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Review

Low Indirect Land Use Change (ILUC) Energy Crops to Bioenergy and Biofuels—A Review

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Abstract: Energy crops are dedicated cultures directed for biofuels, electricity, and heat production. Due to their tolerance to contaminated lands, they can alleviate and remediate land pollution by the disposal of toxic elements and polymetallic agents. Moreover, these crops are suitable to be exploited in marginal soils (e.g., saline), and, therefore, the risk of land-use conflicts due to competition for food, feed, and fuel is reduced, contributing positively to economic growth, and bringing additional revenue to landowners. Therefore, further study and investment in R&D is required to link energy crops to the implementation of biorefineries. The main objective of this study is to present a review of the potential of selected energy crops for bioenergy and biofuels production, when cultivated in marginal/degraded/contaminated (MDC) soils (not competing with agriculture), contributing to avoiding Indirect Land Use Change (ILUC) burdens. The selected energy crops are *Cynara cardunculus*, *Arundo donax*, *Cannabis sativa*, *Helianthus tuberosus*, *Linum usitatissimum*, *Miscanthus × giganteus*, *Sorghum bicolor*, *Panicum virgatum*, *Acacia dealbata*, *Pinus pinaster*, *Paulownia tomentosa*, *Populus alba*, *Populus nigra*, *Salix viminalis*, and microalgae cultures. This article is useful for researchers or entrepreneurs who want to know what kind of crops can produce which biofuels in MDC soils.

Keywords: herbaceous species; forest crops; microalgae culture; marginal soils; degraded soils; contaminated soils; chemical process; biochemical technologies; thermochemical process; energy potential

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1. Introduction

Dedicated energy biomass production, the so-called energy crops, has experienced a rapid expansion in some countries, mostly related to the use of agricultural crops (mainly annual crops), for liquid biofuels production. Energy crops are species that can be produced to generate energy as electricity/heat or biofuels, helping to reduce the generation of greenhouse gases (GHG) mainly by the energy and transport sector [1], due to their inherent photosynthetic capabilities and renewable characteristics. Moreover, their exploitation can help countries achieve energy security and contribute to local and regional development and growth [2], by serving as a source of income for many agricultural producers [3]. In addition, these species should not be considered for food and feed like tubers, grains, and maize, among others [4], to avoid competition for food, feed, and fuel. Moreover, energy crops represent alternative biomass for supply to biorefineries. Moreover, lignocellulosic species for second-generation fuel production [5] and non-food species, represent an important feedstock for many industrial uses.

The advantages of energy crops are also applicable to lignocellulosic residues (part of the species not suitable for harvesting), such as straw, bark, leaves, and bagasse from herbaceous species and long fiber and hardwood from forest species. The reuse of any type of biomass waste material such as forest waste (e.g., wood waste from the wood industries and manufacture of pulp and paper), secondary waste (e.g., animal waste, organic material from food companies, solid waste) and agricultural residues (e.g., short-rotation species, cereals, among others) [6] allow reducing both the fuel load deposited in landfills and the still latent dependence on fossil-based feedstocks [7], creating several environmental, social, and economic opportunities. To comply with sustainability criteria, energy crops value chains must present a reduction of GHG emissions when compared to those released by fossil-based value-chains; the biomass production must not affect or alter negatively the quality of groundwater, soil, or air, and for this reason, it is necessary to limit or to avoid the use of chemical products such as fertilizers and pesticides, the biodiversity of the area where the species are planted must be protected to avoid negative effects directly or indirectly, and, finally, at the local level, the crops must not compete with the food sector and, in parallel, should encourage the economic and social growth of the region [6,8,9].

Herbaceous crops, like the giant reed, switchgrass, reed canary grass (*Phalaris arundinacea*), miscanthus, and perennial ryegrass (*Lolium perenne*) are crop species that can be cut annually after planting and the rhizomes must be left in the ground to ensure continued growth, a procedure that can be maintained for 15 years or longer, therefore, they are also classified as perennial crops. The perennial energy crops (or multi-annual plantations) do not need the incorporation of considerable quantities of pesticides and fertilizers, they help to avoid soil erosion, present low soil fertility requirements [10], and help in the recycling of organic components in the soil [11]. The short cycle coppice like poplar (*Populus* spp.), eucalyptus (*Eucalyptus* spp.), paulownia [*Paulownia tomentosa* (Thunberg) Steudel], and willow (*Salix* spp.) are woody species characterized to be fast-growing and can be cut and regenerated every 3 to 5 years over a 25-year period, with the purpose of obtaining in a short time high yields for energy generation [5]. Microalgae also present high potential as an energy crop because they can accumulate sugars and oils for later direct conversion to biofuels (e.g., bioethanol).

These types of crops when grown in soils with low Indirect Land Use Change (ILUC) risks, namely, soils considered as Marginal/Degraded/Contaminated (MDC), release environmentally clean emissions, and, as compared with fossil fuels, they once represented a negative impact on the atmosphere concerning the quantity of produced carbon dioxide (CO_2) [10]. Yet, these species cannot be cultivated on agricultural terrain with a high carbon (C) soil quantity [5], rather appropriate agricultural and forestry models of these plantation crops should be created [4], and when liquid, solid, and gaseous biofuels are produced (in some cases), the organic by-products can be used as animal feed and fertilizers [10], as a way of continuing the raw material cycle.

The main objective of this review is to present the potential for bioenergy and biofuels from energy crops with low ILUC risk. The potential of energy crops must motivate each producer, entrepreneur, and beneficiary for greater implementation of these species in the diverse processing options (chemical, biochemical, and thermochemical) to generate economic, social, and environmental benefits. It is important that energy crops that present a high potential for bioenergy generation and the recuperation of soils with low ILUC risk are identified to fulfill one of the world's goals, the reduction of GHG.

This paper was developed through a bibliographic search of scientific articles to demonstrate the relevance in several aspects (biofuels, energy, bioproducts, and soils) of the energy crops detailed here. Although there are many more species considered low ILUC energy crops, the selection of the species was carried out based on already known information on crops that grow and adapt to the climatic conditions of Portugal, with the ability to develop in MDC-type soils and with phytoremediation potential (recovery of contaminated land) and phytoextraction (reduces the leaching of heavy metals (HMs) for groundwater) [12]. The keywords used were common (e.g., Cardoon) and scientific (e.g., *Cynara cardunculus* L.) names of each species along with the bioenergy, biomass, and biofuel words. The databases or data sources and journals where the research was carried out were Science Direct, the open-access website Multidisciplinary Digital Publishing Institute (MDPI), Wiley Online Library, Springer, and Google to find relevant information from articles available online. More importance was given to information published in the last eight years and in magazines related to biomass, bioenergy, biofuels, or similar. However, there was relevant information from articles preceding the last eight years because it was referenced in more current articles.

2. Conversion of Low ILUC Risk Energy Crops to Biofuels

2.1. Herbaceous and Other Crops

Herbaceous crops were chosen because they are species that present several environmental benefits such as high nutrient and water use efficiencies, erosion control, soil stabilization, and carbon storage, they contribute to the landscape and biological diversity and have a low need for inputs, namely fertilizers and pesticides [10,13–17], and help in the recycling of organic components in the soil [11]. For example, miscanthus presents an extensive and deep rooting system, a lengthy permanence in soil, and the translocation of nutrients from aerial biomass to the rhizomes at the end of the vegetative cycle, which reduces the need for high application of fertilizers to ensure growth [18]. Jerusalem artichoke is a low-energy intensive crop with several advantages over traditional agricultural crops (grain crops) including rapid growth, elevated biomass generation, and low external production costs (e.g., it needs a low amount of fertilizer, pesticides, or water [19]). All these species are also more widely known from an agronomic point of view and from a commercial point of view they are already on the market, some more present than others.

Virginia fanpetals [*Sida hermaphrodita* (L.) Rusby] is a crop that has aroused great interest by many researchers, mainly in Northern Europe, because it is a species that easily adapts to the climatic conditions of these regions and acts as a phytoremediator [20] in contaminated soils with HMs [21], soil poor in organic matter, and in rocky and sandy soils, and it stores carbon in its roots (hence underground) allowing GHG mitigation [22]. *Sida hermaphrodita* has high potential as an energy crop in solid fuel production such as pellets [23] being burned in combustion processes and for biogas (or biomethane) production [20–22,24], and it is also suitable for the formation of by-products such as fiber, forage, and in pharmaceutical applications [20]. Based on these characteristics, it can be said that Virginia fanpetals is a potential competitor for the herbaceous energy crops that are included in this work. Currently, it is not cultivated in the territory of Portugal, so it can be risky to implement it in the country, however, there is no doubt that for future work, it would be very interesting to develop a study on the viability of this species in Portugal, to investigate its possibilities and increase list of new cultures with potential in the territory as an ILUC crop.

Another advantage of herbaceous crops is that they can be implemented in Wastewater Treatment Plants (WWTP), e.g., *Cynara cardunculus*, giant reed, hemp, linseed, and sorghum. Moreover, some crops can have multi-products, e.g., paper pulp production (giant reed, hemp, miscanthus, sorghum, and switchgrass species), which can help to alleviate the excessive exploitation of eucalyptus. These crops, e.g., sorghum, present also the ability to capture big quantities of CO_2 from the atmosphere, converting it into sugars [25], thus helping to mitigate climate change.

Herbaceous species also present some constraints. For example, crops that have biomass characteristics that are not favorable for energy use, e.g., cardoon due to the amount of N. Giant reed is considered invasive, which can legally prevent its implementation as an energy crop, and for this reason, it is necessary first to use what already exists and then to implement it in a controlled manner. Some crops also present limited yields with low rainfall, and this can compromise production in Mediterranean countries. Even for the production of those crops in soils with low ILUC risk, there are still some barriers to their promotion for energy purposes: e.g., hemp presents legal impediments to its production in many countries, and in other countries, there is a significant market competition in seed use for food purposes, and the suitability of the stalk to several applications with significant commercial value should also be noted. Linseed oil can also be used in the production of vegetable oils for the food sector, a factor that may limit its great expansion as an energy crop, however, when the plantation is applied in soils not suitable for agriculture, its final destiny will be always to produce biofuels or by-products.

The chemical composition of the different herbaceous and oilseed crops is presented in Table 1, for easier comparison between them.

Table 1. Chemical composition of herbaceous and other crops.

Energy Crops	Cellulose (% w w^{-1})	Hemicellulose (% w w^{-1})	Lignin (% w w^{-1})	Ash (% w w^{-1})	Extractives (% w w^{-1})	Other Components (% w w^{-1})
Cynara cardunculus (stalks) [7,26]	34	18.5	(14–23)	(5–11)	(13–21)	-
Cynara cardunculus (seeds) [27]	-	-	-	-	-	Fat content (17–24), protein (26–30), and fiber (20–28)
Arundo donax [6,28,29]	(21–45)	(7–36)	(6.7–34)	(2.3–8)	(12–22)	-
Cannabis sativa [7,30]	(33–74)	(7.6–16.6)	(2.2–29)	(2.6–7.6)	(3.7–20)	(0.3–23.1)
Helianthus tuberosus (tubers) [6,31–33]	(28.5–49.4)	(10.2–16.8)	(14.5–22.2)	4.7	12.1	N (1.45–1.55)
Linum usitatissimum [34]	-	-	-	-	-	Fatty acids [stearic (2–4), palmitic (4–7), linoleic (35–40), oleic (25–40), and α-linolenic (25–60)]
Miscanthus × giganteus [6,29]	(43–58)	(16–34)	(5.8–11)	2	(9–17)	-
Sorghum bicolor [7,25,35]	(23.7–44.6)	(20–27)	(4.4–24.7)	0.4	-	-
Panicum virgatum [7,35–37]	(31.8–45)	(20.3–36) [xylan (25–27)]	(7.4–31.2)	(3.2–5.7)	-	-

As can be seen in Table 1, species such as cardoon and linseed have the potential for biodiesel production since oil can be obtained from the seeds. Another species that also has this characteristic, despite not being specified in the table, is hemp, as oil can also be obtained from the seed. Due to the amount of cellulose and hemicellulose (polysaccharides) present in each species, all herbaceous species have the potential for second generation bioethanol production.

For biodiesel production, the species that have potential as raw materials are cardoon, hemp, Jerusalem artichoke, linseed, and sorghum. Comparing the different crops, hemp is the one that presents a higher yield in oil. [38,39].

Species such as cardoon, hemp, Jerusalem artichoke, giant reed, miscanthus, sorghum, and switchgrass can be applied in biochemical technologies (anaerobic digestion (AD) and alcoholic fermentation) and thermochemical processes (combustion and pyrolysis). Based on studies and related data, some crops, such as sorghum from ensiled sorghum forage [40,41] and giant reed [42], show promising potential for AD technology. In the case of bioethanol, some crops, such as hemp [43] and JA species [44] have also shown promising potential. Biohydrogen production is another promising option, for example, through the exploitation of cardoon and sorghum bark [45].

Herbaceous crops also show promising results with thermochemical processes, such as pyrolysis of miscanthus [46]. Regarding the hydrothermal processes, crops like miscanthus and sorghum have shown potential. Through hydrothermal liquefaction (HTL), it is possible to obtain biochar and bio-oils, with good yields, for example, when sorghum is the feedstock [41,47].

In the following Sections 2.1.1–2.1.8, a revision of promising options for energy with different crops are presented.

2.1.1. Cardoon (*Cynara carduncullus* L.)

Cynara carduncullus is a herbaceous perennial crop [48], belonging to the family Asteraceae, order Asterales, and class Magnoliopsida [49]. The seed productivity can attain 1.3 t ha^{-1} [50].

Traditional use, knowledge, and application of *Cynara carduncullus* are not recent. In the Mediterranean regions, aqueous extracts of cardoon flowers are utilized for human consumption, as coagulants in the traditional fabrication of sheep's milk cheeses, giving them unique characteristics of excellence in texture and taste [51]. The cardoon residues can be utilized for the food sector in the generation of natural preservatives and in the case of oil extracted from the cardoon seed, the surplus material that represents a considerable amount, namely, 81 g 100 g^{-1} of seeds, can be applied as animal feed or as biofertilizer [52]. On the other hand, cardoon leaf infusions are known in folk medicine for regulation of the hepatobiliary system [53], as an anti-inflammatory, antiviral, antimicrobial, antioxidant, antihyperglycemic, antidiabetic, antiproliferative, antibacterial, and anti-HCV, among others [52]. The cardoon stalks are utilized in the paper factories due to the fiber content (cellulose) that can be found in this material [54]. Other applications are the use of cardoon to obtain phytochemical compounds for the pharmaceutical sector (polyphenol-rich sheets that have also been applied in the cosmetic industry [55]), in the fresh green forage production for animal feed, and as reinforcement in structural composites, among other wide variety of uses [51]. It is also possible to obtain a great diversity of bioproducts from *Cynara carduncullus*, such as biolubricants, bioplastics, fragrances, personal hygiene materials, and household items, among others [56]. New uses have been given to various substances that make up the different constituent parts of cardoon, such as obtaining dietary fibers, including inositol, hemicellulose, inulin (fructose polysaccharide extracted from the roots [55]) and cellulose pectin, minerals, and sesquiterpenes lactones such as cynaropicrin, among others [52].

The cardoon is considered a species with high biomass yield with a huge potential for bioenergy production, namely, biodiesel (as cardoon is one of the species with the highest generation of fatty acids) [57], biomethane [58], and bioethanol [48], as well as other processes such as thermochemical [48] like combustion, gasification, and pyrolysis [51], biohydrogen [59], and solid biofuel [51,60] production. Another application is the biokerosene generation from cardoon biomass pyrolysis in which it is possible to achieve a 34.72% yield [61].

Biodiesel production from yeast using the cardoon stalks as raw material within a biorefinery model was studied by Barbanera et al., 2021 being also made a Life Cycle Assessment (LCA) study from the cradle-to-gate for assessing the environmental factors. It was concluded that this type of biodiesel has great environmental advantages, as the emissions of GHG are -1.5 g CO_{2eq} MJ^{-1}, being negative because of the positive credits that the by-products provide [62]. In another study, the obtainment of biodiesel and biolubricants was studied, also in a biorefinery model from cardoon oil, being applied to the transesterification process with methanol and other more complex alcohols (e.g., 2-ethyl-1-hexanol and 2.2-dimethyl-1,3-propanediol). The biolubricants were obtained from fatty acid methyl esters (FAMEs) from cardoon oil with the most complex alcohols. However, to ensure that this type of oil is promising on a large scale (biorefinery), it is required to increase the oxidative capacity of biodiesel (1.35 h). In relation to other materials, the biolubricant yields that are admissible and higher than 92% are also obtained for products with high commercial value such as glycerol and in the case of methanol, this can be reused [63].

Biomethane production through the anaerobic digestion (AD) process was evaluated using cardoon as raw material, using two cultivated species and one wild type. The cultivated species were allowed to obtain higher amounts of both biomass and biomethane, producing 19.1 and 16.8 t DM (dry matter) ha^{-1} $year^{-1}$ and a biomethane volume of 4074 and 4162 Nm^3 when compared to 11.8 t DM ha^{-1} $year^{-1}$ and 2867 Nm^3 of biomethane obtained with wild cardoon. Therefore, *Cynara cardunculus* is considered to be an energy crop with great potential for implementation in biomethane production [64].

The high potential of *Cynara cardunculus* biomass to produce bioethanol [65] has been well studied. Ethanol-water (EW) pre-treatment was implemented for the fragmentation of lignocellulosic biomass present in the cardoon to improve the glucose yield after enzymatic saccharification. A high yield of glucose was obtained (around 72%) after 60 min, at 190 °C, with a liquid/solid ratio of 20 L kg^{-1} and ethanol concentration of 25%, with possible retention of glucans greater than 97%, as well as the removal of xylans greater than 68% and lignin greater than 58% [66]. The thermochemical pre-treatment of cardoon biomass using sodium hydroxide (NaOH) is a very efficient hydrolysis method to obtain a maximum value of methane yield between 0.5 up to 0.6 L methane g^{-1} VS [67]. The alkaline extraction after Cardoon Steam Explosion Pre-treatment (CSEOH) allows for obtaining an ethanol concentration of 18.7 g L^{-1}, with 66.6% of fermentation efficiency and a yield of 26.6 g ethanol 100 g^{-1} CSEOH or 10.1 g ethanol 100 g^{-1} of untreated material (cardoon) [68]. In another study, two processes were studied separately after Steam Explosion (SE) pre-treatment, namely, Semi-Simultaneous Saccharification and Fermentation (SSSF) and Separate Hydrolysis and Fermentation (SHF). SSSF allowed obtaining a yield of ethanol of 13.64 g of ethanol 100 g^{-1} of cardoon, a value slightly higher than that of SHF (13.17 g of ethanol 100 g^{-1} of cardoon) as well as a shorter processing time of 24 h for SSSF, when compared to the SHF [69].

