digestibility of the solid material under mild conditions (low acid concentration, low temperatures, and low processing time). This allows the operation with low or moderate severity factors (temperatures under 150 °C), consequently resulting in energy savings, of great importance under real industrial processing (Shatalov et al. 2017). In this sense, You et al. (2016, 2018) have proposed the use of ionic liquids to pretreat the reed biomass, obtaining up to 50 % hemicellulose removal and increased digestibility of the resulting material (5 g glucose/kg h for untreated material, increasing to 93 g glucose/kg h of initial enzymatic hydrolysis rate, also increasing the total digestibility by twofold). These studies generated glucose concentrations over 10 g/l in 34 min for the pre-treated material and less than 1 g/l for the untreated raw material.

Gavilà et al. (2018) have also proposed using ionic liquids for sugar production, in this case for lactic acid production. This research has found that the use of a switching ionic liquid heated with microwaves can hydrolyze over 60 % of giant reed lignin within 1 h, with minimal amounts of degradation products. More importantly, the solvent can be recovered by precipitation of the remaining pulp. Despite the higher costs of the ionic liquid used in this study, the authors highlight its potential, due to the excellent results obtained and the possibility of reusing the solvent.

4.2.2 Further processing: sugars, cellulose, bioplastics, and lignin production

The products obtained after the fractionation treatment of the reed can also be used to obtain other compounds through biological processes. This cascade approach allows for maximizing the yield and potential of the lignocellulosic biomass.

For example, Ventorino et al. (2017) obtained succinic acid, with a yield of 0.69 g acid/g hydrolyzed material (9.4 g/l succinic acid), through bacterial fermentation using the hydrolysate obtained from the steam explosion of reed and bacteria from the rumen of cows and steers. When reed biomass was supplemented with nitrogen, the same authors found a significant increase in acids recovery, getting up to 12.1, 1.7, and 5.2 g/l of lactate, succinate, and acetate, respectively, using *Cosenzaea myxofaciens* bacterial strain (Ventorino et al. 2016).

For their part, Shatalov et al. (2013) have proposed using the solid residue from acid hydrolysis in an enzymatic hydrolysis process. They obtained a cellulose conversion of 75 % to glucose (26.4 g/100 g dry biomass). Some studies performed by Scordia et al. (2011) used oxalic acid as pre-treatment for ethanol production; 5 % of oxalic acid solution at 180 °C produced maximum glucan conversion, close to 70 %, and enough for ulterior fermentation. Giacobbe et al. (2016) proposed a different approach for biomass pre-treatment, performing an ammonia expansion pre-treatment before enzymatic saccharification using various enzyme cocktails. However, these authors did not run a control saccharification test without pre-treatment, so it is impossible to know the benefits of such a process in terms of enzymatic yields. The production of sugars for bioethanol production is discussed in more detail in the next section, as it is mainly used for energy purposes.

Reed can also be used to obtain cellulosic fibers, for use in different applications. Shatalov and Pereira (2013) suggest conducting an initial hydrolysis step, to remove hemicellulose and lignin, to produce high-purity cellulosic fibers; this method resulted in pulps with around 94 % α-cellulose. Barana et al. (2016) proposed a sequential approach for obtaining lignin, hemicellulose, and cellulose nanocrystals, following a chemical procedure consisting of an alkaline treatment followed by bleaching and acid hydrolysis. These authors recovered around 50 % of the cellulose, hemicellulose, and lignin. Martínez-Sanz et al. (2018) prepared lignocellulosic films by selective removal of lignin and hemicellulose by chemical methods. The films, especially those obtained after hemicellulose removal, showed good mechanical and water barrier properties and high transparency, comparable to thermoplastic starch films, making them interesting for the packaging industry.

Some studies have also used giant reed in biopolymer development, following a multistage approach (Corneli et al. 2016; Calvo et al. 2018). After a chemical pre-treatment and enzymatic hydrolysis, Villegas Calvo et al. (2018) proposed conducting a first fermentation step in dark conditions to produce hydrogen. After this first step, the resulting liquid fraction is transferred into a reactor with the inoculum (solids from the secondary treatment of a Wastewater Treatment Plant) for the production of PHA (polyhydroxyalkanoate). They obtained similar results to those given by other lignocellulosic materials, around 100 g PHA/kg volatile suspended solids (biomass + polymer).