Currently, the application of cardoon to Wastewater Treatment Plants (WWTP) has been of great importance. The behavior of the *Cynara cardunculus* when wastewater (WW) and digested sewage sludge were applied in a Spanish plantation, specifically, in Alcázar de San Juan, was evaluated, aiming at the implementation of this technology for thermal energy production. Five parcels of 100 $m^{2\,w}$ were evaluated, each one with different irrigation, namely, drinking water taken as the control, treated WW, 1 t ha^{-1} of air-dried sewage sludge, 2 t ha^{-1} of air-dried sewage sludge, and 0.7 t ha^{-1} of commercial inorganic fertilizer. The moisture and heating value (High and Low) of cardoon in each parcel were determined. The moisture was in the range [2.08–3.63%] and the Lower Heating Value (LHV) and Higher Heating Value (HHV), were in the following ranges [3.68–3.84) kcal kg^{-1} DM (HHV) and [3.41–3.56] kcal kg^{-1} DM (LHV), respectively. As the difference was not significant, they concluded that it is possible to obtain a similar quantity of energy when the cardoon is irrigated with WW and sewage sludge or commercial fertilizer. The unique problem that can be found in the sewage sludge is the high salinity, thus, it is important to make a continuous characterization of this material [70].

In Portugal, cardoon was proposed for guaranteeing high productivity in the territory, namely, an area of 72,313 ha (0.81% of the total area in Portugal's mainland which corresponded only to degraded and marginal lands), with low requirements concerning the soil and water type, and included energy production in several biochemical and thermochemical technologies [71].

2.1.2. Giant Reed (*Arundo donax* L.)

Arundo donax L., also known as giant reed (family Poaceae, order Cyperales, and class Liliopsida), is an erect, reed-like grass, herbaceous, perennial cane, aggressive and invasive species with the capacity to reproduce quickly, either by seed propagation or by vegetative propagation, being a primary threat to native riparian habitats worldwide and out-competing native plant species in the access to soil-water.

Giant reed is a poly-annual culture that presents average yields of 15 to 40 t DM ha^{-1} $year^{-1}$ [6,28,29]. This species can be applied for energy generation [72], paper pulp, and fiber production (e.g., cellulose for rayon fabrication), and is widely used as an ornamental material for basket-work manufacture, barriers to gardens (trellises and garden fences), crude shelters, construction and roofing materials, livestock fodder, fishing rods, and arrows. Medicinally, the rhizomes and roots have been used for many uses, and culinary uses of the young shoots and leaves, and the rhizome have been proposed [72,73]. It has been also planted along ditches and drainage canals for erosion control or as a bank stabilization agent. Although well known as an aggressive invasive species, the wide commercial applications of *Arundo donax* wide will contribute to further development and adoption of this crop, bearing in mind that the exploitation of this species and its invasive character requires careful reflection [74,75]. With the constant search for biofuels that is expected to increase over time, it is anticipated that the latent interest in this giant reed, considering the high yields it presents, will increase.

Data collected by Corno et al., 2014 show that the giant reed presents major biomass productivity in comparison with other energy crops, allowing a higher generation of biofuel and energy per unit area. Therefore, it can substitute other energy crops, with a diminution in the cost of biomass production. However, there is very little data about the utilization of *Arundo donax* for energy and biofuels generation, therefore, so much remains to be explored [76].

The conversion of *A. donax* into bioenergy has been carried out either by biochemical pathways or thermochemical conversion routes. The biomass of *A. donax* can be used for three types of bioenergy: solid biofuels (in briquettes and pellets including direct biomass combustion [77]), biogas, and biomethane production has been proposed by [78–80], and bioethanol [81–84].

The giant reed represents an adequate species for the biorefineries when its wide utilities are considered. A dedicated *A. donax* crop was subjected to hydrothermal pre-treatment by Di Girolamo, Grigatti, Barbanti, and Angelidaki, 2013 to analyze its potential for biogas generation. Three different situations were applied: without catalyst, during a time (24 h) of substrate impregnation, utilizing 2% w w^{-1} sulfuric acid (H_2SO_4), and instant incorporation of 2% w w^{-1} H_2SO_4 previous steam cooking for pre-treatment parameters; temperature between 150 °C up to 180 °C and time from 10 to 20 min. The results of batch digestion tests, made with 4 g VS L^{-1} on thermophilic conditions, namely 53 °C, during 39 days, presented a methane yield of 273 mL g^{-1} VS incorporated for unprocessed biomass. The no catalytic reactions of biomass reached a yield of 23% for a temperature of 180 °C and a duration of 10 min. The reactors that treated catalyzed biomass were experiencing methanogenic inhibition. This type of inhibition can be caused by the competition with the sulfate-reducing bacteria (SRB) [42]. For Mediterranean conditions, *A. donax* could be an interesting choice as feedstock for biogas facilities [84], concerning profitability, a plant size of 300 kW was referred to as the most beneficial for bioenergy production from *Arundo donax*.

According to Maucieri et al., 2019, the highest biomass, ethanol (3.5 t ha^{-1}), and methane yields (8227 m^3 ha^{-1}) in a four-year study were obtained with *Arundo donax* among thirteen pluri-annual herbaceous cultures previously chosen for their potential biomethane and bioethanol production. This highlighted *A. donax* as one of the most interesting species for biofuel production [6].

The pre-treatment of *Arundo donax* biomass is required for bioethanol production but as this step has been considered the most energy demanding, this should be accounted for in any life-cycle energy balance [84]. Muthuvelu et al., 2019 evaluated giant reed as a novel source of sustainable lignocellulosic residues for bioethanol generation utilizing ultrasound-assisted alkaline pre-treatment. *Arundo donax* presented 214 $\pm$ 3 mg g^{-1} maximum reducing sugar release, yielding a fermentation efficiency of 83 $\pm$ 7% [85].

A microwave–alkali-assisted pre-treatment in one stage has been proposed for *A. donax* pre-treatment with some added benefits, such as less energy consumption, fast heating, and less toxic compound production. The utilization of 5% NaOH solution yielded the highest sugar monomer yield (6.8 g per 100 g of biomass) [86].

Ba, Liu, Wang, and Yang, 2020 carried out pyrolysis studies of *Arundo donax* as feedstock and well as a final potential study of giant reed for alternative sources of materials, energy, and chemicals calculated according to average biomass productivity and marginal soils area in China. An industrial scale (2000 t day^{-1}) would yield 28 MW power, 51.36 t day^{-1} bio-oil, 555.04 t day^{-1} vinegar, and 511.36 t day^{-1} biochar from 9 million t of feedstock obtained in 0.3 million ha of marginal soils at a predicted 30 t ha^{-1} year^{-1} [87]. Moreover, soil remediation and sewage decontamination near aquatic bodies would also occur as *A. donax* was an excellent species to advance the quality of water-polluted bodies and contaminated lands [88], which is of particular significance for the further development of dedicated biorefineries [87]. Finally, Fernando, Barbosa, Costa, and Papazoglou, 2016 concluded that *A. donax* had the big production levels among nine studied species, comparatively an energy balance positive together with the lowest GHG emissions, low nutrient requirements, and the lowest cost per ton of dry biomass or per unit of energy for Mediterranean conditions [88].

The economics of energy crops have been neglected or, to some extent, limited in the literature. The economic aspects of *A. donax* were analyzed from a systematic survey of publications by Jámbor and Török, 2019. Giant reed was proven to have a high potential for a cost-effective biomass generation either in marginal or disadvantageous small areas due to favorable yields and energy balance, high Capital Expenditure (CAPEX) but low Operational Expenditure (OPEX), making its production attractive and potentially economically sustainable (biomass supply and generated revenue) [84].

According to the same publication, giant reed presented the second-highest energy production cost (2.34 € GJ^{-1}), but the highest nutrient-use yield for phosphorus (P) and nitrogen (N) among several studied energy crops. This suggests that *A. donax* is a clear option to utilize further to convert WW (as a source of N and P) into biofuels in the frame of the circular bioeconomy.

2.1.3. Hemp (*Cannabis sativa* L.)

Hemp is a spring crop plant (herbaceous crop) belonging to the family Cannabaceae, order Urticales, and class Magnoliopsida. It has a strong soil structuring capacity, with a strong upright root and its stems are rich in cellulose and lignin. The seeds have a high fat and protein content. Industrial hemp is grown for its stalk, seed, or both. The interior of the stalk is made of woody fibers called “Hurds” that represent a cheap cellulosic residue [89]. The outer part consists of long bast fibers [90]. It is a fast-growing crop [91] and is suitable for production in sandy soils [92]. For centuries, hemp fiber has been very important worldwide, being used in the production of ropes and in the textile sector [93], presenting more advantages than cotton as it does not require as much area for its cultivation and does not need the incorporation of pesticides and insecticides [94].

Currently, new applications of this species have emerged at the industrial level, the most relevant being presented below: in paper production of higher quality than that from wood, thus avoiding deforestation of the forest [95]; construction material industries for the production of sustainable materials specifically isolations from hemp fiber [96]; personal uses like essential oils [97] which can be used to control insects and pests due to their insecticidal and antimicrobial action, in the manufacture of soaps, fragrances and candles [98]; in the pharmaceutical industry for its compounds such as cannabidiol (CBD) [97] and Δ-9-tetrahydrocannabinol both extracted from unpollinated flowers [99]; chemical products such as detergents, varnishes, paints [100], solvents, printing inks, and biopesticides; in WW treatment; in the animal litter production; in the automotive sector as vehicle parts and other internal components; in the fashion industry, and; in the production of jewelry, furniture, nutraceutical, cosmetics (including cosmeceutical), medical and acoustic products [98]. *Cannabis sativa* can be used for biocomposites production [101,102] and innovative and sustainable materials such as bioplastics [98], namely in biodegradable container production with an antibacterial effect [103]. In the food industry, seeds can be extracted from various chemical components such as oil (omega-3 and omega-6 fatty acids) and proteins [99] used in the natural beverages production [98], and the remaining material is often used after the extraction of the oil from the seed for animal feed due to the high presence of proteins [95]. The sectors linked with *Cannabis sativa* that are of greater commercial interest are textile, paper, food, and construction, and those that are under development are the automotive and cosmetics industries [98].

The application of hemp as a raw material to be used in the new industrial units designated by biorefineries for biofuel production [104] has several advantages. In addition, it is also a crop used for energy purposes, either for burning, for the biofuels generation (e.g., bioethanol), and biochemical bioproducts like succinic acid produced in the microbial fermentation stage of sugars from hemp hydrolysate, being an acid that allows the production of other products with high added value such as biopolymers, green solvents, and pharmaceutical products [30]. It is important to know that 1 t DM of hemp makes it possible to produce 149 kg of bioethanol and 115 kg of succinic acid [98]. In relation to the high oil content and the biomass amounts that are generated, there are also environmental sustainability benefits derived either from the possibility of its use as a rotation crop replacing traditional food crops or from the low use of pesticides. Hemp also has the potential of reducing the amount of pesticides in succeeding crops.

There are other energy uses from industrial hemp. Some of them are [105] from chemical processes, and the biodiesel from cannabis seed oil by the transesterification process with methanol [106,107]; in the biochemical process, are the biogas from AD [108–112] and bioethanol obtained through fermentation of biomass [113], and lastly, for thermochemical process, the heat from direct combustion utilizing solid fuels [110] as briquettes [97,108] or pellets produced from cannabis hurds and stems or electricity in systems like Combined Heat and Power (CHP) from cannabis biomass and pyrolysis [114].

Biodiesel production is possible from the oil seed. Assuming a seed yield of 2 t ha^{-1} and an oil seed content of around 35%, and oil yield of approximately 814 L ha^{-1} can be obtained. Due to the high yield of hemp oil in biodiesel (around 97%), a total biodiesel yield of 789 L ha^{-1} is reached [38]. Other studies have integrated into a single system the two types of liquid biofuels production (biodiesel and bioethanol) with *Cannabis sativa* as an industrial raw material. Biodiesel was obtained through the extraction of lipids from the material and followed by transesterification. The remaining biomass, therefore, the one free of lipids, was submitted to two pre-treatments: a hydrothermal (free of chemical compounds) and another of disk refining, and finally, enzymatic hydrolysis was applied to obtain bioethanol [104,115]. In this type of process, industrial hemp is seen as a solution to reduce GHG emissions, motivating economic growth at any level [95].

The production of biomethane through AD from hemp crop residues (e.g., parts of the species such as flowers and hurds) was studied by Matassa, Esposito, Pirozzi, and Papirio, 2020 [116]. The highest biochemical methane potential (BMP) obtained was 422 $\pm$ 20 mL methane g VS^{-1} from pre-treated and crude fibers. However, the many commercial uses of the crude fibers make their application for biomethane production less appealing. For the remaining waste material, it was determined that when applying two pre-treatments, one physical (grinding) and the other alkaline (dilution with NAOH) to the hemp hurds, there is an increase of 15.9% of BMP (initial value of 239 $\pm$ 10 mL methane g VS^{-1}) and for hemp flowers mixed with inflorescences when the pre-treatment of dilution with NaOH was applied, there was a 28.5% increase in BMP (initial value of 118 $\pm$ 8 mL methane g VS^{-1}). In conclusion, the application of alkaline pre-treatment increases the production of biomethane (of BMP) and hemp residues represent the potential for its generation [116]. Harvest time influences the amount of material collected as well as the biogas yield obtained [117], therefore, it is important to consider this aspect for further implementation of biomethane production from hemp.

Two scenarios for bioethanol production and eight scenarios for biomethane generation from the *Cannabis sativa* stalks harvested in autumn were evaluated to compare the gross energy production. Two pre-treatments were applied: a physical one that consisted of grinding the material and another physical-chemical process with steam. The two scenarios to produce bioethanol were as follows: In the first, the stems were subjected to a steam pre-treatment, and then, with the hexoses produced, a Simultaneous Saccharification and Fermentation (SSF) was applied (in this step enzymes and yeasts are added) to obtain bioethanol; the second scenario was the same as the first, with the difference being that before the SSF, the material is separated into two phases, one liquid and the other solid, with only ethanol obtained during the solid separation. For the case of biomethane produced by AD, eight different types of raw materials were used separately: crushed leaves, crushed stems, milled stems, stems subjected to steam pre-treatment, stems subjected to enzymatic hydrolysis (pre-treated with steam), the residues obtained in each bioethanol production scenario, and, finally, the liquid phase not used in the second bioethanol scenario. All materials that were subjected to steam pre-treatment were allowed to obtain a higher methane production and, in turn, it was found that the methane yields were very similar in cases where the materials were or were not pre-hydrolyzed. This study shows that the bioethanol and biomethane co-production is doubly advantageous (double energy generation) in a single process because enzymes and yeasts incorporated before SSF for the bioethanol production can be converted into biomethane [118].

Several studies were carried out in order to maximize the cellulose content, by the use of steam and enzymes (pectinase), obtaining cellulose contents of about 78% [119]. Other studies confirm that the high cellulose content present in hemp guarantees a much higher potential for bioethanol production compared to other energy crops like sorghum, kenaf, and switchgrass [89,120].

To get the highest glucose yield in the enzymatic hydrolysis for transformation into ethanol, an optimization of steam pre-treatment parameters under different conditions was performed [43], using hemp silage (leaves and stem) and dry hemp. The SSF process was also applied in both cases. Results showed that the optimal pre-treatment conditions for both materials maximizing the glucose yield were the saturation with 2% SO_2 before the steam pre-treatment at 210 °C for 5 min. The obtained ethanol yields were 163 g kg^{-1} of ensiled hemp DM and 171 g kg^{-1} of dry hemp. These results correspond to the values between 206 and 216 L ethanol t^{-1} hemp (based on initial dry material).

Four types of hemp were evaluated to obtain bioethanol using three types of pre-treatments: Liquid Hot Water (LHW), diluted acid (1% H_2SO_4), and diluted alkali (1% NaOH). The LHW allowed obtaining between 85% to 98% of glucan and between 67% to 71% of xylan. The acid pre-treatment allowed the decomposition of glucan between 5.9% to 10.6 g L^{-1}. The alkaline pre-treatment allowed extracting between 58.6% to 75.3% of the lignin with lower production of inhibitors, with a high amount of glucose and ethanol being obtained, unlike the other two pre-treatments where there was a higher production of compounds inhibitors and low yields of glucose and ethanol due to the amount of recondensed lignin. In the alkaline pre-treatment (which gave the best results), similar ethanol yields were obtained for the four typologies of hemp studied [121].

Spectroscopic determination of several distillates from a slow pyrolysis system with hemp hurds was carried out to evaluate the potential of this process as well as the main products obtained. Crude distillates were collected in three process stages: drying, roasting, and slow pyrolysis, with the system at the initial stage at room temperature up to the maximum operating temperature of 350 °C. The slow pyrolysis process allows increasing the energy yield of biochar by 15%, therefore, it can be seen as a solution to optimize the quality of the product. Biochar can be used as a fertilizer and soil remedial, in filtering processes, and as a composite [100].

For a hemp plantation to be initially applied as a phytoremediator for use in the bioenergy sector such as in transesterification, AD, fermentation, or combustion, it is necessary to evaluate the presence of HMs, radionuclides, and organic contaminants in each process [122] as these components can affect the equilibrium of the system.

2.1.4. Jerusalem Artichoke (*Helianthus tuberosus* L.)

Jerusalem artichoke (JA) belonging to the family Asteraceae, order Asterales, and class Magnoliopsida, have so many names such as sunroot, sunchoke, or topinambur. It is an herbaceous perennial tuberous plant, despite often being managed as an annual, with the sunflower (*Helianthus annuus* L.) being included in the identical genus as the sunroot [19,123,124].

Helianthus tuberosus is a great feedstock to be applied in consolidated bioprocessing, therefore, each part of the plant can be used, e.g., the aerial biomass (stalk) and the tubers. The JA tubers are constituted by two types of carbohydrates: inulin which is a linear polymer [D-fructose units that present β (2→1) bonds, with a terminal of D-glucose molecule that have a α (1→2) bond], and sugars such as glucose and fructose; while the cellulose and hemicellulose are the principal's carbohydrates located in the aerial part of the species. Besides the carbohydrates from the whole plant, the tubers present an N content that can be utilized in the fermentation bioprocesses with the objective of not needing to incorporate additional nutrients [6,31–33].

Conventionally, JA has been applied for food and feed generation and folk medicine, for example, inulin soluble dietary fiber used to replace sugar and fat, and also for its anticancer and immune system boosting properties [125]. However, for the past two decades, an awareness of its significant health benefits led to the exploitation of alternative uses such as the production of functional food ingredients and bioactive compounds. The functional food ingredients derived mainly from JA tubers, such as inulin, fructooligosaccharides (FOS) (considered a probiotic for its bifidogenic properties [126]), and fructose, are particularly beneficial in the treatment of obesity and diabetes type 2 and are also constituted by a high protein value, namely, most of the essential amino acids for life. In addition, several valuable bioactive compounds have been extracted in the aerial part of this species (leaves and stalks), serving as antifungal, antioxidants and applied in medicine for the treatment as an anticancer with pharmaceutical effects [123,124,127–129], with the inulin considered as an excipient and stabilizer (as a drug delivery vehicle to reduce the dose amount and side effects) [125]. Another use that can be given to JA is in the production of cement composites for application in the civil construction sector [33].

Currently, an enhanced interest has arisen in the JA as a potential energy crop for biofuels and bioproducts through biorefinery [19,124,127,130–132] because it has a diversity of characteristics that offer great competitive advantages, like a fast-growing species that adapts very easily to different climatic conditions, with a high yield and amount of inulin [133]. With respect to biofuel production, there are numerous studies describing different approaches to producing bioethanol from JA tubers inulin [130,132,134–136], from JA stalks [137,138] or from the whole plant [19,32,124,127,131,139]. Besides bioethanol, other biofuels have been obtained through JA fermentations, such as butanol [124,140], 2,3-butanediol [141,142], single-cell oil, methane from AD (yields up to $\leq$590 L kg^{-1} VS) [131,143–145], and biogas from pyrolysis [32]. In addition to biofuels, *Helianthus tuberosus* has been used to produce several biodata-based chemicals, like various types of acids such as succinic, butyric, citric, propionic, poly-(L-malic acid), poly-(γ-glutamic acid), and L-lactate among other compounds like 5-HMF and sorbitol [124,126,132]. Moreover, JA crop residues can also be burnt for power and heat generation in the combined form [19], and to produce solid fuels (briquettes and pellets) from the aerial part of the species [133]. Indeed, this species represents a potential biorefinery crop and can be considered a crop with multi-purpose utilities for the generation of various bioproducts (chemicals and fuels) from the whole plant (aerial part inclusive of the tubers) providing elevated economic value. Nevertheless, the advantages of JA as an energy crop for the bioeconomy have only come to light in the last decade.

Biodiesel production from JA tubers and *Chlorella protothecoides* microalgae were studied by Cheng et al., 2009. The tuber hydrolysate was used as a substrate for the selected microalgae species, to produce lipids in a total of 4 days. After this time, a lipid concentration of 44% in dry mass was reached, which was extracted and later transesterified for the biodiesel generation that consisted of the methyl ester of the linoleic acid, oleic acid, and cetane acid. However, 82% of biodiesel corresponds to the methyl esters of unsaturated fatty acids. This study allows us to conclude that it is possible to obtain biodiesel using the tubers of *Helianthus tuberosus* as a carbon source in microalgae cultivation, with a reduction in costs due to the low price of the feedstock [146]. In another study, lipid extraction was also performed using JA tubers hydrolysate as raw material and *Rhodosporidium toruloides* Y4 as a culture medium, obtaining a lipid titer of approximately 40 g L^{-1} and a number of cellular lipids close to 57% w w^{-1}, being demonstrated once more that the hydrolysate of the tubers of JA represents a material with high potential for the production of lipids through microbial pathways or for other biologically based chemical products [147].

In a pilot plant, biogas production was studied using only JA (material available above ground), and the production was analyzed when the biomass was freshly harvested, dried in the open air, and stored in silos (ensiled). The measurement of the BMP determined that the dry biomass in the open air was the one that allowed the production of a greater amount of biogas (including the largest volume of biomethane), with the ensiled material being the one with the lowest biogas production. The microbial community inside the reactor was very similar in both cases (outdoor dry material and ensiled). Thus, it is apparent the conditions in which the biomass is found to achieve greater biogas production from species such as JA [148].

In the biofuel production process where the main objective is to produce or increase the inulin quantity, the removal of the flowers was studied [149]. Between 33% and 100% of the flowers were removed in order to evaluate, for different percentages of removal, the distribution of carbohydrates in the tubers, a factor that increased the amount of material produced in the species (from 20.5% to 44.4%), being distributed approximately was 12% to 37% for the stems, 57% to 218% for the leaves, and 29% to 43% for the tubers, with the latter being where the largest amount of inulin present in the species is concentrated. Removing the flowers also allowed for reducing the amount of ash (from 25% to 100%) as well as increasing the calorific value of the tubers (from 33% to 100%). When the flowers were 100% removed, the greatest amount of biomass in the tubers was obtained, being 228 g tuber $plant^{-1}$, therefore, aiming at producing a greater amount of inulin to subsequently produce biofuel such as bioethanol, as well as to improve the chemical properties of the species, the flowers should be removed entirely, and these should be used to produce other value-added products.

Jerusalem artichoke is a raw material suitable for bioethanol production and other products such as D-psicose, which allows the production of other types of sugars such as D-glucose and D-fructose. The process comprises the steps of hydrolysis and enzymatic conversion, fermentation by yeast, and pervaporation, and, after this last phase, the collection of D-psicose and bioethanol takes place with an approximate yield of 15 mg mL^{-1} and 14 mg mL^{-1}. From the 56.47 mg mL^{-1} of D-fructose present in 100 mg mL^{-1} of *Helianthus tuberosus,* 18.2 mg mL^{-1} of D-psicose were produced, [150], therefore, the products with high added value can be obtained from a raw material considered to be of low cost.

Jerusalem artichoke ethanol yield reported ranges from 1500 to 11,000 L ha^{-1} from tubers and from 2835 to 11,230 L ha^{-1} from aerial biomass [44]; while sugarcane ethanol yield ranges from 2800 to 8764 L ha^{-1} and corn ethanol yield ranges from 2000 to 6698 L ha^{-1} [44,132]. Paixão et al., 2018 made a comparison between the total energy consumption and the CO_{2eq} emissions of the *Helianthus tuberosus* tubers for the ethanol production that was produced in the refinery of sugar beet, sugarcane, and corn, concluding that this species represents a feedstock with a high value to be utilized as an additive in the blend of ethanol/gasoline. Therefore, it represents a promising sustainable alternative [136].

A Jerusalem artichoke plantation of 1 ha can produce between 18 to 28 t of residual material specifically for foliage, with the tubers harvested from the species being used for other purposes. To use these residues at the bioenergy level, they will be subjected to a pyrolysis process with various heating rates, namely, 10, 20, 30, 40, and 80 °C min^{-1}, in an oxygen-free (inert) atmosphere, reaching better thermal transformation conditions at a temperature between 270 °C to 430 °C. At temperatures above 430 °C, lignin degradation and coal formation were achieved. An analysis carried out on the gaseous fraction found the release of phenols, aldehydes, esters, carboxylic acids, methane, and aromatic hydrocarbons, therefore, products with a high energy content for energy production, and other valuable products such as solvents were also verified (toluene and acetic acid). This system (maintaining the same temperature conditions) can also be extrapolated to an industrial scale whenever it is optimized to obtain products with high-energy load, bio-oil, and syngas. Considering this system, it can be said that JA residues (without considering the tubers) represent a crop with broad advantages for chemical and energy production [151].

2.1.5. Linseed (*Linum usitatissimum* L.)

Linseed is utilized for linseed oil generation, textile fiber, and seed [152] and is an easy crop to grow, and does not require high soil nutrients.

It also has a high content of unsaturated fatty acids and the seeds have a low cost when compared to others of the same genus (oily) [153]. Flax oil is a relevant vegetable oil utilized in the food industry (cooking oil) and in other applications like natural oil, the generation of omega-3 fatty acid obtained from the high content of α-linolenic acid, and the medicinal sector for the control of several diseases as rheumatoid arthritis, blood pressure, and cholesterol [154]. There exists a high interest in *Linum usitatissimum* for utilization in dietary supplements and functional foods [155], with an increasing need to identify strategies to increment its productivity to meet the growing demand [156]. Flax, apart from linseed oil production, can also be used as fiber and as feed for livestock [154].

Linseed oil is utilized too for biodiesel generation [157–159], and its utilization in diesel engines results in high-performance parameters namely, brake thermal efficiency (BTE), low brake-specific fuel consumption (BSFC), and power output [160]. Biodiesel produced from *Linum usitatissimum* L. can also be used in blends with other fossil fuels such as petrodiesel in combustion systems and it has been found that this type of biodiesel achieves high efficiency at the maximum compression ratio (18:1) without that this could cause engine problems [161]. Characteristics like low volatility, high viscosity, and polyunsaturated are problems that arise when it is made to be the substitution of vegetable oil for a diesel engine as fuel. These parameters can be changed with other options such as pyrolysis, microemulsion, dilution, and transesterification. Several production systems can be applied for biodiesel generation [152].

Data of linseed oil methyl and ethyl esters such as viscosity and flash point are values that are strongly reduced after the transesterification phase. Several chemical parameters of linseed ester fuel were analyzed, being 0.03% free fatty acids value, 27.8 m_{eq} kg^{-1} for peroxides, and, lastly, the free glycerol was 0%. After the transesterification reaction, it was verified that the density value, specifically, of linseed oil and linseed oil methyl ester was similar to the density of conventional diesel fuel and in relation to other parameters, the linseed oil heating value was 10% lower than diesel because of the presence of a higher oxygen content [152].

A high value of polyunsaturated fatty acids characterizes linseed oil fatty acid methyl esters (LMEs); they oxidize fast, and, therefore, such products can be blended with other FAMEs to be utilized in diesel machines [162]. Linseed oil methyl ester characteristics are comparable with diesel fuel and present a lower carbon monoxide (CO) emission when compared to conventional diesel. It is utilized in diesel machines yielding very good results, like high BTE, high power output, and low BSFC.

Linseed oil was submitted to a continuous transesterification process, in a fixed bed reactor, using calcium oxide (CaO) as a catalyst, to evaluate the yield of FAMEs under these conditions. The main idea was to compare the behavior of the system with and without the presence of the co-solvent, with three variables analyzed: the molar ratio of diethyl ether (DEE) (co-solvent) in relation to methanol (most relevant variable), the molar ratio of methanol to oil, and the volumetric flow (ml min^{-1}) based on the yield of FAMEs. The presence of the co-solvent allowed obtaining the maximum yield of FAMEs (98.08%) with a molar ratio of DEE to methanol of 1.19:1, a molar ratio of methanol to oil of 9.48:1, and a volumetric flow of 1.37 mL min^{-1}, at a temperature of 30 °C and 160 g of CaO. When the reaction took place without the presence of the DEE, the maximum yield of FAME was 75.83%, therefore, the absence of agitation and incorporation of a co-solvent into the system effectively increased the yield of FAMEs [39]. In another study, the transesterification process with and without the presence of a co-solvent [tetrahydrofuran (THF)] was also evaluated, but the agitation was applied in both cases and with a potassium hydroxide (KOH) catalyst. The effectiveness of the co-solvent in biodiesel production systems from *Linum usitatissimum* was demonstrated once more, as it allows a greater mass transfer between the steps of the system, facilitates the occurrence of the transesterification reaction, with lower temperatures, reaction time, and agitation rates (40 °C, 90 min, and 700 rpm), achieving a high biodiesel yield (93.15%) and high FAME purity (99.8%). When THF (co-solvent) is not present, the results are less desirable as it requires higher temperatures, reaction times, and agitation rates (50 °C, 120 min, and 750 rpm), achieving a lower biodiesel yield (84.3%) and lower purity of FAME (99.7%) [163].

It was published that a maximum biodiesel yield of 93% can be obtained with linseed oil that presents 4% moisture [164]. Thus, there is a research gap in biodiesel generation from linseed oil, namely in the optimization of the main preparation parameters, like the reaction temperature (transesterification phase), catalyst proportion, the methanol to oil ratio (M/O), and the reaction time. The yield of biodiesel production over transesterification depends on several operating aspects, like the reaction time and temperature, catalyst weight percent, and alcohol/oil molar ratio.

Linum usitatissimum has been used in the last 40 years as a crop with high potential for soil phytoremediation [165–167] and WW, specifically in terrains with a high load of HMs, being highly resistant to these components [154], and managing to store a greater amount of HMs in the aboveground part of the plant (aerial) and less in the roots.

2.1.6. Miscanthus (*Miscanthus* × *giganteus* Greef et Deu)

Miscanthus spp. is a C4 perennial rhizomatous lignocellulosic crop, with a good potential for bioenergy, biofuels, and bio-based product generation [168,169]. The plant *Miscanthus* × *giganteus*, belongs to the family Poaceae/Gramineae, order Cyperales, and class Liliopsida [170]. In Europe, this crop is gaining relevance as an energy grass given its aptitude to grow under a large spectrum of climatic conditions, its high yields, and an estimated productive lifetime of at least 15 to 20 years [171].

Miscanthus × *giganteus* is an attractive material for many uses, such as thatching, animal bedding, pulp for paper, fibreboards, nanocellulose production, and inclusion in composites and building materials, among others [7,170,172,173].

Yet, its most current use is as solid fuel as the heat capacity of the miscanthus biomass is very high (18.5 GJ Mg^{-1} [174], LHV of 16.4 GJ Mg^{-1} [175]). Indeed, the benefits of this crop rely on the fact that its cultivation on marginal soil and its use for stationary power and heat generation can attain substantial greenhouse gas emission and non-renewable energy savings, up to 13 Mg CO_{2eq} ha^{-1} $year^{-1}$ and 230 GJ ha^{-1} $year^{-1}$, respectively. In addition, in relation to energy and GHG emission savings, miscanthus was the crop that performed better when used in a small CHP, compared with other perennials, namely, giant reed, cardoon, and switchgrass [176]. Moreover, experiments with miscanthus conducted in a pilot-scale gasification plant also indicated a high potential for energy generation and friendliness from an ecological standpoint [177]. Besides, this crop benefits from the fact that it presents low ash and nitrogen content (respectively 1.96% and 0.09 % w w^{-1} DM, [175]), which are two important parameters when evaluating the adequacy of biomass as feedstock for combustion to generate electricity, heat, or CHP. Yet, miscanthus biomass usually presents a high slagging propensity because of its high chloride (Cl) and potassium (K) contents when compared to wood biomass, which may limit its conversion with processes operating at high temperatures, such as combustion and gasification [175]. In addition, the lower yields and the increase in biomass ash and nitrogen content that can be achieved when the biomass is being harvested from marginal or contaminated soils can compromise its technological and economic exploitation [178].

Other conversion technologies of miscanthus to energy can be either thermochemical (torrefaction, pyrolysis) or biochemical (AD, fermentation to ethanol). In the torrefaction process, the biomass is pre-treated with heat in an oxygen-free environment, and the resulting solid and energy-dense material can be pelletized, being suitable for direct combustion in boilers, co-firing in large power plants, or gasification to syngas. Hydrothermal carbonization (HTC) and slow pyrolysis are the other two pre-treatment processes that can also be applied to miscanthus. In the study of Wilk and Magdziarz, 2017, the effect of these pre-treatment processes (slow pyrolysis, torrefaction, and HTC) on the properties of *M. giganteus* were analyzed and the results indicated that there was an improvement in the combustible characteristics of the obtained biochar when compared to raw biomass by the increment of carbon content. Pyrolysis is a conversion technology where the biomass is heated rapidly to a high temperature in an oxygen-free environment, converting the lignocellulosic-rich biomass into pyrolysis oil which can be used for combustion or could be further upgraded to a range of higher-value products [179]. Lakshman, Brassard, Hamelin, Raghavan, and Godbout, 2021, found out in their study that the optimal pyrolysis parameters to generate a bio-crude oil from miscanthus with a biomass residence time of 81 s, with a low water content was a temperature of 510 °C and a nitrogen flow rate of 5.1 L min^{-1}. The bio-crude oil obtained under these conditions presented a water content of 25.3% and a higher heating value of 15.8 MJ kg^{-1}. The process yields bio-crude oil (18.8%), biochar (22.1%), the aqueous phase of bio-oil (18.3%), and non-condensable gases (40.8%) [46].

In current commercial digesters, the agricultural residues can be supplemented with a feed of energy crops (which includes miscanthus). The AD converts biomass/miscanthus to biogas (with a high methane content), and this biogas can be applied in CHP units or it can be upgraded to methane, and the remaining digestate can be applied as fertilizer [180]. Yet, because the digestion of the lignocellulosic material of miscanthus is difficult due to the complex chemical structure, its degradability should be increased by using a physical, chemical, or biochemical pre-treatment. Miscanthus also represents an option for the second-generation ethanol production. In this case, the cellulosic material needs to be separated from the lignin and then hydrolyzed to its sugars, for fermentation. Therefore, the material needs to be pre-treated with biological, chemical, or physical methods, or with a combination of these methods, to minimize the recalcitrance of lignocellulosic biomass to transformation into sugars. Different studies are currently being done to optimize the bioethanol production from miscanthus which can yield between 0.10 and 0.13 L kg^{-1} [181], although improved yields can be obtained depending on the chosen pre-treatment and fermentation strategies.

2.1.7. Sorghum (*Sorghum bicolor* L. Moench)

Sorghum (family Poaceae/Gramineae, order Cyperales, and class Liliopsida) is a C4 plant. The most cultivated sorghum varieties are biomass (or energy) sorghum, grain sorghum, and sweet sorghum, which are distinguished by their chemical composition, morphological characteristics (size and amount of grain), and applications [7,25,35]. The specific fractionation of sorghum hemicellulose to obtain xylose-rich solutions which can be further converted into added-value products can also be a good alternative for using this abundant resource [182]. Although there are not many examples in the literature regarding the utilization of sorghum pentoses for bioproducts, their conversion to xylitol was previously reported [183,184].

Sorghum bicolor presents three constituent parts (leaves, panicle, and stalk), and every part may be utilized for the generation of a diversity of products. In many countries on the Asian and African continent, sorghum is considered a food crop, specifically sorghum grains due to its high nutritional value in terms of micronutrients and antioxidants, being also gluten-free, therefore, it is a food option for those intolerant to this protein, becoming a food considered healthy in many developed countries. It also has a high potential for genetic improvement although this feature has only been partially explored [25]. The gasification process was also studied for the sorghum stover [185] and the sorghum straw [186].

Energy sorghum can be transformed into energy carriers by biochemical processes like bioethanol [187,188], and in European temperate regions, also by thermochemical pathways like gasification, pyrolysis, and combustion, for electricity, heat, biofuel, and biochar generation [189,190]. Biochar, for example, has been successfully used for soil remediation and for the diminution of GHG emissions and as soil fertilizer [111,190]. Sorghum biomass as well as grains can be used in the production of enzymes, microbial lipids, bioproducts for industrial use, bioactive compounds to improve human health, and to be applied as a phytoremediator in contaminated soils [41].

Sorghum oil extracted from grains has a high potential for biodiesel production as demonstrated by several studies [191–194]. The alcohols used for the transesterification reaction were in some cases methanol and in others ethanol, with different molar ratios of alcohol to oil (e.g., 3:1, 5:1, 6:1, 8:1, 12:1, and 24:1), with temperatures between 30 °C to 67 °C, different types of catalysts such as NaOH, KOH, and zinc ethoxide and NaOH oil weight percentages ranging from 0.25% to 1.5%. The most relevant aspects found in these studies were that when both methanol and ethanol are used with a NaOH catalyst, a very similar ester yield is obtained of 92% and 92.9%; when it is applied in a 6:1 molar ratio and a 1.5 wt% NaOH oil, there is a decrease in the formed ethyl esters caused by soap formation [41]. In another study by Wyatt, Jones, Johnston, and Moreau, 2018, the sorghum grain bran was subjected to a transesterification process using methanol, with temperatures of 25 °C and 40 °C and sodium methoxide ($NaOCH_3$) catalyst, where the highest yield of ester was obtained equal to 98.3% [195].

Sweet sorghum can be separated into three forms: grain, extraction from soluble sugar broth, and lignocellulosic biomass [35]. Wet and dry grains from sorghum distilleries can be used for the generation of livestock feed and energy [41]. Sweet sorghum in India is used to produce brown sugar and for lighting in remote areas through lanterns that burn bioethanol (from sorghum). After extracting the juice, the dry fibrous waste material called bagasse can be used in combustion systems [196] to subsequently generate heat and electricity in CHP systems, produce paper, compost, bioplastics, bioethanol [197], butanol, pellets, plastic, and wood compounds, biofertilizer, and animal fodder [35]. The sorghum silage (from bagasse) can be utilized as food for dairy cattle due to its high amount of minerals and micronutrients [197] and for biogas generation [198]. After concentrating the juice in syrup, the foam produced can be processed to produce biofertilizers and feed cattle. The material known as vinasse (distilled obtained after the ethanol production from the juice) is used in AD systems to produce biomethane and as a soil biofertilizer in agricultural areas, thus seeking to reuse as a residue [197].