On the other hand, the study by Corneli et al. (2016) proposed using different lignocellulosic materials, including reed, to obtain the biopolymer through a silage pre-treatment. Polylactic acid (PLA) can also be obtained from reed hydrolysis and fermentation to yield lactic acid (Gavilà et al. 2018). Finally, the char recovered from acid hydrolysis for levulinic acid production has been used to synthesize flexible polyurethane (Bernardini et al. 2017). To obtain this, the solid was liquefied by microwaves at low temperatures, using glycerol and PEG as solvents, and water as a foaming agent. The obtained polyol was used at a concentration of 7 wt % of the final foam, which showed properties suitable for packaging applications.

Sterols, lipids, and fatty acids have been produced from the rhizome, along with other compounds such as terpenoids, alkaloids, xanthones, xanthene, and phenolic compounds (Liu et al. 2021b; Pansuksan et al. 2020).

As summarized in Figure 6, the reed is an excellent source of lignin (contains about 20–25 % Klason lignin), made up of p-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid units linked predominantly by β-O-4′ aryl ether linkages (~70–80 %), with the remainder being β-β′, β-5′, β-1′, y α,β-diaryl ether bonds (You et al. 2013). Different authors have investigated composites based on this complex compound (Thakur et al. 2014; Vaidya et al. 2019) due to its excellent mechanical, antioxidant, and biodegradable properties. Besides, lignin can be used to produce polymers, carbon fibers, or phenolic compounds (Savy and Piccolo 2014; Licursi et al. 2015) with antioxidant properties, such as vanillin or syringaldehyde (Pinto et al. 2015). Other authors highlight the importance of lignin valorization for improving biorefineries' economic and ecological performance; the final aim is the production of green molecules and biofuels (Cotana et al. 2014; Molino et al. 2018).

For example, Cotana et al. (2014) have proposed three routes for getting lignin from the residues of bioethanol production from giant reed. They found that a rich-lignin material (around 73 %) with high thermal stability, suitable for composites manufacturing, can be obtained with a simple NaOH treatment, followed by an acid step to precipitate the lignin.

Savy and Piccolo (2014) characterized lignin fractions from *Arundo* stem obtained by acid hydrolysis and alkaline oxidization. These authors obtained higher lignin recovery from sulfuric acid hydrolysis, although the lignin obtained from the alkaline process showed higher oxidized lignin, which is also water-soluble.

Also, Pinto et al. (2015) proposed pulping *Arundo* stalks in an alkali solution at a moderate temperature (160 °C) to obtain cellulose pulp and being able to recover lignin from the black liquor, thus allowing for its further valorization. Around 100 g lignin/kg of dry matter was obtained by this method. These authors consider giant reed a good option for producing low molecular weight phenolics, favorable for aldehydes production, as the ones already mentioned.

4.3 Bioenergy production from giant reed

Regarding energy production from the lignocellulosic materials derived from giant reed, Krička et al. (2017) obtained the heat value from direct burning of the dry plant, obtaining higher and lower heating values (17.5 and 16.1 MJ/kg, respectively) similar to those obtained for other widely used crops for energy production, such as *Miscanthus* (18.2 and 16.8 MJ/kg). These authors state that the high lignin content of this plant makes them more suitable for direct burning instead of transformation into other energy products. However, this option should be discouraged, due to the low recalcitrance of this biomass and the good yields obtained for biochemicals and bioenergy production, as demonstrated by other authors and discussed below. Biomass direct burning should only be contemplated in those cases where the obtaining of bioderived products would need energy consumption higher than the value to be obtained from such bioproducts.

Several authors have evaluated the potential of reed for ethanol production. The process proposed begins with acid hydrolysis, as mentioned in the previous section, followed by alkaline treatment. Lemons e Silva et al. (2015) performed simultaneous saccharification with cellulase and fermentation with *Saccharomyces cerevisiae*, obtaining 42 g glucose/l in 30 h which was thereafter transformed into 39 g ethanol/l in 70 h. These authors worked with relatively high enzyme loadings (25 FPU g/solids) and supplemented the medium with urea, potassium dihydrogen phosphate, yeast extract, and a salt solution. The biomass was added in five batches every 12 h.