Sweet sorghum, in particular, is very interesting because, after the extraction of the soluble sugar, the residual biomass is a typical lignocellulosic feedstock adequate for producing: ethanol [188,196,199], methane [200], or both [201]; AD and biohydrogen production [202], and: biobased products such as butyric acid which can be obtained from sweet sorghum stalks after being subjected to enzymatic liquefaction using *Clostridium tyrobutyricum,* as bacteria, with a possible yield obtained of butyric acid equal to 0.39 g g^{-1} consumed sugars [203]. As the sweet sorghum stalks contain juice with high sugar content, the ethanol produced from this juice is claimed to be cheaper than corn ethanol [204]. Furthermore, the cost to cultivate sweet sorghum is inferior to sugarcane [205,206]. These advantages have certainly contributed to the increased number of works dealing with ethanol production from sorghum [207–211]. Although despite the important advantages mentioned, there is still no commercial plant based on this feedstock.

Biogas from different parts of sorghum (ensiled sorghum forage, trunk, sweet sorghum stalks, among others), has been widely studied. With ensiled sorghum forage [40] a maximum methane yield of 316 mL methane g^{-1} VS (Volatile Solids) was obtained using sludge as inoculum from a plant of sugar [41]. Sweet sorghum stalks [212] were also used as a feedstock for biomethane generation, with a maximum yield of 284.37 mL methane g^{-1} VS being utilized in the sludge from a biogas industrial unit [41]. For the biogas production from the sorghum trunk [213], sludge from a WWTP was used as an inoculum, which obtained a maximum yield of 478 mL biogas g^{-1} VS [41]. Finally, with the sludge from a WWTP used as inoculum, a maximum methane yield equal to 303 L methane kg^{-1} sorghum biomass was obtained [41] using as raw material sweet sorghum biomass [214].

Bioethanol is the biofuel that presents the largest number of studies using sorghum as a raw material, most of which are presented in Stamenković et al., 2020 [41]. The juice extracted from sorghum stalks [215,216] has a high potential for the formation of bioethanol, having greater potential than the juice extracted from sugarcane. However, the factors that limit obtaining a higher yield of bioethanol are the low amount of monomeric sugars, high cell growth, and the need to clarify the juice. For the broth extracted from sorghum stalks, the highest maximum yield of bioethanol obtained was 0.51 g g^{-1}, in processes that used the yeast *Saccharomyces cerevisiae* and the bacteria *Escherichia coli* [41]. Sorghum bagasse [217] is a by-product that comes from the juice extraction process with a high amount of cellulose, hemicellulose, and lignin being pre-treated through several processes such as washing, drying, milling, sieving, pasteurization, and hydrolysis. Enzymatic hydrolysis and ammonia fiber expansion were the two hydrolysis methods that allowed obtaining the highest maximum bioethanol yield of 0.495 g g^{-1} using *S. cerevisiae* as yeast [41]. Sorghum stalks (without leaves) [218] are usually dried and ground to be subsequently hydrolyzed and fermented, with the highest maximum yield of bioethanol (0.48 g g^{-1}) obtained when it was performed a direct fermentation with the fungus *Mucor indicus* [41]. The sorghum stover [219], sorghum grains [220], the whole plant [221], and sorghum liquor waste [222] were also studied for bioethanol generation.

Biohydrogen production from different parts of sorghum (sweet sorghum extracts and syrup, bagasse, stalks, bark, among others) has been widely studied. With the extract of sweet sorghum [223] a maximum hydrogen (H_2) yield equal to 0.93 ± 0.03 mol H_2 mol^{-1} glucose was obtained using indigenous microflora as a culture medium in the fermentation [41]. Sweet sorghum syrup was also utilized as a feedstock for biohydrogen generation, obtaining a maximum yield of 0.68 mol H_2 mol^{-1} hexose and using a mixed culture medium [224]. Sorghum stalk was subjected to a fermentation process using mixed anaerobic sludge collected from a landfill as inoculum, with the maximum H_2 yield equal to 127.26 mL g^{-1} TVS (Total Volatile Solids) [225]. For the biohydrogen production from sorghum bark, the bacterium *Clostridium beijerinckii* was used, which allowed obtaining a maximum yield of 1.051 mol H_2 mol^{-1} RS (reducing sugar) [45]. With sorghum bagasse [226], a maximum H_2 yield equal to 4.68 mol H_2 kg^{-1} degraded substrate was obtained using as a culture medium the microflora from buffalo manure [41]. Finally, using sludge from a WWTP, a maximum H_2 yield of 47.3 mL g^{-1} glucose and xylose [41] was obtained, a process that was subjected to sorghum leaf waste [227].

The thermochemical processes that can be applied to sweet sorghum (stalks or bagasse) are rapid pyrolysis [228–231] and the torrefaction [232] to the formation of products with high added value like bio-oil and biochar and finally, hydrothermal liquefaction (HTL) [233].

The slow pyrolysis process was also applied to sorghum [234], sorghum bagasse [235], and sweet sorghum [236] to evaluate in the first two the potential production of an aqueous product such as bio-oil and another solid such as biochar, and in the last one, only biochar formation. Additionally, for energy sorghum, a conventional pyrolysis process was applied, in a batch-type reactor operating at high pressure (6.9 bar or 100 psi), to evaluate at 400 °C, 500 °C, and 600 °C, and a heating rate of 4 °C min^{-1}, the yield of the products obtained in the different phases (liquid, solid and gaseous) for each temperature. The bio-oil yield was equal for the three temperatures (400 °C, 500 °C, and 600 °C) being 3 wt%, and for the case of biochar, the highest yield was obtained at 400 °C being 40 wt%, therefore, as the process temperature increases, the production of the solid product decreases [237].

Hydrothermal liquefaction was applied to sweet sorghum bagasse to obtain energy products like biochar and bio-oil. The material was subjected to washing with water and subsequently dried at room temperature, ground, and sieved. In the HTL process, six different types of catalysts were used [KOH, Ni/Si-Al, Zeolita Socony Mobil-5 (ZSM-5), potassium carbonate (K_2CO_3), formic acid, and nickel phosphide (Ni_2P)] with some homogeneous and others heterogeneous, with temperatures between 300 °C and 350 °C. According to the results obtained, the best bio-oil yield was obtained with K_2CO_3, KOH, and Ni/Si-Al at 300 °C, with values of: 61.8%, 42.3%, and 45%, respectively [47]. Regarding the biochar yields obtained when using these catalysts, the values were approximately 20%, 25%, and 40% [41].

Sorghum has been shown to be an excellent soil decontaminator [238]. After the restoration of the soil has been achieved, the species can be used to produce bioethanol and other products with high added value. However, as in the study by Xiao et al., 2021, due to the accumulation of cadmium (Cd) in the stalks, further studies should be carried out to eliminate the Cd present in the species as it is an element with high mobility and toxicity, and if the material is used in biorefineries, it can generate pollution [239]. For these reasons, the accumulation of HMs should be in the roots in order to make the aerial part of the species useful [41].

2.1.8. Switchgrass (*Panicum virgatum* L.)

Switchgrass belonging to the family Poaceae/Gramineae, order Cyperales, and class Liliopsida is considered a C4 plant and perennial grass that develop in hot seasons, able to grow under different climates, weather conditions, and soil types, with great longevity, adaptability, and versatility. It has low water and nutritional requirements, needs less intensive agricultural management practices, needs low herbicide input requirements together with the capacity to generate biomass that presents a high content of carbohydrates (cellulose and hemicellulose), and lastly, outstanding resistance against pests and diseases that occurs naturally in this species [240], with no annual reseeding [241].

Switchgrass has been reported to show a tremendous potential for being a cost-effective and sustainable bioenergy feedstock. The ethanol obtained from switchgrass reveals that the energy return is meaningly negative (around 50%) compared to ethanol from corn [242]. The same authors reported the following: for each unit of non-renewable power input required to generate biofuel obtained from *Panicum virgatum*, 6.4 units of renewable power are produced. Considerable benefits from switchgrass cultivation and processing concerning CO_2 emissions have been highlighted by most LCA studies [243–245]. *Panicum virgatum* was recently mentioned in an EU Directive 2018/2001 (RED-II- Annex IX) list as 'non-food cellulosic material' toward the promotion of biogas to be utilized in the transport sector and in advanced biofuels generation, due to its minimum contribution of twice its power amount which is not the case for first-generation biofuels. Bustamante-Silveira, Siri-Prieto, and Carrasco-Letelier, 2021 have analyzed the water footprint (WF) of different bioethanol cropping systems (maize-wheat-sorghum rotation, continuous sweet and switchgrass). The latter presented the lowest values per hectare and per liter of ethanol (12,735 m^3 ha^{-1} $year^{-1}$ and 3.8 m^3 L^{-1} ethanol, respectively), being the best choice for bioethanol crop generation [246].

Considering energy-based biorefineries, two different conversion pathways can be used. Following the biochemical conversion pathway, a list of proposed technologies is as follows: fermentation after pre-treatment and enzymatic hydrolysis unit operations for bioethanol [247] or biomethane [if a dark fermentation (DF) is chosen] or in alternative AD towards biogas [240,248]. When directed to fermentation of its sugar fraction, a pre-treatment step has been suggested to increase the production of fermentable sugars. Depending on the pre-treatment type, glucose and xylose yields have been reported from 70% up to 90% and from 70% to 100% after hydrolysis, respectively. Considering pre-treatment followed by hydrolysis, ethanol yielded from 72% to 92% of the theoretical maximum [240,248]. The application of an enzymatic hydrolysis step with cellulase and b-glucosidase incremented maximum ethanol production by 211.9% when compared with the control that does not present enzymes [240]. Continuous ball milling during fermentation by *Clostridium thermocellum* allowed more than 85% total carbohydrate solubilization of switchgrass without exposing the feedstock to high temperatures or chemicals. This cell disruption method improved cellulosic-based biofuels production, especially bioethanol [249]. Switchgrass was applied to steam explosion pre-treatment in a semi-continuous pre-pilot reactor to obtain a pre-treated solid with significant digestibility for enzymatic hydrolysis. The residence time (5–15 min), different temperature conditions (170–200 °C), and severity factors (2.76–4.12) were utilized for steam explosion pre-treatment, which were combined through a 22-central composite design. The results obtained showed both variables had a big influence on the process, affecting the structure of the biomass and the saccharification yield. Considering the values analyzed in this study, the temperature effect was more eminent than the residence time effect. The best saccharification yield (88.3%) was obtained with the biomass pre-treated at 200 °C for 10 min. A similar result was obtained utilizing a cellulose pulp (commercial) as raw material for enzymatic hydrolysis, confirming that the bestt conditions for switchgrass pre-treatment in the pre-pilot scale were satisfactorily successful [37].

Material and energy balances taken from previous experimental data as well as real switchgrass compositions and enzymatic hydrolysis loads and yields were the starting point for a detailed techno-economic study [250] and a sensitivity analysis. The economic viability of liquid hot water pretreated switchgrass biorefinery was evaluated. Under the scenario of ethanol and electricity coproduction, the generation costs were in the same order of magnitude as other advanced biofuels with competitive oil prices above 100 $ per barrel. Moreover, when other high added value co-products such as furfural, acetic acid, and formic acid are also considered, the minimum ethanol selling point decreased. Plant size, as well as switchgrass composition strongly affect biorefinery economics [250].

Following the thermochemical conversion pathway, four technological options have been previously reported: torrefaction, pyrolysis [251,252], combustion, and gasification, from which the principal energetic products are solid biomass (torrefied), bio-oil, CHP, and syngas [248].

Switchgrass was reported to be pelletized to be utilized as a solid biofuel, having a 14.6:1 power output-to-input relation, which is considerably superior than other liquid biofuel choices from farming [36]. Finally, having in mind biobased product biorefineries, switchgrass can be processed using chemical, physical, and biological conversion routes in order to obtain fine chemicals, pulp, or fiber for paper production and construction materials, including proteins, sugars, and pectins [248], besides its primary use as forage production. Other applications include environmental services such as soil conservation and CO_2 biosequestration due to its remarkable profound root system with a high content of fiber.

Switchgrass was thermochemically converted through pyrolysis (500 °C) or gasification (700–800 °C) [253]. The obtained biochar was proven to be used as an inexpensive pH buffer and source of mineral as well as trace metal nutrients in acetone-butanol-ethanol (ABE) fermentation, replacing very expensive conventional buffers, yielding 18.1 g L^{-1} ABE, which was higher than the control, without biochar. Moreover, using a non-detoxified switchgrass hydrolysate medium, an ABE production enhancement was observed (18.5 g L^{-1}) compared to the control (10.1 g L^{-1}), highlighting savings in the costly detoxification process [253].

2.2. Forest Crops

Forests crops like the short cycle coppice such ss poplar (*Populus* spp.), paulownia [*Paulownia tomentosa* (Thunberg) Steudel], and willow (*Salix* spp.) are woody species characterized to be fast-growing, can be cut and regenerated every 3 to 5 years in a 25-year period, with the purpose of obtaining in a short time high yields for energy generation [5]. This species also serves as protection for many more sensitive areas and in a wide diversity of soils, avoiding in some cases an increase in erosion. They are highly viable for converting into bioenergy and can be used to produce a variety of by-products (information that is confirmed and described in the main text of each culture) which brings numerous advantages for their implementation as feedstock for biorefineries. Based on their characteristics, namely, low S, N, and Cl amounts, the use of ligneous biomass for energy purposes has environmental benefits compared to herbaceous biomass, in particular regarding NO_2 emissions. Another advantage is related to a lower risk of corrosion phenomena in combustion boilers [254].

The advantage of forest crops is that the species like acacia that are invasive crops could be used for biofuel production because they reduce the occupied area, control the reproduction of this species [255], minimize the cost of the removal of this species, and reduce the fuel load that can generate fires in sensitive areas [256]. Acacia dealbata allows a wide variety of products to be obtained, such as the production of paper pulp, like the paulownia and willow species. Other advantages of forest crops are that they can reduce erosion in the areas where they are planted, as seen with the poplar, and their extracts show less inhibitory effects on the fermentative processes of bioethanol production, with higher efficiency for conversion into biofuels compared to other species such as pine (softwood) [257]. Moreover, trees like poplar also present a low ash content and a high amount of cellulose (greater than corn straw and switchgrass [258]). These trees can also retain leachate from landfills and be applied in WW treatment [259], as in studies with poplar and willow. *Populus nigra* has a high value from a bioeconomic perspective, being widely used in the creation of new hybrids in Europe such as *Populus* × *Euramericana* (*Populus deltoites* × *Populus nigra*), and they are fast-growing energy crops with greater advantages [260]. An advantage of the willow is that it is an excellent phytoremediator because it removes between 40% and 80% of nitrate-nitrogen compounds present in groundwater, being a species that serves as a regulator of the chemical composition of the water and the functioning of the soil [261].

Forest species also present some constraints such as acacia which presents an invasive character, an aspect that causes a loss of biodiversity by changing ecosystems and creating competition between species [262]. Additionally, acacia requires well-drained soils [263]. *Pinus pinaster* presents a high concentration of N and S, these elements could generate atmospheric pollutants in combustion systems [264]. Moreover, the main species causing fires in Portugal are *Acacia dealbata* and *Pinus pinaster* [265]. There are food applications that use food-grade grown willow, however, willow produced from marginal lands and, especially contaminated soils, may prevent the usage of its biomass for food and feed purposes.

The chemical composition of the different forest crops is presented in Table 2, for easier comparison between them.

Table 2. Chemical composition of forest crops.

Energy Crops	Cellulose (% w w^{-1})	Hemicellulose (% w w^{-1})	Lignin (% w w^{-1})	Ash (% w w^{-1})	Extractives (% w w^{-1})	Other Components (% w w^{-1})
Acacia dealbata (wood) [266,267]	(42.4–50.9)	(17–29) [xylan (16.4–19.3)]	(19.3–20.1)	(0.5–1.1)	(3.1–5.85)	-
Acacia dealbata (bark) [266,267]	19	21.6	18.6	3.3	37.5	-
Acacia dealbata (leaves and flowers) [266,267]	43.1	(21.6–22.2) [xylan: 18.7]	25.9	(0.5–1.1)	8.3	-
Pinus pinaster [268,269]	[40–50]	[15–24]	[25–33]	0.16	2.9	-
Paulownia tomentosa [270–274]	(39.2–49)	(17.98–28.1)	(17.8–37.6)	(0.5–4.6)	(5.6–8.8)	Holocellulose (39.2–61.5)

Table 2. *Cont.*

Energy Crops	Cellulose (% w w^{-1})	Hemicellulose (% w w^{-1})	Lignin (% w w^{-1})	Ash (% w w^{-1})	Extractives (% w w^{-1})	Other Components (% w w^{-1})
Populus [258,275]	(42–49)	(16–23)	(21–29)	1.8	-	-
Salix viminalis [276–282]	(37–56)	(13–26.7)	(12–37.4)	(0.6–2)	(6.3–7.75)	Holocellulose (63.7–64.5)

As can be seen in Table 2, all the forest species studied [acacia (wood), maritime pine, paulownia, poplar, and willow] present a high cellulose and hemicellulose (polysaccharides) content, and therefore they all have the potential for second generation bioethanol production. All these species also present a high potential for combustion systems because they present a low ash content facilitating the conditions applied inside the boiler, without the need for continuous cleaning of the ash.

In biochemical technologies such as AD and alcoholic fermentation, maritime pine, poplar, and willow have shown potential. However, acacia and paulownia are also considered suitable raw materials for bioethanol production [274]. Some forest species have also been tested for biohydrogen production, with promising results, e.g., paulownia stalks [283].

These forest species described in this study have also the potential for energy production (electrical, thermal, or both), e.g., in combustion processes as solid fuels (woodchips, pellets, and briquettes), for example, the ones produced from maritime pine [284]. Additionally, they can be used to produce bio-oil through pyrolysis, e.g., with acacia [285] and paulownia [286].

In relation to other thermochemical systems like gasification, species such as maritime pine [287], poplar [288], and willow can serve as a raw material in this process. Or in hydrothermal process, e.g., with willow.

More details are described in the following Sections 2.2.1–2.2.5.

2.2.1. Acacia (*Acacia dealbata* L.)

Acacia-mimosa (family Fabaceae/Leguminosae, order Fabales, and class Magnoliopsida) with the scientific name *Acacia dealbata* Link is an allochthonous or introduced woody tree with a large shrub and erect stem [263].