Loaces et al. (2017) followed a similar approach and compared the sugars and ethanol yields obtained in simultaneous and separate saccharification and fermentation. These authors used liquid hot water treatment (or autohydrolysis) and dilute acid as pre-treatment and obtained up to 33 g glucose/l and 24 g ethanol/l in the separate process and a similar value (35 g/l) for the simultaneous process. This research used *Escherichia coli* in the fermentation process, and the ethanol yields were higher than those obtained for other strains, such as *S. cerevisiae*, *Scheffersomyces stipites*, or *Saccharomyces carlsbergensis*, which led to 19.0, 18.0, and 16 g ethanol/l, respectively (Ask et al. 2012; Scordia et al. 2011, 2012, 2013).

A different study (Sidana et al. 2022) that used *Meyerozyma guilliermondii* yeast on reed hydrolysates following a two-step acid/alkali hydrolysis process, obtained ethanol yields of 33 g/l in 72 h. The *Arundo* biomass has been signaled as a valuable source of pentosans as its xylose content is similar, or even higher, than glucose. Moreover, it has higher xylose content than other biomasses, such as sugar cane bagasse (Neto et al. 1997). Both *E. coli* and *M. guilliermondii* can metabolize pentoses during fermentation. Viola et al. (Viola et al. 2015) reported higher ethanol yields, using *S. cerevisiae*, on hydrolysates obtained by autohydrolysis of fresh ripe reed (no prior drying step). Other authors have also studied the rhizome as a raw material for potentially obtaining green energy, in the form of ethanol, as this part of the plant contains over 30 % sugar (Proietti et al. 2017). The use of reed provides higher bioethanol yields than those obtained from other energy crops, such as cassava, *Miscanthus*, sugar cane, or beet, with the additional advantage of not being a food crop (Corno et al. 2014).

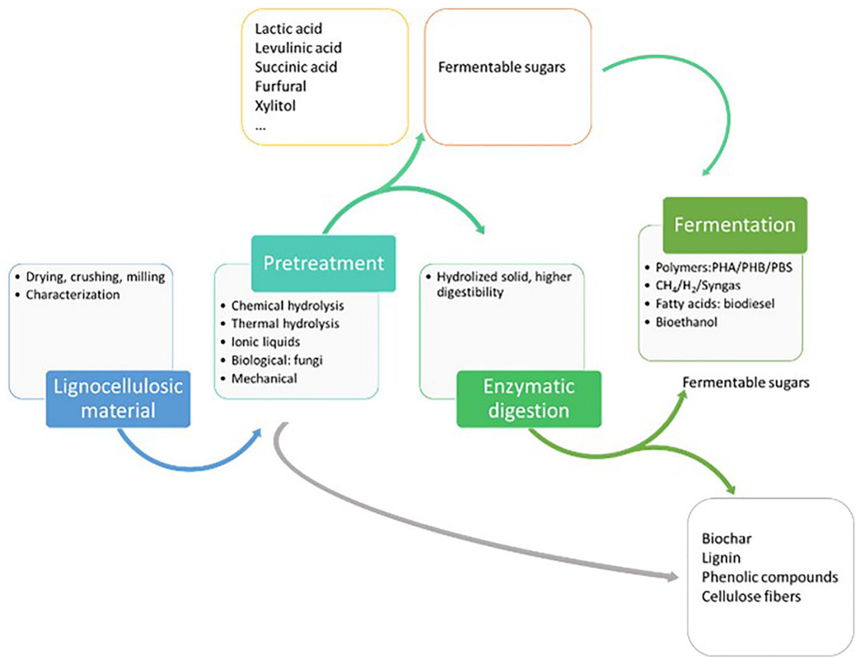

Figure 6: Different biorefinery processes combined to produce several compounds of interest, starting from *Arundo donax* L. PHA, polyhydroxyalkanoate; PHB, polyhydroxybutirate; PBS, polybutylene succinate.