Acacia-mimosa plays an important commercial role since its wood can be used for the paper production through the kraft process by the amount of cellulose present in the material [267], allowing the elaboration of several products like cardboard, the paper for writing and printing, which gives it a special shine, considered of high quality, and more advantageous than eucalyptus due to the low amount of alkali it presents [263], and finally, acacia wood is also used for the production of construction materials and furniture, compounds of interest to the medicinal sector [289,290], xylooligosaccharides [291], syringaldehyde, vanillin [292], and solutions rich in glucose [293,294]. The bark is used for the production of tannins (substances of plant origin) due to the high amount present in the species (greater than 74%) [295] and other compounds such as absorbents [296], those with an antimicrobial and antioxidant capacity [266,297] and the anti-quorum sensing [298]. In the perfume industry, flowers are processed to produce fragrances, as well as perfume fixatives [263], in the production of compounds with anti-inflammatory properties [299,300] as well as other types of products such as bioherbicides [301]. In the ecosystem, the pollen in the flowers presents a relevant function for the continuity of sleep [263]. The extracts from the leaves of *Acacia dealbata* are excellent as a raw material in natural products beneficial to health due to their antioxidant activity [266,302], and the antimicrobials present in the extract [302] are also used for herbicides production [301]. Concerning the timber sector, acacia is considered of high quality for the manufacture of furniture and poles and is also used as fuel for heat generation. Two liquid biofuels that can be produced from *Acacia dealbata* [263] are bioethanol [303,304] and bio-oil. Some studies researched the implementation of acacia for bioproducts and biofuels production in a biorefinery-type system, either from the residual material of the species [305] or from all constituent parts of the species [306].

Muñoz et al., 2007 studied the pre-treatment with two fungi (*Ceriporiopsis subvermispora* and *Ganoderma australe*) maintained at a temperature of 27 °C, moisture of 55% for 30 days, and the organosolv delignification was performed at 200 °C, with 60% of ethanol for 1 h. In this first phase, the pulp yield in the case of acacia was between 31% and 51% and obtained 93% of glucan and 2% of lignin. With the objective of producing bioethanol, it was applied to the pulp material with two process types SSF or SHF being utilized for the *Saccharomyces cerevisiae*. For the SHF and SSF processes, the best conversion to bioethanol was obtained for acacia in the first process from 40% to 48%, and in the second process, it was 44% to 65%. These results concluded that each stage must be improved to obtain a higher conversion of this species into bioethanol, namely, in the pre-treatment through a decrease in the incubation time and in the stage of saccharification/fermentation to utilize a material with a higher pulp consistency [307].

Another study that evaluated the possibility of producing bioethanol with *Acacia dealbata* through a diluted acid pre-treatment, with this phase the most important because it is where the transformation of the lignocellulosic material in sugars for bioethanol production occurs. It was evaluated for two different systems: SHF and SSF, which included a wash with residual Water Insoluble Fraction (WIF). The *Acacia dealbata* presented a high potential to produce bioethanol with 10.31 g ethanol L^{-1} obtained during 24 h with the SHF process and with the other process, SSF, it obtained 7.53 g ethanol L^{-1} over 48 h, so, under these conditions, SHF obtained the best results. However, it is possible to obtain 12.18 g ethanol L^{-1} when the fermentation is made over the soluble fraction of undiluted water in parallel with the SHF process [308].

To evaluate the potential of *Acacia dealbata* in a biorefinery, this species was submitted to an ionic liquid 1-ethyl-3-methylimidazolium acetate pre-treatment for 30 min at a temperature of 150 °C, with 66% of the xylan (20 times higher when compared to untreated raw material) recovered and 88% of cellulose (13 times higher than untreated material). The remaining solid part (substrate) was processed in an enzymatic hydrolysis system (cellulose conversion) for 48 h, which allowed obtaining high yields of fermentable glucose (carbon source) suitable for the biofuels generation like bioethanol and other bioproducts [294], therefore, the application of acacia in an industrial scale system such as a biorefinery is guaranteed.

In Spain, a study was carried out in which several *Acacia dealbata* plantations were evaluated (by the high invasive degree of this species in the south of Galiza and north of Portugal) to characterize the species in relation to the moisture content, volatile percentage, HHV and LHV to determine its energy potential, in several constituent parts of the species such as the trunk and the thin leaves and branches. According to the values obtained, the average moisture content (35.29% for the trunk and 35.22% for the leaves and branches); volatiles (83.58% for trunks and 77.28% for leaves and branches); ashes (0.80% for the trunk and 2.32% for the leaves and branches) and HHV when the material is free of water (without moisture) is 4797.93 kcal kg^{-1} for the trunk and 5181.10 kcal kg^{-1} for the leaves and branches. In turn, the LHV is 4478.65 kcal kg^{-1} for the trunk and 4865 kcal kg^{-1} for the leaves and branches. With these results, the viability of acacia-mimosa as fuel in combustion systems for heat production or in cogeneration systems, due to the values obtained of the calorific power [309] is guaranteed.

In Portugal, the main species for producing wood pellets for burn-in boilers is the *Pinus pinaster* and for this cause, it is important to compare this type of material with other species like acacia-mimosa for the quantity of material that can be found in the territory [262]. It can serve as a carbon reservoir because it is a fast-growing species, it also rapidly removes the carbon present in the atmosphere through CO_2, mitigating climate change, thus confirming its potential for the production of material with high carbon content [310] such as biochar that can be obtained through the pyrolysis process at 450 °C for 8 h [311].

An acacia plantation with 2 ha can yield 140 t of biomass for wood pellets production that has a similar quality to those produced with *Pinus Pinaster* Aiton and *Eucalyptus globulus* L., with the only exception being the amount of Cl which was slightly higher [255]. In another study, on the contrary, it was found that the chemical composition (ash content, N and Cl) of *Acacia dealbata* and *Eucalyptus globulus* are the main factors that hinder their use for producing certified pellets. The use of the waste material of these species serves as a solution for the collection and reuse of the material, and it should be used in processes where certified products are not required [312], creating a system that complies with the criteria governed by the circular economy. In a fluidized bed reactor with a turbulent regime, two different types of pellets were burned: one produced with maritime pine and the other with acacia-mimosa, and the contaminants [CO_2, CO, and nitrogen oxides (NO_x)] formed in each case were verified and compared. The pellets produced by both species presented a lower emission of contaminants and a better combustion behavior due to the type of reactor used (fluidized bed) [313].

Vicente et al., 2019 analyzed the emissions of pellets produced from Acacia seen as an invasive species in Portugal, specifically located in the coastal areas, to be utilized like fuel at a residential level. Among the properties evaluated were the particulate matter PM_{10} (anhydrosugars like levoglucosan 284 µg g^{-1} PM_{10} and polyaromatic hydrocarbons 8.77 µg g^{-1} PM_{10}), CO (2468 ± 485 mg MJ^{-1}), sulfur dioxide (SO_2) (222 ± 115 mg MJ^{-1}), and NO_x (118 ± 14 mg MJ^{-1}). All these values were considered elevated because the acacias trees were grown in zones with high salt concentrations. For this reason, to obtain a solid fuel from acacia with minor production of emissions, the pre-treatment of the material before the pelleting including the drying step must be optimized, mixing the acacia with other materials to obtain a biofuel with other properties, to incorporate additives that allow major compaction of the particles and to control the air supply during the combustion [314].

In another study, Amutio et al., 2013 evaluated several types of wastes from *Cytisus multiflorus* (50%) and *Spartium junceum* (50%) both identified as Bio1, *Acacia dealbata* identified as Bio2, and, lastly, *Pterospartum tridentatum* identified as Bio3 in the pyrolysis technology. The process occurred in a Conical Spouted Bed Reactor (CSBR), with a temperature of 500 °C, continuous biomass input in the system, and continuous removal of the char. In the liquid phase, the bio-oil (main product) was constituted of water, phenols, ketones, acids, furans, and a lesser quantity of saccharides, aldehydes, and alcohols. The results showed that the yield of bio-oil was 79.5% (Bio1), 72.1% (Bio2), and 75.1% (Bio3) being higher for the Bio1 due to the higher quantity of hemicellulose and cellulose in this species, that favors the bio-oil production. The char yield was 16.6% for Bio1, 23% (Bio2), and about 20% for Bio3. In the relation to the gas phase, the quantity produced was between 4% and 5% for the three species. These results showed the high benefits of these species for the bio-oil generation in a CSBR reactor, being possible to maximize the yield of the liquid phase with high heat and mass transfer rates, a low residence time of the volatile elements, and continuous removal of char, conditions that were maintained in this process [285].

2.2.2. Maritime Pine (*Pinus pinaster* Aiton)

Pinus pinaster Aiton is a woody fast-growing species [315] belonging to the family Pinaceae, order Pinales, and class Pinopsida, which requires a lot of insolation and is able to resist shade only in the first months after germination [316].

This species presents a fundamental function in the economics and rural development in the commercialization of wood, namely for carpentry in exterior and interior areas (floors and parquet), as well as in the real estate sector for the high quality of the material, wood treated for the production of poles, scaffolding shipyards, packaging and pallets for the storage and transport of goods, bodyworks [315], fiber and particle agglomerates in the phosphorus industry, in the manufacture of fence fencing, toys, blinds [317], in the pulp production through the amount of cellulose present in the trunk, of resin for the generation of a great range of chemical products by the presence of terpenic oils of good quality [318] and firewood, in their simple form for the production of heat at the domestic level. Other uses applied to this species are in the manufacture of poles, furniture, and building materials like particle boards [319] and they serve as shading for recreation and picnic areas. The resin is utilized to make rosin and turpentine, the main components in the production of soaps, glues, oils, waxes, medicines, and varnishes. The bark is used to produce tar [320], polyphenols, tannin, antioxidants, adhesives, bio-oil, and particle boards (from the bark partially liquefied) [321].

Maritime pine can be used for several biofuels production using the biochemical process like biogas and bioethanol and in thermochemical conversion [322] through solid fuels production of pellets [323,324] and briquettes in heating, gasification, and pyrolysis systems. *Pinus pinaster* is the principal material in the pellets production in Portugal as it is made of soft wood, an aspect that facilitates grinding, due to its low ash content and greater amount of extractives when compared to other species such as Eucalyptus [323], and because of the availability of the species in the territory.

Pinus pinaster wood was studied for its viability for biofuel production in a biorefinery. The pre-treatment for the material was carried out for aqueous fractionation to obtain the hemicellulose saccharides solution (liquid) and another phase, the solid-state composed of cellulose and lignin. The liquid solution (constituted for polymeric or oligomeric hemicellulose saccharides) was treated with H_2SO_4 (up to 4 wt%) and heated (up to 130 °C) to transform substrates into sugars. The saccharification was achieved almost totally under certain conditions for possible fermentation. After the solid phase (conversion of cellulose) is mixed in the acid medium under microwave irradiation, levulinic acid is obtained to produce valeric biofuels and formic acid for further use in the fuel cell. In the case of the lignin, it was recovered like solid residue using a method with acid [325].

The main species causing fires in Portugal are *Genista tridentata*, *Cistus ladanifer*, *Cytisus* spp., and *Acacia dealbata* (species that make up the first mixture), coming from marginal lands, and *Pinus pinaster* and *Eucalyptus globulus* (constituting the second mixture) integrated into the forest system, therefore, it was proposed to study the fractionation of each mixture as feedstock in a biorefinery for a year, to assess their potential to produce biofuels and other bioproducts. Each mixture was subjected to an autohydrolysis between 190 °C and 240 °C (non-isothermal conditions) to compare the two: the effects of fractionation of each mixture (solubilization of hemicellulose in oligosaccharides and the achieved recovery of lignin and cellulose), the heating values obtained to evaluate their potential as biofuel, and the behavior of enzymatic cellulose hydrolysis for the glucose formation. Excellent results were obtained for both mixtures, such as high oligosaccharide recovery, HHV (the solid part can be used as fuel), and improved glucose obtention (from 45% to 90%) [265]. This type of mixture represents a suitable material for biofuel production (including bioethanol) and products of high commercial value in a biorefinery-type installation, being seen as an alternative to reduce the material load causing fires.

A study about the heating values from different species, allowed us to know what species are most significant to solids biofuel production, namely, wood pellets. It was evaluated that several species like *Castanea sativa*, *Eucalyptus globulus*, *Quercus robur*, *Salix babylonica*, *Populus* × *canadensis*, *Pseudotsuga menziesii*, maritime pine, among other types, were classified as softwoods and hardwoods. The results show that hardwoods had an HHV between 17,631.66 and 20,809.47 kJ kg^{-1} and the softwoods had values ranging from 19,660.02 to 20,360.45 kJ kg^{-1} (the value for the maritime pine is 20,237.89 kJ kg^{-1} i.e., below the species with the highest HHV). In relation to the LHV, the hardwoods had a value between 14,411.54 and 17,907.85 kJ kg^{-1} and the softwood values were between 15,629.71 and 16,935.72 kJ kg^{-1}, with the last value corresponding to the maritime pine, namely, the highest LHV. This study considers the *Pinus pinaster* to be one of several species having the best conditions for application in the thermochemical processes, mainly, combustion [326].

In the District of Bragança in Portugal, a study was conducted on the energy generation (electricity and heat) from the maritime pine because it is a forest species most common in this region. The destination of the energy produced includes several sectors (residential, service, and industrial). The total forest area in Bragança of the *Pinus pinaster* is 89,024 ha with an energy content of 4170.5 TJ. However, consider the data of a power factory, 22% of efficiency, a heating value of 18 GJ t^{-1}, and an operation time of 7200 h $year^{-1}$ which can obtain electricity power of 254.9 GWh. Consider the annual yield of this species, and it can be concluded that it is possible to supply the Bragança District with almost 49% of energy and 60% of its electricity demands for each sector, and 84% of the total energy demands of the several sectors mentioned before [327].

In Spain, the study by Álvarez-Álvarez et al., 2018 was made with the purpose of investigating the potential of different species including maritime pine. the maritime pine obtained the values as follows: the highest HHV of 19,366.277 kJ kg^{-1} (mean); the lowest value of ash of 0.602%, and in the ultimate analysis; the percent of C, sulfur (S), and N were 47.775% C, 0.650% S, and 0.494% N. Once again, it can be concluded the importance of *Pinus pinaster* in the energy production for the HHV and ash values, although the high concentration of N and S are elements that generate atmospheric pollutants [264].

Viana, Rodrigues, Godina, Matias, and Nunes, 2018 performed the analysis and evaluation of several characteristics such as density, moisture, proximate and ultimate analysis, HHV, energy density (E_d), Fuelwood Value Index (FVI), and a dimensional value, among others. The most important results obtained for the different parts analyzed of the maritime pine (wood stem, pine needles, and top of the specie) were: 0.22% to 1.92% of ashes, 19.57 to 21.61 MJ kg^{-1} of HHV, 2.06 to 8.9 GJ m^{-3} of $E_{d,}$ and the values of the FVI were superior in the case of the wood stem (4658) and top of the species (2861.8). Based on these results, it is guaranteed that the maritime pine represents a biomass with a very high potential to create energy in the form of woodchips, briquettes, and pellets [284].

Following the previous study, one of the co-authors, Leonel Nunes, published another work where the woodchips produced from maritime pine were analyzed but it also incorporated the bark. It is important to highlight that in almost all species, the bark contains a very high amount of inorganic material that contributes to the superior values of the ashes. Later on, some problems can arise in the industrial boilers and during the combustion as the bark can cause, the incrustation of the scobs in the bottom of the equipment, a factor that increases the number of times that it is necessary to undertake maintenance requiring the boiler to stop [328].

Several types of materials were studied in Spain, like maritime pine pruning (forestry), grapevine and olive tree pruning (agriculture), and sawdust and marc of grape (industry residues), for its use in the circulating flow gasifier, to evaluate different typologies of biomass, independent of the provenance in the same equipment and conditions, with the objective of determining which materials can be used in gasification systems, whether combined or not. The results show that agricultural pruning wastes (olive and grapevine) presented higher gasification efficiency and yield than forestry (*Pinus pinaster* pruning) and industrial (marc of grape and sawdust) wastes, therefore, in the case of gasification, the agricultural wastes are more capable to produce a gas with high potential to be used for heat production or in the alternative, as power using the gas as working fluid through internal engines or gas turbines [329].

In Montpellier, two-stage gasifiers with a fixed bed were installed (the equipment can be used in pyrolysis and gasification) with the *Pinus pinaster* species as raw material. The pyrolysis was studied concerning different operational parameters. In relation to the biomass flow rate, when increased, a low quality of char was obtained. The best efficiency of the process (involving cracking, the heating value, and quality of the solid phase or charcoal and the gaseous phase) was obtained between 650 °C and 750 °C of temperature, 30 min residence time, and 10 and 15 kg h^{-1} of biomass flow rate, as the best conditions to optimize the pyrolysis process and obtain some products with high added value as charcoal production with an HHV of 33 MJ kg^{-1} and gases with an HHV of 15 MJ Nm^{-3} [287].

2.2.3. Paulownia [*Paulownia tomentosa* (Thunberg) Steudel]

Paulownia tomentosa is a tree of deciduous hardwood type (family Scrophulariaceae, order Scrophulariales, and class Magnoliopsida) that grows very fast [330]. Its high cellulose content (about 440 g cellulose kg^{-1}) and its rapid growth have led to the development of studies showing its feasibility for use both in bioenergy and for utilization in the industry that processes the pulp and in lignin enforcement, combining delignification with autohydrolysis processes [331,332].

The *Paulownia tomentosa* leaves, consisting of glycerides, sugars, and flavonoids, are highly resistant to herbivores [270], being a strong species against pest attack. The C-geranylated flavonoids present in flowers have several functions such as anti-inflammatory, antimicrobial, and inhibitory on some types of enzymes related to various diseases such as type 2 diabetes and Alzheimer's. Terpenoids, also present in flowers, also fulfill several neuroprotective functions [333] and are cytotoxic, attacking various types of cancer cells [334]. A wide variety of essential oils such as benzyl alcohol and 1,2,4-trimethoxybenzene [270] with antibacterial, antiviral, antioxidant, and anti-inflammatory effects were also found in the flowers [335]. The paulownia wood was subjected to the supercritical CO_2 technique, obtaining an extract that has excellent properties to be used as an insecticide, specifically, to combat flour larvae [336]. Some processes applied to paulownia wood have allowed the extraction of a greater amount of lignin and extractives such as heat treatment, with temperature conditions equal to 210 °C and a time of 3 h, in turn causing the wood to darken [271]. *Paulownia tomentosa* wood also has a great potential for obtaining activated carbon from a chemical activation method with zinc chloride ($ZnCl_2$), the product being used as an industrial absorbent, namely, in the separation and purification of liquid compounds and gas, as well as for the control of contamination generated by polluting gases [337].

The energetic valorization of woody species, like paulownia, is possible over its direct utilization such as solid biomass fuels [338] for the electricity and heat production or as feedstock for biofuels of second-generation [272]. Its main use is in wood production for industrial applications, because of its elevated ignition point, dimensional stability, and lifetime maintaining its properties [273].

In a biorefinery-type system, two species of paulownia (*P. tomentosa* and *P. elongata*) were analyzed, and the hot water extraction (HWE) pre-treatment was applied to achieve two major objectives: the first was to extract the largest amount of hemicellulose (liquid phase), and the second was to access the largest amount of lignin present in the wood. After the extraction of hemicellulose (first objective) after membrane separation, the recovery of products such as furfural, acetic acid, methanol, formic acid, hydroxymethylfurfural (HMF), and lignin extractives occurred. However, the main products obtained at this stage were through hydrolysis of hemicellulose and part of the cellulose produced in delignification, to subsequently ferment sugars and produce several neutral solvents such as ethanol, butanol, and acetone, as well as other products, namely, bioplastics. Before delignification (second objective), it was possible to use the material for CHP systems, solid fuel production such as pellets, and reconstituted wood products. Subsequently, in the delignification with acetone and water in an oxygen atmosphere, lignin and cellulose were produced, the latter being used for paper production, nanocellulose, and the hydrolysis described above [339]. In this way, the scheme that characterizes this biorefinery is complemented, with paulownia being a crop with high potential to be applied in this type of industrial unit.