The pyrolysis of reed to obtain biogas and phenol-rich chars has also been assessed in the literature. Bartoli et al. (Bartoli et al. 2016) produced biochar and bio-oil by microwave-assisted pyrolysis. They found that rhizomes and leaves provided large bio-char quantities (up to 60 %), due to the different ash contents in the three fractions, which would catalyze the biochar formation. In comparison, stems produced a larger amount of bio-oil (around 40 %). The pyrolysis reactions are quick for the three materials (about 20 min for 100 g of biomass). The bio-chars showed a calorific value of about 31 MJ/kg, similar to other solid fuels. The obtained bio-chars showed a very low hydrogen content, demonstrating the extent of the thermal process; they also had an important amount of volatile organic compounds (around 25 %), attributed by authors to the batch processing and the low temperatures reached in the pyrolysis process (lower than 700 °C). Moreover, the bio-oils consisted significant amount of aromatic compounds (over 200 g/l) and acetic acid (around 120 g/l). Slow pyrolysis at lower temperatures (300–400 °C for 60–90 min) of *Arundo* stems revealed carbon contents over 80 %, with a similar composition to the biochar obtained by Bartoli and collaborators (2016), although with higher content in volatiles (over 50 %) (Carnevale et al. 2022). Zheng et al. (2018) obtained biochar as by-product of pyrolysis vinegar (mainly acetic acid and phenol-derived compounds) production by *Arundo* stems at different temperatures, finding that higher temperatures let to lower biochar and similar vinegar yields. These authors did not further characterize the char. Ribechini et al. (2012) have found that pyrolysis at 150 and 190 °C results in the total conversion of hemicellulose and cellulose, with partial depolymerization of lignin The result of their solid analysis suggests the potential of the char as an antioxidant source instead of fuel, as it is mainly derived from the lignin fraction, thus getting a high-added value product. As mentioned in Section 4.2.1, the solubilization of hemicellulose produces an important amount of biochar, rich in phenolic compounds and with antioxidant properties, which can be further valorized (Licursi et al. 2015, 2018).

A different approach consists of the anaerobic digestion of giant reed biomass. For example, Amaducci and Perego (2015) obtained a biochemical biogas potential ranging from 345 to 506 ml/g volatile solids (VS), with a methane content of about 50 %, highly influenced by the lignin and ash content of the raw material. Yang and Li (2014) obtained similar methane production values with fresh *Arundo* (150.8 ml/g VS); methane production yields were lower with dried *Arundo*, particularly with solid contents by 20 %. However, other authors have reported the need for pre-treatment to get acceptable yields of methane production; for example, Baldini et al. (2017) applied ensilage as pre-treatment, before the anaerobic digestion, with biochemical biogas potential similar to the results of Amaducci and Perego (Amaducci and Perego 2015), which equates to approximately 50 % of the theoretical biomethane production.

Di Girolamo et al. (2014) reported an increase in methane production yield (up to 30 %) when reed was treated with a low concentration NaOH solution (0.15 N); these same authors also used maleic anhydride as pre-treatment, which led to higher methane yields (Di Girolamo et al. 2016). Methane production values were similar between the silage and the NaOH pre-treatments, while maleic anhydride ones reached higher values, comparable to those of *sorghum* or barley straw. Liu et al. (2015, 2016a,b) performed similar studies, comparing methane production yields for giant reed pre-treated by ensilage, fungus, and urea application. Urea pre-treatment yielded 173 ml/g VS in 30 days (production took place in the first 5 days), which indicates an increase of 18 % when compared to the untreated raw material (Liu et al. 2015).

The effect of fungus was opposite to that expected due to the degradation of cellulose and solid contents reduction (Liu et al. 2016b); the ensilage pre-treatment resulted in a 15 % increase in the methane yield, while fungal pre-treatment resulted in a 30 % decrease. In addition to the effect of pre-treatment on the methane yields, these authors also found some differences with regard to the harvest time. *Arundo* harvested in December contained higher water cellulose carbohydrates while the ones harvested in August had a higher lignin content, which resulted in lower biomass digestibility (Liu et al. 2016b; Ragaglini et al. 2014). The results from these authors suggest that urea pre-treatment provided higher yields than the ensilage pre-treatment (173 ml/g vs. 165 ml/g, respectively).