Bioethanol from lignocellulosic crops encompasses higher production costs than using first-generation technologies. With the idea of converting the process to a system is economically more favorable, the valuation of paulownia from a biorefinery perspective is an important asset. As for other woody species, the initial pre-treatment phase is a determinant of the overall yield of the conversion processes. The use of autohydrolysis processes allows the solubilization of hemicelluloses. The insoluble phase, consisting of lignin and cellulose, is subjected to saccharification and fermentation processes, through two separate processes SHF or in one-step simultaneously SSF. Experimental results for the valorization of *Paulownia tomentosa* for bioethanol production allowed a comparison of the two strategies (SHF and SSF) and the quantification of the global balance and the energy recovery of the several fractions obtained. After the autohydrolysis process, the liquid phase consists essentially of xylooligosaccharides (60% of the identified compounds), allowing a concentration of 15.7 g L^{-1} in these compounds. When processing the solid phase, which contains essentially lignin and glucan, the use of the SSF process at a solids content of 20% allowed a value of concentration in ethanol of 52.7 g L^{-1}, which corresponds to 80% of the ethanol yield. The obtained results correspond to a possible production between 10,779 and 13,300 L bioethanol ha^{-1} $year^{-1}$ if the hemicellulosic bioethanol production is included. The energy analysis of the process revealed that the burning of lignin is decisive for increasing the energy conversion efficiency, reaching global values above 80% when this option is taken into account [274].

Biohydrogen production from the leaves and stems of paulownia was studied by Yi et al., 2020 to make a comparison between this species and wheat straw. The pre-treatment consisted of an ultra-fine grinding where it was possible to modify the microstructural, thermal, and optical properties of the biomass, and the biohydrogen production process was through photo fermentation. After pre-treatment, paulownia stalks showed a high yield in biohydrogen production (51.75%) when compared to corn straw (20.59%) caused by the change that the treatment itself caused in the chemical composition of the materials, namely, in hemicellulose, cellulose, and lignin [283].

Based on these characteristics, namely, low S, N, and Cl amounts, the use of ligneous biomass for energy purposes has environmental benefits compared to herbaceous biomass, in particular, regarding nitrogen dioxide (NO_2) and S emissions. Another advantage is related to a lower risk of corrosion phenomena in combustion boilers [254].

Paulownia flowers have already been studied in the process of pyrolysis (carbonization) and alkaline activation to produce porous activated carbon used as a supercapacitor. Due to certain specific properties present in the material, such as its high specific capacitance, it was possible to use the porous activated carbon produced as a mechanism to store energy through a low-cost and high-performance system [340].

Paulownia tomentosa wood was submitted to a slow pyrolysis process for the bio-oil production through a fixed bed reactor with the incorporation of N, being studied was the state of the raw material (particle size) and conditions of the system (temperature, heating rate, and N flow) and how it interfered in the formation of the products. The pyrolysis conversion increased with temperature, the maximum conversion value (77.4%) was obtained at a temperature of 773 K, therefore, at this same temperature, with a heating rate of 50 K min^{-1}, N flow equal to 100 mL min^{-1} and a particle diameter ranging between 0.425 and 1 mm, the highest net yield (bio-oil) equal to 54% was obtained. The yields of pyrolysis products are greatly affected by the system conditions and not by the state of the raw material [286].

2.2.4. Populus (*Populus* spp.)

Poplar is a fast-growing species, therefore, an SRWC crop, belonging to the family Salicaceae, order Salicales, and class Magnoliopsida, being many of the hybrids formed from European poplars such as *Populus tremula* L., *P. alba* L. and *P. nigra* L. [341].

There are many species of poplars that are used in the bioenergy sector. However, *Populus alba* L. (white poplar) and *Populus nigra* L. (black poplar) are most relevant as an energy crops. *Populus alba* L. is little used commercially, however, it is of great interest in creating a diversity of hybrids for various economic sectors, including bioenergy. At the soil level, it allows the recovery of land (marginal/degraded) and polluted soils (phytoremediation with hybrids *P. alba* × *tremula* and *P. tremula* × *alba*), in the energy production [342] it can be used as firewood due to its high calorific value 19.133 MJ kg^{-1} [343] in combustion systems [344] and lastly, for the liquid biofuel production like bioethanol [345].

There is a strong importance of the hybrids generated between the genera *Populus* spp. and *Salix* spp. as both belong to the same division, class, order, and family. However, the poplar presents excellent qualities such as energy crop or SRWC due to its physical and genetic variety, sexual compatibility between several species of the same genus creating hybrids with different and improved properties, when compared with the species that originate them, being reproducible in a vegetative way, facilitating their commercialization in the bioenergy sector [346,347] for the several biofuels production from biochemical conversions like bioethanol [275,348,349] and thermochemical conversions like combustion [350], gasification [351] and pyrolysis, among others like biobutanol [352,353]. Other advantages of the Populus are that in terms of its initial treatment, it is easy to harvest, handle and store [354], a factor that reduces the complexity of the harvesting process, as well as the expenses associated with it. Other products can be obtained from cellulose such as textile materials, cosmetics, and pharmaceuticals, among others, and also from lignin such as biopolymers, fertilizers, biopesticides, and vanillin compounds [355].

One of the gases produced in AD systems is hydrogen sulfide (H_2S) which causes problems within the reactors. In a digester that processes manure as raw material, two different experiments were carried out to measure the reduction of H_2S present in biogas. In the first experience, three components were added to a gas measurement system: poplar wood biochar, steam-treated wood chips, and poplar chips (without any extra treatment). In the second experience, only a biochar sulfate ($SO_4{}^{2-}$) was incorporated directly into the digester. In the first experience, it was necessary for 3 g of poplar wood biochar for every 500 g of manure to guarantee a considerable decrease in H_2S (final concentration was up to 205 ppm) in biogas, with an absorption of 78% for each gram DM fed, without affecting the methane production. In the second experience, there was a decrease in H_2S not caused by $SO_4{}^{2-}$ [consumed by sulfur-reducing bacteria (SRB)], but by other mechanisms such as SRB inhibition, and direct H_2S absorption, among others. The first experiment suggested that the poplar wood biochar absorbed H_2S in AD systems [356].

In the study by Negro et al., 2003 with *Populus nigra* L. it was possible to obtain ethanol through the SSF process with two types of hydrothermal pre-treatment LHW and SE [357]. The latter yielded the best results with reaction times and temperature of 4 min and 210 °C, respectively, with a recovery of 95% cellulose and 41% xylose in the liquid, SSF yields of 60% (theoretical), and enzymatic hydrolysis close to 60% [358].

Rosso, Facciotto, Bergante, Vietto, and Nervo, 2013 determined which hybrid from *Populus alba* L. and *Salix* spp. (*S. jessoensis*, *S. matsudana*, *S. alba* and *S. fragilis*) had greater advantages to be utilized as a feedstock for the biofuels generation, like bioethanol highly dependent on cellulose present in the material or others such as heat through combustion and electricity from CHP type systems. The results showed that some hybrids showed high values of specific gravity (0.5 g cm^{-3}) and others were lower (0.4 g cm^{-3}), coinciding with the results found in the literature. These hybrids have a high potential in the Mediterranean regions and may guarantee, in the future, a progressive replacement of fossil fuels [359].

As an SRWC species, there are many poplar plantations that can be directed to thermochemical processes like combustion in automatic boilers for heat production, which is necessary for two-family houses of 15 ODT ha^{-1} $year^{-1}$ to produce the same amount of heat as a heating system that uses 7000 L of oil and the steam produced can also be injected into a high-pressure turbine to generate electrical energy. Concerning gasification, the gas is fed into a CHP system (joint heat and electricity generation) and the production of solid fuels such as briquettes. In both systems, the raw material must be in the form of chips [358].

Bartoli, Rosi, Giovannelli, Frediani, and Frediani, 2016 used a wide variety of fast-growing poplar clones to produce bio-oil using the Microwave-Assisted Pyrolysis (MAP) process, with a high heating rate, to obtain a high yield and product quality, which can also be directed to coal, gas or bio-oil production. The bio-oils obtained showed small proportions of water up to 17.5% (by weight), low viscosity (lower than those reported in other studies), and low density (close to 1 mg ml^{-1}), being fluid at room temperature and with yields up to 32% (considered high). Finally, in relation to acetic acid, a high concentration of 543.3 mg ml^{-1} and a yield of 69.9 g kg^{-1} were obtained in one of the trials [360].

In the study of Chen et al., 2016, pyrolysis was evaluated at the laboratory scale using the sawdust of poplar wood to obtain bio-oil (used as biofuel or bioproduct), biochar (used as a contaminant absorber, activated carbon as an additive in the soil to improve the quality) and non-condensable gases (methane, CO, CO_2 and H_2 used for the formation of syngas or burned to produce energy) with different heating rates (10 °C min^{-1}, 30 °C min^{-1} and 50 °C min^{-1}), with several temperatures (400 °C, 450 °C, 500 °C, 550 °C, and 600 °C). The best results were obtained with the maximum values, being the HHV of the bio-oil 14.39 MJ kg^{-1} at 550 °C and 50 °C min^{-1}, the specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) for the conditions of 600 °C and 30 °C min^{-1} and finally, the HHV of the non-condensable gas was 14.56 MJ m^{-3} at 600 °C and 50 °C min^{-1}. High mass and energy yields were obtained: for bio-oil at 500 °C and with high heating rates; for biochar with lower temperature and heating rate, and, lastly, for non-condensable gases with higher temperature and heating rates. Poplar wood sawdust is an industrial residual material with a high potential to produce biofuels and bioproducts [361].

In a study by Selvi Gökkaya, Çokkuvvetli, Sağlam, Yüksel, and Ballice, 2019, the poplar chippings were gassed through a hydrothermal process (sub and supercritical water), to evaluate how the system conditions [temperature (between 300 °C and 600 °C) and catalytic variety], with a time reaction of 1 h, affect the conversion yield. The catalysts used were minerals, commercially available alkaline KOH, dolomite, trona, borax, and those produced in the laboratory such as ruthenium/activated carbon (Ru/AC), nickel/activated carbon (Ni/AC), and active carbons impregnated with metals. Each catalyst directs the reaction to form products of greater interest such as methane and H_2. As the temperature increased, the efficiency of the gas phase increased (from 29.7% to 79.3%), with the opposite occurring in the liquid (from 27.6% to 1.1%) and solid (from 38% to 15.6%). The gaseous compounds with the highest yields were H_2 with 20.1 mol kg^{-1} C and methane with 12.7 mol kg^{-1} C, both present in the biomass when the Ru/AC catalyst was applied. The Populus has the potential as a raw material to be applied in gasification processes for the generation of gaseous biofuels [288].

Soares Dias et al., 2019 studied nine Populus hybrids from SRWC plantations that were evaluated in a pyrolysis reactor (fixed bed with several solid catalysts). In another system, pine bark was used in a non-catalytic reactor, as a comparison. Pyrolysis was applied in both systems, with temperatures between 425 °C and 500 °C. In all experiments carried out on hybrids, the results were similar, with bio-oil production having the best yields (53%) at 500 °C (maximum temperature). All the catalysts used, namely, the basic ones [magnesium carbonate ($MgCO_3$) and sodium carbonate (Na_2CO_3)) and acids (H-ZSM-5 and Fluid Catalytic Cracking (FCC)], reduced the number of acids present in the bio-oil. For biochar, better yields were obtained (approximately 21% by weight) when applied to pine bark (containing a greater amount of lignin) in a non-catalytic system, than in the case of Populus [362].

In a bench-type pyrolytic reactor at two temperatures, namely, 500 °C and 600 °C, two biomass typologies were analyzed, namely, poplar (hardwood) and spruce (softwood) to assess the potential of both species in obtaining bio-oil. The results showed that with softwood, bio-oil yields of 65.40% (at 500 °C) and 71.20% (at 600 °C) were obtained, and in the case of hardwood, these yields were 62.50% (at 500 °C) and 68.40% (at 600 °C), therefore, the best results were obtained with softwood at 600 °C. When both species were subjected to a temperature of 500 °C, several phenolic compounds were obtained for the case of softwood, and sugar-rich components, acids, and furans for the case of hardwood. As methanol was used, it showed greater efficiency in the process when compared with the water and toluene, as it allowed a greater extraction of chemical compounds (greater than 90%) in bio-oil caused by its high polarity [363]. Although the highest yield of bio-oil was obtained with softwood, it is also considered that poplar has a high potential for liquid biofuels production like bio-oil.

In Romania, for 10 years (from 1999 to 2009), several agricultural areas (arable and pasture) with an extension of 1.03 million ha were abandoned, without having been converted into a forest area. If poplars would be planted in these areas, a total amount of energy of 194.3 PJ would be obtained (17.5% of total consumption energy in this country) [364].

2.2.5. Willow (*Salix viminalis* L.)

Energy willow (family Salicaceae, order Salicales, and class Magnoliopsida) encompasses a great variety of high-yielding genotypes and hybrids cultivars, most noteworthy based on the *Salix viminalis* L., commonly known as basket willow, among other species [365,366]. As a culture, it grows everywhere in Europe and it is naturalized in eastern North America [367].

As a promising energy crop, it is being utilized as a direct source of energy such as a solid biofuel. Willow presents a significant calorific value, between 17 and 19.5 MJ kg^{-1} (dry basis) [368], being sold to the final user like wood chips whose cost depends on the moisture amount and on particle size. Willow use can be further used as a feedstock for biofuels generation, as it can be an advantageous feedstock for biorefineries.

The conversion of the polysaccharides into biofuels, namely bioethanol [3,279,369–373], and biogas [277] from the material harvested in the vegetative growth stage, which has a low lignin content and a high amount of soluble elements that favor the AD process, since with the material still green, the collection process is easier, a factor that reduces costs of production [374], and biobutanol [375], has been studied during the past years, since the 1990s, with much of the focus being extensively directed into bioethanol. Willow used in soil phytoremediation systems has been applied for energy recovery in thermochemical processes such as gasification [376], pyrolysis [377,378], and combustion [379,380].

As an alternative, autohydrolysis has been studied by other groups [381], paying special attention to the upgrade of hemicellulose which is mainly composed of xylan-type polysaccharides, substituted with arabinose, mannose, and galactose [371]. Under autohydrolysis, the hydrolysates obtained mainly contained oligosaccharides, some monosaccharides, and low amounts of sugar degradation products that increased with process severity. These oligosaccharides may be potentially used as prebiotic food and feed additives, which are added-value products. Furthermore, oligosaccharides can also be converted into other added-value products, namely surfactants, such as novel glycosyl surfactants as described in [382]. This work uses microwave-assisted autohydrolysis to produce oligosaccharides that are later converted into surfactants using the co-produced solid biomass as catalyst (after a simple activation), in a complete integrated valorization loop.

The food applications may imply the use of food-grade grown willow, however, willow produced from marginal lands, especially contaminated soils, may prevent the usage of its biomass for food and feed purposes. A similar discussion can be made for the upgrade of willow bark, a source of salicin that can be used in pharmaceutical [383], nutraceutical, or cosmetic applications, even though energy willow cultivars typically have a lower content of salicin as compared to other cultivars [384]. Conversely, activated carbon production does not seem to suffer from this limitation, especially if its applications move away from food applications. For instance, it is possible to produce activated carbon from willow leaves [385] by pyrolysis, presenting a good capacitive performance as a supercapacitor electrode, with potential applications in automobiles, buses, trains, cranes, and elevators. Willow fiber has also been used for paper manufacturing because of the amount of cellulose that is in the material [386].

The bioethanol ground case considers an overall transformation yield of 310 L ethanol t^{-1} (dry willow biomass) based on the utilization of steam-explosion [282,369,387] as the pre-treatment process, conservative cellulose to glucose yield of 75% [388], and fermentation conditions and yields for a *Zymomonas mobilis*-based process [389]. A preliminary LCA [370] showed that willow-based ethanol can be an effective biofuel to help to achieve GHG emission goals. This can be further enhanced by the utilization of other pre-treatment methods, and several studies have been carried out to improve the selective recovery of polysaccharides and lignin from willow biomass. Among others, acid [375,390], alkali [277], and organosolv pre-treatments have been studied, and higher enzymatic cellulose digestibility has been achieved, namely for the ethanol-based organosolv, using H_2SO_4 as catalyst [391]. This process enabled to obtain a cellulose digestibility of 87%, a 116% increase over the ground case, but the overall sugar recovery is a function of xylose and glucan recovery in the liquid and solid streams, respectively.

Willow has been shown to be a species with high capacity and potential as a soil phytoremediation material, storing trace elements [e.g., Cd and zinc (Zn)] in the aerial part (above the ground) of the species [392]. Considering this aspect, willow harvested in an area contaminated with trace elements of manganese (Mn) and Zn was applied to a SE pre-treatment to eliminate the contaminating elements present in the material and to produce bioethanol. The contaminated material was impregnated with H_2SO_4 (2% concentration) to be subsequently performed the SE pre-treatment at a temperature of 220 °C, with 80% of the trace elements being extracted. The remaining material was again submitted to a SE pre-treatment but this time at 180 °C to be subsequently applied to the enzymatic hydrolysis process (total time of 75 h) in which a conversion of 80% of the cellulose into glucose was achieved. Using *Saccharomyces cerevisiae,* bioethanol was obtained in the fermentation stage. With this study, bioethanol is guaranteed to be obtained from a material contaminated (willow) with elements such as Mn and Zn, without any change in these yeasts and enzymes (biocatalysts) [281].

In another study, a willow plantation was irrigated with WW to assess both the behavior of the species and the use of these waters in a sustainable way, being seen as a solution for the WW treatment. The evaluation of the chemical composition of the species determined that 8% of willows irrigated with WW obtained an increase in the amount of glucan, a decrease in arabinose and galactose, and no changes in the values corresponding to xylose, mannose, and lignin. When the pre-treatment with ionic liquid and the enzymatic saccharification process was applied, it was determined that the yield was not significantly changed, with an amount greater than 95% of glucose found in the cell wall being emitted and a recovery of 35% was obtained of lignin, therefore, there was an increase of more than 200% in the yield of the material irrigated with WW. With this study, it can be stated that it is possible to use this type of water in willow plantations when it is desired to produce biofuels such as bioethanol in a biorefinery-type facility [393].

For the bio-oil production from willow contaminated with certain HMs, several studies have been implemented. These studies differ in the type of contaminant present in the material, the type of pyrolysis reaction, the process conditions regarding temperature and reaction time, the scale of the process, and whether or not there is a pre-treatment phase [394]. Stals et al., 2010 applied flash-type pyrolysis, at a laboratory scale in a semi-continuous fluidized bed reactor, with a very fast reaction time and at different temperatures (between 350 °C and 550 °C), in a willow contaminated with Cd, copper (Cu), Zn, and lead (Pb), the best results being obtained at a temperature of 450 °C, with a bio-oil yield of 48%, a temperature at which a smaller amount of contaminating elements (Zn and Cd) were transferred to the bio-oil, these being reduced to a greater extent when a post-treatment with a hot gas filter was applied [395]. Kuppens et al., 2015 [396] studied the rapid pyrolysis of Cd-contaminated willow at a temperature that lies between 350 °C and 650 °C in a full-scale reactor to obtain a bio-oil yield of 65%, suitable for the heat production due to the LHV obtained, namely, 17 GJ t^{-1}, which is subsequently the electrical energy produced in a CHP system.

Crushed and dried willow that is contaminated with Cd, Cu, chromium (Cr), aluminum (Al), magnesium (Mg), Sn, Zn, Pb, nickel (Ni), cobalt (Co), iron (Fe), and Mn was submitted to a gasification process in a fixed bed reactor at laboratory scale, with CO_2 with a flow of 5.40 L h^{-1}being used as gassing agent, at temperatures ranging between 450 °C and 950 °C. The temperature at which a complete transfer of elements such as Pb, Cd, and Zn to the gas phase (syngas) occurred was 750 °C [394].

HTL has been studied to obtain the generation of the bio-crude product. Here the relevance of the pre-treatment process is evidenced. The use of autohydrolysis yielded interesting results, especially if a two-step dissolution process is applied using a semi-continuous flow reactor [278]. More recently, alkaline pre-treatment enabled the generation of a bio-crude with an oxygen amount lower than 8 wt% and a higher concentration of aromatics and phenolic compounds [397].

2.3. Microalgae

Microalgae are photosynthetic unicellular organisms, many are microscopic, and they are found naturally in water systems (freshwater, sea, brackish, and WW). These organisms need the elements of CO_2, sunlight, and H_2O to generate lipids, carbohydrates, proteins, and other types of bioactive components in a short time. Microalgae are mostly divided into four groups: *Chlorophyceae* (green algae), *Bacillariophyceae* (diatoms), *Chrysophyceae* (golden algae), and *Cyanophyceae* (blue algae). This kind of biomass (microalgal) is constituted from 9.5 to 42% lipids, from 17 to 57% carbohydrates, and from 20 to 50% protein, on a dry weight basis, depending on the species [398] and culture conditions (e.g., [399–401].

The microalgal biomass has a great variety of advantages as a raw material for biofuel production when compared to traditional biomass resources:

- Microalgae present an elevated growth rate in a short time when they are compared to the terrestrial energy crops and it is a culture that can be developed at any time of the year. Its productivity is by far higher when compared with other cultures, converting the sunlight and CO_2 into power and doubling in times shorter than 6 h under optimal conditions. In fact, certain types of species can double their biomass in times as short as 3.5 h [402];
- The photosynthesis mechanism in these microorganisms is similar to higher species. However, they have an elevated photosynthetic efficiency (between 4% and 7.5%) far above the 0.5% for terrestrial cultures [398];
- Microalgae implementation needs a low water quantity including the land resort than the other types of cultures (terrestrial). It can be utilized in marine or freshwater, brackish and the non-arable land, decreasing the environmental impingement, without creating competition with food crops [400];
- This microorganism can get nutrients such as N and P from WW, making available, in parallel, a solution for the agro-industrial effluents [400]; Microalgae is capable of fixing CO_2 from the environment, however, it can also use the CO_2 of energy plants and of industrial sources. The typical value of this microorganism is that it can fixate 1.83 kg CO_2 kg^{-1} (dry algal biomass) [398];
- Microalgal biomass is utilized to produce many valued products like fuels (inclusive aviation gas, jet fuel, gasoline, biodiesel, and bioethanol, among others), feed, food, and other products like nutraceuticals and cosmetics. Waste biomass can be utilized as fertilizer and feed [398];
- The possibility of manipulating the biochemical characteristics of the biomass microalgal over a variety of developmental conditions [400].

Different microalgae species have been studied for their biofuel generation potential and in the fixation of CO_2, to reduce the high production of GHG in the world, caused by the massive use of fossil fuels [71].

The transformation systems vary with several factors like the desired biofuel product, the composition of biomass, economics, time, and operation conditions from microalgal-based biofuels that can be obtained through chemical (Table S1), biochemical (Tables S2–S4), and thermochemical (Tables S5–S7) conversion pathways [398,400]. All these tables are presented in the Supplementary Materials.

At first sight, the high lipid content in some microalgae species makes them a potentially appealing source for biodiesel production. However, high production costs, scalability, limited growth rates, and the need for stress to induce lipid production are challenges to industrial-scale microalgae-based biodiesel. Biodiesel production with acid or base catalysts in a homogeneous phase employs a two-step method: oil extraction using solvents followed by transesterification, resulting in high water consumption and energy input [403–406]. On the other hand, in situ transesterification is a single-step process, which avoids the need for a prior oil extraction step [405,407–409] (Table S1).

Biogas is mainly composed of CH_4 and CO_2. The biogas yield and quality depend on the feedstock composition, temperature, pH, solid and hydraulic retention time, and feeding rate (Table S2). The C:N ratio plays a crucial role in an effective and stable anaerobic digestion process. The optimal C:N ratio for biogas production ranges between 20:1 and 30:1 [410,411]. Too low a C:N ratio can be overcome by co-digestion of microalgal biomass with organic substrates poor in nitrogen, such as sewage sludge [412].

Bioethanol production from algae biomass is based on the fermentation of algal polysaccharides which are starch, sugar, and cellulose, either through SHF [413–418] or SSF [419,420]. Different bioethanol yields have been reported depending on the feedstock substrate whole or pre-treated microalgal biomass (Table S3). In 2010, Harun et al. (2010) showed that lipid-extracted *Chlorococum* sp. generated a 60% higher ethanol concentration compared with the dried/intact biomass [414].

In recent years, photobiological H_2 production from algae biomass has become a novel research field. Some microalgae species, such as *Chlamydomonas reinhardtii*, *Chlorella sorokiniana*, *Chlorella vulgaris*, and *Scenedesmus obliquus*, have been shown to be able to modulate their genetic, enzymatic, and metabolic expression to produce H_2 through biophotolysis after S deprivation [421–425]. Another way to produce H_2 can be through a dark fermentation process using anaerobic bacteria [426–433] (Table S4).

Gasification is a versatile chemical technology in fair, oxygen, or steam at 700–1000 °C, producing a mixture of gases known as syngas (mainly composed of H_2, CO_2, and CH_4) [434]. Steam gasification may be a promising way to produce hydrogen from algae [435–437]. The use of catalysts promotes the production of H_2 while declining tar formation [435,437–440]. An overview of results obtained from the gasification of algae is shown in Table S5.

The pyrolysis of microalgae biomass is usually done at temperatures between 300 °C and 700 °C but may be performed at lower temperatures using a catalyst [441]. The amounts of gas, oil, and char obtained from pyrolysis of algae biomass can vary considerably depending on the microalgae species and growth conditions (Table S6). For example, significant differences were found in bio-oil yields from autotrophic and heterotrophic *C. protothecoides*, 16.6 and 57.9%, respectively. A 3.4 times higher heating value was obtained for heterotrophic compared to autotrophic *C. protothecoides* [442]. Slow pyrolysis is easier to carry out, producing bio-oil yields between 30% and 60% [441,443–447]. Fast pyrolysis can reduce the amount of biochar [448], and the gaseous product is mainly composed of CH_4 and CO_2.

Unlike the previous thermochemical processes, HTL occurs in a wet environment and, thus, does not require an energy-intensive dewatering step of the biomass [449]. HTL occurs at temperatures ranging between 300 and 400 °C [449–457]. The oil yields from the different species are n, and on the microalgae chemical composition, differences in bio-oil yields were reported, ranging from 21% for *Porprydium creuntum* [454], to 66% for *Nannochloropsis* sp. [458]. An overview of microalgae liquefaction studies is available in Table S7.

3. Benefits and Constraints of Bioenergy Technologies Applied to Energy Crops Cultivated in Contaminated and Marginal Soils

Various daily anthropogenic activities are known to deteriorate the state of the soil, increasing its degree of pollution due to the massive discharge of HMs into the environment [178], causing changes in the ecosystem, affecting its balance and the health of all living beings that subsist in it [459]. Among these activities are industries that operate and produce fossil fuels such as refineries and petrochemicals, those linked to various sectors such as metallurgy (including foundry), mining (causes excessive soil depletion), agriculture (due to the incorporation of fertilizers and pesticides in the soil) [178], the automotive industry by the exhaust gases of light or heavy vehicles, urban waste, and sewage sludge [394], among others.

For these reasons, many areas, after being productive land for the agricultural and food sector, have soils that are considered degraded by human action, reducing their organic and biological load, enriching it with HMs which leads them to be considered contaminated, or become marginal areas because of the low quality and unproductiveness of the land, being poor, with poor groundwater quality, as well as inconvenient climatic conditions and unfavorable reliefs [460]. Marginal soils, in some cases, are also abandoned territories where threatening species often develop that only destroy the soil by excessively absorbing its nutrients, later causing a decrease in the productivity of any species that wishes to develop. The countries that present a larger area (greater than 20% of the total area) of land considered marginal are Norway, Albania, Italy, San Marino, Lithuania, and Portugal [461], standing in the Mediterranean with the biggest amount of abandoned agricultural area and saline soils [462].

Soil degradation is synonymous with a variety of terms such as contamination or pollution by HMs, desertification, erosion, wear, salinization, deterioration, undue occupation of invasive species, and abandonment, among many others. However, all these factors can be characterized into three different typologies, such as biological, physical, and chemical. The biological one manifests itself when it happens with land thinning or deforestation, the excessive presence of water often caused by high rainfall, and, finally, the destruction of biodiversity. The physical occurs when there is a loss of organic material, mainly carbon, the land relief is affected by external environmental agents causing the phenomenon known as erosion and, finally, the physical state of the soil is altered, causing the appearance of a hard and thick layer on the surface, compacting, and waterproofing the soil. The chemical happens when there is salinization and acidification of the soil, accumulation of HMs, leaching of nutrients (loss of fertile matter), or of HMs into groundwater, among others [463].

Contaminated soil pollutants in Europe include on average, 35% of HMs, 10% of polycyclic aromatic hydrocarbons (PAHs), and 24% of mineral oils, a [394]. The origin of HMs comes both from anthropogenic activities (as explained above) and from processes that occur naturally at the geological level [178]. HMs are characterized by being inorganic elements such as Cu, Pb, Ni, Zn, Cd, Cr, Fe, Mn, and arsenic (As), among others, with a density five times higher than in the case of water, as well as presenting a high atomic weight [394] being distributed to the environment by different routes. The soil is where the greatest storage of HMs occurs, being caused by factors such as precipitation, the humus present in the soil, and the accumulation of minerals on the surface. The distribution of HMs can occur in several ways. In biomass, some contaminants are only retained in the roots, but in other cases, they are later transported to the aerial part of the species (i.e., Cd and Zn) as in the stems and leaves (i.e., Cr and Pb) [178]. When the contaminants remain in the roots, the aboveground part can be used for bioenergy as the release of metallic pollutants will not occur, but, in this way, the contaminants remain in the soil. Otherwise, when the pollutants are no longer in the roots, the decontamination of the soil takes place there (after a physicochemical analysis), requiring the application of bioenergy treatments or processes that allow the recovery or elimination of these contaminants located in the part aerial view of culture.

The benefits and constraints of energy crops from contaminated or marginal soils, when implemented in conversion processes to produce biofuels, are presented in Table 3, including applied pre- and post-treatments to reduce the presence of pollutants in the process or in the products formed.

Table 3. Benefits and constraints of bioenergy technologies when energy crops are applied in contaminated and marginal soils.

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
General aspects	*Cynara cardunculus* has been shown to be an ideal energy crop to be cultivated and grown in land with low fertility (marginal [56,462] and degraded), serving as protection against soil degradation and erosion caused by intense rainfall [55] improving the fertility of this type of soil [464]. Cardoon is a species with the capacity to serve as a phytoremediation plant in the recovery of soils contaminated with potentially toxic elements (PTE) [e.g., Pb, arsenic (As), Cu, Zn, Cd e antimony (Sb)] [465] and with trace elements [466]. Cardoon was also studied in contaminated soils with As and Cd, proving to be a species that tolerates this type of terrain. The Cd was retained in the aerial part of the plant (old leaves) and the As in the roots, therefore, cardoon is a useful crop to extract the Cd present in soil, and, in the case of land highly contaminated with As, it serves as a stabilizer for that land [467,468]. Giant reed presents wide diversity advantages in relation to other energy crops such as the adaptation to many environments, soils, and cultivation conditions, not requiring fertilizers, and lastly, the high yields and productivities of the crop [76]. Giant reed can be applied for the phytoremediation of contaminated soils [29,469,470]. *Cannabis sativa* is a crop that does not require the incorporation of pesticides and nutrients, a factor that ensures the proper use of the soil, prevents the development of weeds, and allows the extraction of HMs from the soil [471], and organic contaminants and radionuclides, acting as an excellent phytoextractor of contaminants and soil phytoremediator, namely in the roots. *Helianthus tuberosus* is utilized for soil recuperation in disturbed industrial sites (e.g., soils such as salting, alkaline, coal-mining, and oil-polluted) and to prevent land erosion [130,472,473], and is a species that resists the attack of pests and the appearance of diseases [133]. Jerusalem artichoke due to its agronomic characteristics, like tolerance to salt stresses and dry conditions, presents a great	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	resistance to frost and plant diseases [31,474–477], being a species that tolerates alkaline soils and grows easily in cold and dry climates [149] including very high temperatures [133]. *Helianthus tuberosus* can grow well on marginal lands [19,143] and in poor soils [478], therefore avoiding the contest for arable lands that present food cultures. One of the HMs that linseed can remove more easily is Cd, however, it can also remove metals such as Cu, Zn, Ni, and Pb from the soil. *Linum usitatissimum* is a species that also tolerates, absorbs, and stores high amounts of petroleum hydrocarbons present in contaminated soils, and is widely used in oil countries in the Middle East. After its application as a phytoremediation material, it can be used as a fiber and for the production of linseed oil [154]. It has been claimed that cultivation of the miscanthus in marginal [12,460,479–481] and contaminated soils [482–485] has the potential to restore soil properties, halting degradation [486], desertification, and contamination [9,178,462,487]. Some sorghum genes present high productivity in marginal soils, a low amount of nutrients, and do not require high water requirements [41]. Sorghum can grow on land considered marginal [188] due to the multiple advantages of this species, such as high tolerance to water stress, it has short growth cycles, namely, between 3 to 5 months, and can achieve high carbon sequestration rates equal to 50 g m^{-2} day^{-1} [460]. Sorghum has been shown to be an excellent phytoremediator and phytostabilizer of contaminated soils [238] due to the several advantages it presents, such as high biomass formation, easily adaptable to different types of environments and withstands various types of contaminants among them HMs (such as Cd and Zn), being able to accumulate them in the species itself, therefore, decontaminating the soil [41]. *Sorghum bicolor* is mainly characterized by its ability to grow in arid soils, being drought tolerant, producing high biomass yields [41], and presenting a low need for fertilizer, therefore, it can develop in marginal soils [197,488].	For a hemp plantation initially applied as a phytoremediator to be used in the bioenergy sector, it is necessary to evaluate the presence of HMs, radionuclides, and organic contaminants in each process [122] as these components can affect the balance of the system. Despite the wide advantages of linseed as soil phytoremediation, as the accumulation of HMs in the species occurs, its growth is lower, however, their biomass formation [154]. In arid areas it is also possible to use WW in sorghum plantations, being necessary an adequate use and control of the soil to avoid the accumulation of sodium (Na) present in the waters [500] reusing low-quality water that does not compete with drinking water and still has some nutrients [501]. Acacia leaves present a high amount of N that, after falling, nourish the soil and fixes this nutrient [502]. However, if this component is very high, it can have harmful consequences for the ecosystem, increasing the growth of invasive species that densify largely the forest, preventing the passage of water, a factor that increases the degree of erosion, avoiding the development and continuity of other species like the indigenous *Populus* when applied as SRWC in silviculture, it cannot be applied to degraded soils, as its productivity and yield are low, and the investment is not very profitable [503]. *Populus* to increase productivity in plantations destined for bioenergy, it is necessary to apply water, fertilizers, and examine the appearance of weeds, factors that increase the overall costs of the installation. To make it viable and profitable, one must select the most appropriate hybrids and apply appropriate silviculture measures to reduce costs [257]. A benefit is the reduction of GHG emissions since [504] evaluated that fast-growing woody species can produce 9 to 161 times less GHG than coal, producing 14.1 to 85.9 times more energy than coal. The only disadvantage is the need for irrigation to ensure the economic viability of the plantation [505].

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	Acacia is tolerant to soils of little fertility [263]. *Pinus pinaster* is considered a species of fast growth and tolerant to poor soils, being applied to reforest degraded areas and in the stabilization of dunes, to protect intensive plantations (including agricultural fields), in the conservation of soils mainly in areas at risk of erosion [320], to combat soil degradation and control hydrological systems [489]. *Paulownia tomentosa* has a high potential to be implemented in contaminated soils for later recovery, in abandoned land (previously used for agriculture) with low water needs, in soils that may suffer from erosion for its later stabilization, and in marginal soils [490]. Hybrid species of Paulownia (*P. tomentosa* × *fortune* and *P.elongata* × *fortune*) have great advantages in the absorption of HMs in contaminated soils, being seen for its phytoremediator potential. In these varieties, the accumulation of K and calcium (Ca) occurs in the stems, the Pb, Zn, and Cu occur in the leaves, and the accumulation of Cd, Na, magnesium (Mg), and Fe is given in the roots [491]. At the soil level, the Populus is often applied for phytoremediation in the recovery of contaminated areas [492] and agricultural land that has suffered degradation over time [493], increasing the organic matter in the soil. *Populus alba* L. at the soil level allows the recovery of land (marginal/degraded) and polluted soils (phytoremediation with hybrids *Populus alba* × *tremula* and *Populus tremula* × *alba*) [342]. *Populus alba* L. has been shown to have a high potential for decontaminating water bodies with high amounts of nitrates (NO_3^-), namely, between 100 and 300 mg L^{-1} [367]. In terms of the environment and the soil, *Populus nigra* L. plantations reduce the degree of pollution, balancing the microclimate [260]. Willow can successfully grow in many types of soil ranging from periodically flooded to marginal lands and polluted soils, with the optimal conditions being well- drained sandy and wet loamy soil with a pH range of 5.5 to 7.5 [367]. Dry soils are not suitable for willow cultivation.	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils			
Treatment or Conversion Process		**Benefits**	**Constraints**
		Currently, willow is used for protecting soils from water erosion [368] and phytoremediation [494]. *Salix viminalis* is applied to marginal lands [495], in contaminated soils for the phytoextraction of heavy metals such as As, Pb, Sb [496], Zn e Cd [497,498] through the wide extension of its roots and in degraded soils (poor in nutrients) [499] being in all cases for its subsequent recovery.	
Pre-treatment	General	It allows reducing the quantities of contaminants [HMs, minerals, persistent organic pollutants (POPs), among others] present in the raw material to avoid its propagation in the following stages of the process or in the formed products [394].	If the application of pre-treatment is not efficient in eliminating the contaminants, in the following steps, the processes that use catalysts will also be contaminated or the degradation of biological products may occur [394].
	Phytomining	It allows the recovery of HMs with high added value at an industrial level (e.g., battery production) [506] that are accumulated in the aerial part, leaves, or roots of certain species, closing the life cycle of these metals.	
	Extraction treatment	It extracts the HMs found in the waste material from phytoremediation, using an extracting agent such as ammonium (acetate, nitrate, and oxalate), pure water, ethylenediaminetetraacetic acid (EDTA), and H_2SO_4. Before submitting the material to the extracting agent, it can be squeezed to obtain a liquid phase or heat-treated to obtain a solid phase, both rich in HMs [507].	When the HMs are in the liquid phase, a previous treatment is necessary to extract the metals, for example, the application of a coagulant in the liquid squeeze to reduce the concentration of Cd. Biomass reduction from phytoremediation is lower when the extraction is applied before heat treatment [507].
	Microbial treatment	It allows for the microbial stabilization of biomass as well as the incorporation of moisture into the organic material and can be applied under anaerobic (fermentation) and aerobic (composting) conditions. When any of the two types of microorganisms (anaerobic or aerobic) are used, the decomposition of organic matter always occurs into substances such as alcohols, microbial, organic acids, H_2O, H_2S, CO_2, ammonia (NH_3), methane, SO_4^{2-}, phosphate (PO_4^{2-}), as well as an energy release. The HMs stored in the extraction solution can be recycled. This is a technology that has multiple advantages, being highly efficient. It has low energy requirements, and protects the environment, through different types of extraction: semi-bionic, microwave, ultrasonic, and supercritical fluid, among others [507].	The reduction of biomass from phytoremediation is lower when a microbial treatment is applied before heat treatment. Other methods are recommended when the content of HMs found in the species is high. For the reason described above, the microbial treatment is more efficient for biomass with low HMs. Treatment that presents a high risk of producing secondary contaminants, a factor that limits its environmental sustainability [507].