Lignin from giant reed stems, separated after the steam explosion and alkaline hydrolysis, has been used to obtain syngas via supercritical water gasification (Molino et al. 2018). Operating at 550 °C and 250 bar, Molino et al. (2018) generated a gas rich in syngas (>90 %) with no carbon dioxide, a hydrogen content of 65 %, and a higher heating value of 43 MJ/kg, similar to conventional methane. Besides, an organic-rich liquor with valuable chemicals, such as glucose, xylose, formic acid, acetic acid, and syringaldehyde, was also obtained.

Yang et al. (2020) also evaluated the pyrolysis of residual lignin from *Arundo* hydrolysis and fermentation for ethanol production, obtaining biochar and biogas. They obtained 7.5 % of biogas and 16.7 % of ethanol for the fermentation plus pyrolysis route versus 26.6 % of biogas production for direct pyrolysis. This approach increases the overall process yield and provides a more valuable utilization of the lignocellulosic materials compared to direct pyrolysis.

Reed hydrolysates rich in xylose and glucose can also serve as a substrate for the growth of oily yeasts (*Lipomyces starkeyi*) to obtain fats at a concentration of 30 %, with a good yield of transformation of sugars to lipids (15–24 %) (Di Fidio et al. 2021). In this approach, the hydrolysates are first obtained using microwaves or acid/enzymatic hydrolysis processes; afterward, a yeast strain capable of transforming the obtained xylose into fats is used. These authors follow a cascade approach, using both the hydrolysate and solid residue. For the solid, enzymatic hydrolysis is proposed, followed by a process where the same yeast strain is used to transform glucose into single-cell oils. Other authors followed a similar strategy, starting from acid hydrolysis of the reed to obtain the hydrolysate (Pirozzi et al. 2014) and getting yields that are comparable to those obtained in biodiesel production plants. Also, Pirozzi et al. (2013) performed different studies using the hydrolysates from *Arundo* to grow oil yeasts. They obtained 110 g lipids/l, with oleic acid as the major component. However, if a two-step process was applied to the biomass (steam explosion followed by enzymatic hydrolysis), the oil yield could increase up to 150 g/l (Pirozzi et al. 2014).

4.4 *Arundo donax* biorefinery: current limitations and future opportunities

From the literature review performed, it can be concluded that *A. donax* L. has great potential as biorefinery feedstock, due to its composition, year-round availability, and fast growth rate. As summarized in Figure 6, there are several paths for the transformation of reed biomass into building blocks, energy products or cellulose fibers. The relatively high content in hemicellulose, around 25–30 % for the aerial parts of the plant (stems and leaves), suggests performing a first hydrolysis step, under mild conditions (140 °C and low acid concentration) for the recovery of xylans, also degrading the amorphous part of cellulose into glucose. More severe conditions are not recommended, due to the degradation of these monomers into furfural or HMF, which means the hydrolysates would need of further purification stages. The obtained solid, with improved digestibility, could be later processed by enzymatic means to increase the glucose yields. This is a procedure commonly followed in literature, although assays are usually performed at small scale. The cost of enzymes on a large scale would reduce the economic profitability of such installations, so other options, such as further chemical treatments or pyrolysis, should be considered. Something similar happens for the thermochemical treatments; it is generally considered that moderate temperatures are required for biomass fractionation, although there are several paths to achieve so, from pressurized reactors, conventional heating, or microwaves. Again, assays are mainly performed at lab-scale, and some of these procedures might not be fully scalable. On the other hand, the use of ultrasounds and cavitation has not been fully explored and might also provide good yields. Energy efficiency should be considered, and cavitation is one of the techniques with higher energy efficiency and shorter processing times (Poddar et al. 2022).

Despite the wide availability of studies on the potential use of giant reed, scalability assays have not been found. The cultivation of fungi that produce enzymes for the ulterior processing of the reed biomass would be an exciting option although, again, this needs to be further assessed. So, the alternative is the use of chemicals, in the lower proportion possible, to allow the separation of the original biomass into profitable products. This is, in the authors' opinion, the next steps to undertake: shifting from the grams scale used in the lab to a pilot-scale plant, working with at least kilograms, and optimizing the procedures to maximize yields. The comparison between lab and pilot-scale plant conditions and yields would allow for a later design of appropriate industrial facilities for the processing of such biomass.

On the other hand, only 7 % of the arable land in the EU is devoted to industrial crops (Eurostat 2019), most of it being occupied with cereals. It is important to note that, despite the interest of the scientific community and the strategies settled by different organisms to increase the availability of raw materials for biorefinery development and reduce the oil dependence, food production is prioritized, and energy or industrial crops cannot displace it. The use of by-products or residues from food production are undeniably a valuable resource and they should be reintroduced into the industrial value chain to maximize the use of resources.

Based on *Arundo*'s specific resistance to salinity, droughts, pathogens, etc. a strategy to increase the cultivated lands for industrial purposes could be the use of marginal or degraded soils, using low-quality waters. This would allow for reducing soil loss and restoring their quality while, at the same time, getting valuable lignocellulose material for further industrial use. It is estimated that about 60–70 % of European soils are degraded, while over 25 % are identified as with a high or very high risk of desertification, especially in southern Europe. The Mediterranean basin is particularly sensitive to soil loss, also having low levels of organic matter and high salinization (Ferreira et al. 2022). Even if the yields obtained in such conditions are not optimal, the low requirements of such plant species could provide additional environmental benefits, regarding soil restoration and preservation. Besides, not only degraded soils could be used; a recent study has estimated that over 8 million hectares of EU agricultural soil are not used due to non-optimized conditions and is considered marginal agricultural land (Reinhardt et al. 2022), while about 40 % of such surface can be considered as profitable land (Sallustio et al. 2022). An assessment performed in China for a plant processing 2000 t/day would lead to 28 MW power, plus over 50 t/day of bio-oil, 555 t/day of vinegar and similar values of biochar (Abreu et al. 2022), showing the potential of *Arundo* for producing several fractions at high-scale. Considering the use of only 1 % of such area, and the estimated yields for this plant of 30 t/ha, about 2.4 million tons of *Arundo* biomass could be obtained yearly, which can be translated into over 70 MW energy, over 125 t of bio-oil and almost 1500 t of biochar and pyrolysis vinegar. The use of unused soil for the obtaining of biomass feedstock would also help reduce the dependence on external sources to produce chemicals or energy, advancing the SDGs objectives on sustainable and responsible consumption, green energy, soils preservation, etc. while, at the same time, would not have any impact on food production, as no crop substitution would be required.

The European Strategy for Bioeconomy has as its main aim the production and commercialization of food, forestry products, bio-products and bioenergy obtained from environmentally friendly competitive processes. The commitment to the achievement of SDGs and the advancement toward more sustainable and efficient processes and products can be reflected in the growing number of biorefineries installed, among other factors. In Europe alone, over 2300 installations are identified, mainly located in central Europe (Germany, France, Sweden, and Italy) (Parisi 2022). Most of them are devoted to bioenergy products (biomethane in particular), although chemical production has gained importance in the last years. Most of these installations in Europe is one platform biorefinery, focusing on oil products, while the non-EU ones (led by China and the USA) are mostly devoted to sugars platform, starting from sugar and starch crops (Baldoni et al. 2021). Most of these plants operate with a commercial purpose, although at different scales (Parisi 2022), from a few to hundreds of thousands of tons of input raw material. The casuistic is so wide (type of raw materials, main product, type of process) that there is no guide on the potential scale to reach a certain level of profitability, and this is particularly one of the exciting challenges to still undertake, the demonstration of the profitability, at different levels, of such installations.

Finally, the potential selection and modification of the plant species to improve this adaption to the aforementioned degraded soil conditions and poor-quality waters would also pose significant improvements on the dry matter yields obtained, although this path is still in the very early stages of development (Danelli et al. 2020).

The last Global biorefinery status report points out the use of marginal land and the cultivation of resilient species as a solution to overcome the current limitations of lignocellulose material availability and foster the growth of the bioeconomy (Annevelink et al. 2022). In this sense, considering the inputs required for the cultivation, the plant species' resilience, the availability of marginal and degraded soils, and the potential ability to remove pollutants from soil and waters, *A. donax* L. can be considered as a convenient species and its cultivation should be promoted, even over other species more commonly cultivated such as *Miscanthus* or switchgrass. A recent study has proven that *Arundo* provides higher efficiency for syngas production than *Miscanthus*, from exergy analysis (Manić et al. 2023), although both species are more favorable than corn stalk or municipal wastes, which are more commonly used as feedstock for methane or syngas production. The potential invasive character of this plant species is certainly a thread to consider, although the potential benefits from the cultivation, also from an environmental point of view, should not be disregarded.

5 Conclusions and outlook

5.1 Conclusions

The extensive literature published on this topic shows the interest in the use of giant reed for several purposes in a bioeconomy scenario. The abundant biomass generated by this plant, its fast-growing rate, and the low inputs needed for its cultivation has made several authors propose *Arundo* as a promising source of lignocellulosic biomass. The extensive range of applications for products obtained from its cultivation, from sugars to a wide range of chemicals, besides the traditional hand-craft products, have made policymakers refer to this plant as a high-interest crop. This non-food crop is considered to have great potential as an energy crop, especially in the Mediterranean basin, although it can also adapt to colder and wetter climatic conditions.

The biorefineries' growth potential is linked to their sustainability, considering its three aspects (environmental, social, and economic). The cascade approach is seen as the most interesting to maximize the potential of the biomass and, thus, its profitability, showing giant reed a suitable composition to follow such an approach and exploit the different fractions. Hemicellulose-derived products are usually the first compounds obtained, as it is a relatively easy compound to degrade, and it accounts for a major fraction of the raw biomass. need of a pre-treatment stage to ease the separation of the different fractions, thus maximizing the range of products to obtain and yields, has been demonstrated. These pre-treatments also induce an increase in the material's digestibility. The low recalcitrance of *Arundo* biomass allows for conducting such pretreatments with low-concentration solutions, especially acids, and mild conditions. These are suitable for the solubilization of hemicellulose and partial depolymerization of lignin and cellulose. Acids are used to catalyze such reactions in concentrations below 2 %. Other options include using ionic liquids, which can be reused several times. Microwave pre-treatment has also been proposed to pretreat the biomass rapidly while releasing sugars simultaneously, although heating in semicontinuous or continuous mode should be further explored in order to increase process scalability and profitability.

5.2 Outlook

Even if the invasive potential of *A. donax* is clear, an adequate management strategy would bring significant environmental improvements, especially in areas with soil erosion risk and affected by droughts, due to the resistance of this plant to saline or low-quality waters and soils. This strategy should not only include the adoption of the processes for maximizing the yields of bioproducts obtained at lower energy requirements but also crop management, only using marginal or degraded soils, low-quality waters, or even wastewaters to reduce the need for nitrogen fertilization. The cultivation of giant reed appears then as a potential strategy to reduce the risk of soil loss and desertification risk, especially in the Mediterranean area.

Different strategies can be employed for reed valorization depending on the intended end. However, the sugars platform seems to be one of the most promising ones, considering the wide range of bio-products that can be obtained: polymers, such as PLA, PHA, or PBS, fats for biodiesel production, bioethanol, and other chemicals used in synthesis, especially xylose and levulinic acid. After sugar production, the residual solid biomass can be fed into further processes to obtain lignin and cellulose fibers or further processed to maximize sugar production. Antioxidant compounds, biochar, bio-oils, and energy products can be obtained at the later steps of the value-chain. The high yields obtained under relatively mild conditions and the wide range of products potentially produced from *Arundo* materials make direct energy valorization (burning) a non-desirable strategy, making the refining a more efficient and sustainable approach.

Even though some authors have performed environmental analysis on the crop, the inputs required, and the performance of bioproducts obtained (mainly related to bioethanol), more studies on the environmental and economic impact of *Arundo* cultivation and its processing are still required.

The scaling-up of such infrastructures to cover the gap between demonstration plants and large-scale production ones still needs to be undertaken, as recognized in the Global Bioeconomy Summit in 2020. Thus, there is a promising field of study, framed on the green deal strategy of the EU and the sustainable development goals, to optimize not only the technical feasibility of biorefineries but also the environmental, economic, and social performance of such installations.

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