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils			
Treatment or Conversion Process		**Benefits**	**Constraints**
	Compression landfill treatment	It has been widely used, being easy and simple to apply. When the species used for phytoremediation are compressed, a high concentration of HMs and chelating substances are obtained [507].	Treatment that presents a high risk of producing secondary contaminants [507], a factor that limits its environmental sustainability.
	Synthesis of nanomaterials (treatment)	This new treatment has a lower cost and lower environmental impact when compared to the traditional method of metal nanoparticles. The biomass used for phytoremediation can be reduced up to 100% when this method is applied. The reduction of biomass from phytoremediation is greater when this treatment is applied as well as other thermochemical conversion technologies such as pyrolysis, gasification, and combustion. It is a technology with a low level of second-degree contamination, therefore, in this sense, it has no environmental impact [507].	There are not enough studies or applications of this type of treatment when it comes to biomass applied in phytoremediation systems (including its residues), therefore, containing HMs. When residues from phytoremediation are used, the application of this type of treatment is costly and complicated [507].
Thermochemical conversion process	General	Metals such as Zn and Pb can be largely retained (greater than 90%) in the solid phase and at temperatures ranging between 220 °C and 900 °C. In the by-products, several metals can be found, being later used for other applications as in the case of Zn, used as a catalyst to obtain furans and acetates; gaseous by-products can be used as synthesis gas (high presence of methane and H_2); by-products obtained in the solid phase can be used as adsorbents for metals (after their leaching). Finally, the Cd can be applied for the photodegradation of contaminants present in water bodies [506].	In any thermochemical process, the main constraints are the translocation of contaminants in the different phases of the products and by-products, as well as the possibility that they return to the environment, therefore, to the air, soil, or water bodies. The As (metalloid) and Cd (metal) in this type of process can completely leave the system at 900 °C [506], without its recovery being possible, causing an environmental risk.
	Combustion	From all the thermo- and biochemical conversion technologies of contaminated biomass into energy, combustion presents the greatest environmental advantages, especially when compared with pyrolysis and composting [394]. Some additives incorporated into the system such as kaolin allow the removal of metals such as Zn (88.1% removed) and Cd (91.2%) and others such as activated carbon, allow the elimination of polycyclic aromatic hydrocarbons (99%) and metals such as Cd (97.6%) and Zn (99.1%), all of which are from the gaseous phase. Kaolin also helps to lower NO_x in the gas phase to environmentally acceptable levels.	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	In some studies, ash from contaminated biomass with HMs contains less metal than the legally permitted limit value, so this type of ash can be reused as fertilizer for application in agricultural and forestry systems and is no longer considered a hazardous waste [507]. During combustion, NO_x compounds are formed and released. However, when the nitrogen uptake of biomass from contaminated soils is very similar to the biomass that develops on uncontaminated soils, the amount of NO_x emitted will also be similar in both cases and therefore, cannot be considered a greater environmental impact when it comes from contaminated soils [178]. When the raw material is contaminated biomass with HMs and for cases where energy (heat and electricity in a cogeneration system) is produced in a closed-type cycle, in which there are no leaks in the system, the release of contaminated gases does not occur to the atmosphere. However, metals can also be present in the solid phase, requiring proper treatment of the material. *Miscanthus* × *giganteus* applied in polluted soil with several types of HMs such as Cu, Ni, Zn, Cd, Cr, Pb, and K presents a diversified distribution of metals throughout the plant as in the aerial part (stems and leaves), rhizomes, and roots. Ni and Cr are not stored throughout the plant and the remaining metals (with the exception of K) accumulate mainly in the roots and rhizomes, a factor that facilitates the use of the aerial part (the least contaminated) to bioenergy, in combustion systems by the generation of contaminants to be lower, mainly in the gas phase [508]. *Arundo donax* L. was evaluated in soils contaminated with several HMs, including Cu, Cd, and Zn. In the third year of planting, the giant r managed to remove 2.09 kg ha^{-1} of Cu from the soil; 0.007 kg ha^{-1} of Cd, and 3.87 kg ha^{-1} of Zn. With these results, it is possible to guarantee the potential of this species for phytoextraction and later be applied in energy conversion processes such as combustion and anaerobic digestion [509].	If residues from biomass used for phytoremediation are burned, many components such as CO, HMs, NO_x, among others, are released through fly ash causing a second-degree of contamination. For this reason, it is necessary to properly handle and capture the ashes, making them unsuitable for reuse due to the amount of metals in them. Some additives incorporated into the system prevent part of the HMs from phytoremediation residues from being transported to the gaseous phase. Treatment that presents a high risk of producing secondary contaminants, a factor that limits its environmental sustainability. Regarding biochar as a fertilizer, when it has high amounts of HMs, these metals may leach into groundwater and even into the soil, and for this reason, it is necessary to carry out a physicochemical analysis of the biochar (in terms of the amount of HMs) to ensure environmental safety before its application [507].When biomass that is contaminated with HMs is subjected to a combustion process, strict care is needed to keep the conditions as controlled as possible to avoid those metals or other contaminants are not emitted in gases and fly ash that are released without any type of control, it being also required that the solid material is disposed of the system with due care and safety [178]. Combustion (also including anaerobic digestion) are the two technologies that pose the greatest risk of emitting metals into the environment without them being fully retained. When biomass contaminated with HMs is used, pollutants (metals) are released into the atmosphere, at the point where energy is produced [510]. Considering the study by Laval-Gilly et al., 2017 [508], when high amounts of K are stored in the aboveground part of the biomass, this decreases the efficiency of the combustion process due to the formation of slag and scale inside the reactor. Combustion is considered an inappropriate technology when it comes to biomass from soils not suitable for agriculture (marginal). This only happens when yields are low and there is a higher concentration of ash and N, which leads to a heavier emission of pollutants such as NOx, particles in fly ash and CO_2 [460].

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
Gasification	When a temperature below 1000 °C is applied, elements such as Pb, As, Cd and Zn are volatile. However, to prevent this, compounds such as silicon dioxide (SiO_2), calcium sulfate ($CaSO_4$), and aluminium oxide (Al_2O_3) can be incorporated into the system as they reduce the volatilization of Pb, Cd, and Zn. Likewise, when a temperature below 1000 °C is applied, elements such as Cu, Ni, Mn, and Co are not volatile [507]. Several species including *Miscanthus* × *giganteus* and *Panicum virgatum* L. contaminated with HMs (Zn, Pb, and Cd) were processed in a fixed bed gasifier that operates at atmospheric pressure to produce synthesis gas with a certain calorific value to be used in cogeneration systems. The species that best supports the Pb and Zn contained in the soil is miscanthus, however, both species have potential as phytostabilizer material for soils polluted with HMs. The LHV value of gases obtained with miscanthus was 3.68 MJ m^{-3} and in the case of switchgrass, it was 2.77 MJ m^{-3} [511]. Mn is a type of metal that can be condensed from the gas phase after the application of a gas cleaning or purification system [394].	The metals found in greater proportion in the gas phase are Pb, Cd, and Zn. Factors such as operating conditions (pressure and temperature), pre and post-treatment, the type of gasification agent, the type of reactor (gasifier) used based on the bed (fixed, fluidized, dragged, among others), the reactor construction material, and finally, the chemical speciation of metals, affect the quality of the synthesis gas and the distribution of HMs, when contaminated biomass is used as raw material. Sometimes high concentrations of HMs such as Ni, Fe, Cr, Cu, and molybdenum (Mo) are found in the synthesis gas. This occurs due to the release of these from the gasifier caused by several factors such as the type of material in the reactor, the functioning of the refrigeration system, and the type of additives or lubricants, among others [394]. In this system, metal oxides are released from the contaminated biomass, which must be stored in the slag and the metals found in fly ash must be subjected to a cleaning system such as that are applied in the gas phase of the combustion process [178]. In the gas phase, there are several HMs, being present in different ways: Hg and Cd can be found in large quantities; Co can be partially or totally in this phase with temperatures around 500 °C and 800 °C and finally, metals such as Zn, Pb, Ni, vanadium, As, Cd, Cr, and Sb are present when temperatures are below 500 °C [394]. As this is the phase of interest in this type of system, a gas cleaning process or separation of these metals is always necessary.
Pyrolysis	To produce biofuels as well as other forms of energy such as thermal (heat recovery) and electrical (large scale), this thermochemical conversion technology is the most promising when biomass contaminated with HMs is used as a raw material [506]. The pyrolysis of leaves and branches of contaminated species can be carried out mixed rather than separately, to facilitate the process and take advantage of all the constituent parts of the cultures, providing greater environmental safety [394]. It is advisable for proper implementation of the process a solid particle size of the contaminated biomass smaller than 0.50 mm to guarantee the production of a liquid product (bio-oil) free of metals as well as the concentration of volatiles and refractories in the bio-coal.	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	When Cu-contaminated biomass is treated (with 1% in the material), the best option is rapid pyrolysis, in a type of fixed-bed reactor, and at a temperature of 500 °C. To guarantee the presence of HMs in the biochar, a fluidized bed reactor can be used at a temperature of 600 °C or flash-type pyrolysis operating at lower temperatures can be applied in the same type of reactor (coupled to a hot gas filter), therefore, around 350 °C. The selection of the optimal operating temperature will depend on the boiling or melting point as well as the amount of HMs present in the biomass. For these reasons, it is important to emphasize that elements such as As, Pb, Hg, and Cd are very volatile, Mo, Zn, Cu, and Ni are semi-volatile and finally, Cr, vanadium, Co, and Mn are not volatile. Fast pyrolysis allows the pyrolytic decomposition of biomass contaminated with HMs, obtaining a bio-oil with excellent properties, therefore, high yield and HHV value as well as low concentration of HMs. When it is desired to accumulate HMs in the waste material, the application of pyrolysis is more promising than in the case of combustion and gasification [394]. In this type of system, when biomass contains metals such as Ni, Zn, and Pb, they react as catalysts, boosting the hydrogenation reaction to produce organic acids, accelerating the formation of bio-oil, and improving its properties. When residues from biomass used for phytoremediation are subjected to a pyrolysis process, there is a distribution of HMs between the 3 resulting phases (solid, liquid, and gas) of the system. The HMs amount in each phase will depend on the conditions (such as temperature) under which the process is carried out. For example, in a pyrolytic system, as the temperature was increased, the presence of Cr in the bottom ash was also higher when compared to a combustion-type system. The amount of Cr in the gas phase in a pyrolysis process was slightly lower than the obtained in the combustion residue of the same biomass at the same temperature (350 °C). When flash-type pyrolysis is applied, it is possible to recover part of the HMs in the solid phase, therefore, in the charcoal. The incorporation of additives [NaOH, Al_2O_3, calcium dihydrogenphosphate ($Ca(H_2PO_4)_2$), calcium carbonate ($CaCO_3$), iron(III) chloride ($FeCl_3$), among others]	Slow pyrolysis of biomass contaminated with HMs presents a high content of HMs in the bio-oil (with low yield) and produces a low amount and variety of organic compounds. Factors such as particle size, typology of contaminated biomass, pyrolysis (including operating conditions), and pre and post-treatment can affect the transfer of solids and HMs and the main properties of bio-oil such as quality, yield, and HHV [394]. When a hyperaccumulator (contaminated biomass) that contains Ni was used, the composition of the bio-oil was changed, forming a greater amount of other compounds that contained N, such as triacetoneamine [507]. When this type of system processes contaminated biomass, great care must be taken with the coke produced in the solid phase as it concentrates a large part of the HMs [178]. Fast pyrolysis systems cannot use different types of catalysts in the same process because the catalysts themselves are deactivated. Other metals such as K, Mg, Na, and Ca that are stored in lignocellulosic-type biomass significantly affect pyrolysis processes because it modifies both the material structure and the different pyrolytic reaction pathways [512].

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	allows to reduce the leaching of HMs from biochar, therefore, these additives can react with the HMs and produce stable compounds while the pyrolytic process takes place. Some types of biochar can be used as additives in phytoremediation systems in soils contaminated with HMs, boosting the growth of the species, and improving the biochemical characteristics of the soil. When the bio-oil has a certain amount of HMs, it can be removed using different types of treatments such as extraction, cation exchange, and separation through solvents, among others [507]. In the case of biomass contaminated with metals such as Zn and Cd, this technology has more advantages when compared to combustion because it presents a smaller amount of metals in the exhaust flow (or outflow of gases) [510]. Pyrolysis allows the storage of up to 80% of metals in the solid phase (coal) and the production of a liquid phase (bio-oil) suitable for bioenergy [510]. Elements contained in biomass such as Ni and Cu can act as catalysts within a pyrolytic reactor to produce bio-oil and gaseous compounds. Most of the HMs are found in the solid phase known as biochar, supporting metallic nanoparticles, used to catalyze and eliminate contaminants and as an energy converter and accumulator. When the metallic nanoparticles production is required and the biomass consists of elements with a pyrolytic behavior such as Ni, Co, Cu, and Zn, the system has a lower operating cost, is more sustainable, as it avoids the use of extra chemical components, simplifying the process. Fast pyrolysis systems require soluble catalysts that can penetrate the biomass, to ensure greater control over biomass decomposition [512]. The two most suitable technologies for high productivity of bio-oil and biochar rich in HMs (Cu, Zn, Cd, Pb, and Ni) are flash and fast pyrolysis. Fluidized bed reactors can retain a greater amount of HMs (Cu, Zn, Cd, Pb, and Ni) in the solid phase when operating at higher temperatures and ablative type reactors store a greater number of metallic pollutants in the biochar at a lower temperature [513]. When slow pyrolysis is applied to contaminated biomass (rhizomes of	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	Arundo donax L. and leaves and branches of *Populus nigra* L.) with Pb, Zn, Cd, and Cu, it is possible to achieve a mass and volume reduction of the material, producing a vapor phase (fuel) free of pollutants, being the storage of metals in the solid or biochar phase. However, when the material contains essentially Cd, it is required to operate the reactor at low temperatures (below 430 °C) to obtain a fuel vapor without metals. If the biomass presents a greater proportion of the remaining HMs (Pb, Zn, and Cu), the system must be operated at higher temperatures (maximum value of 600 °C) to produce charcoal with a greater surface area and lower mobility of the metals [514]. Grass species such as *Panicum virgatum* L. used in phytoremediation systems for soils polluted with Pb underwent a rapid pyrolysis process without affecting the distribution of products in the system by the presence of the metal [515]. Pyrolysis of the *Arundo donax* L. species contaminated with metals such as As, Cd, and Pb was applied to determine if there was pollution to the environment. The system required the incorporation of other compounds such as $CaCO_3$, NaOH, Al_2O_3, and $FeCl_3$ to ensure the fixation of metals in the biochar. The results showed that 97% of Cd and 37% of As were stabilized in the biochar using 5% Al_2O_3, at a temperature of 250 °C and a reaction time of 2 h. In the case of Pb, 57% of it was fixed in biochar using 5% $CaCO_3$, at 400 °C for 1 h [516]. It can be stated that the giant reed cultivated in contaminated soils has the potential to be applied in pyrolysis systems since in most of the studies, the HMs are retained in the solid or biochar phase, being possible its later recovery.	
Hydrothermal	The HTL process can be used to chemically extract as well as separate the HMs from the bio-oil obtained through pyrolysis when using biomass contaminated with HMs. Afterward, the solid residue obtained can be reused as fertilizer [394]. For a hyperaccumulator with a high humidity value, a highly efficient system is HTC. Elements such as Zn and Pb, in this type of process, tend to accumulate in more than 50% of solid waste, the remaining amount being converted into oxidizable compounds or more stable residual goods, therefore, at an environmental level, the ecotoxicity values were reduced almost entirely [507].	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils			
Treatment or Conversion Process		**Benefits**	**Constraints**
		HTL is a process that allows the recovery (greater than 95%) of metals such as Cu and Cd in the residue obtained in the solid phase, despite the large amount of C that may still contain the resulting material. The HTL has a high potential to process microalgae and macroalgae used for the phytoremediation of polluted waters with HMs, allowing the storage of metals in the solid phase (compact and inert) to be later recovered, as well as the production of a liquid phase (bio-crude) with the proper characteristics for bioenergy. The HTL process allows for the breakdown of macronutrients such as P, N, and K in an aqueous-type medium to achieve extra nutrient recovery [510]. When applied to liquefaction in grass species developed in marginal soils, there are many advantages found in this type of system as they present a lower operating cost caused by the easy disaggregation of the material inside the reactor at lower temperatures [460].	When compared to other thermochemical technologies (combustion, gasification, and pyrolysis) hydrothermal reactions need higher pressures. When applied to HTC the reduction of biomass from phytoremediation is lower than in other thermochemical technologies. When a hyper-accumulator containing Ni, Pb, and Zn is used as raw material, the metals are retained in the bio-oil, making it impossible to recover or isolate the HMs. Both HTC and HTL are technologies that can present blockages in the reactor's internal system, increasing its operating costs [507].
Biochemical conversion process	Anaerobic digestion	*Arundo donax* L. was evaluated in soils contaminated with several HMs, including Cu, Cd, and Zn. In the third year of planting, the giant reed managed to remove 2.09 kg ha^{-1} of Cu from the soil; 0.007 kg ha^{-1} of Cd, and 3.87 kg ha^{-1} of Zn. With these results, it is possible to guarantee the potential of this species for phytoextraction and later be applied in energy conversion processes such as anaerobic digestion and combustion [509].	Anaerobic digestion (also including combustion) are the two technologies that pose the greatest risk of emitting metals to the environment without them being fully retained. When biomass contaminated with HMs is used, pollutants (metals) are released from other commercial products produced [510] in this type of system such as the compost used for agriculture.
	Composting	It reduces the organic matter present in the residual material from phytoremediation, accumulating the HMs in another fraction that can later be applied in anaerobic digestion. It is a technique used for many centuries, with low cost and with a closed carbon cycle because the carbon that is released has already been captured [506].	Metals can be transferred naturally from the system by the microbial action itself, especially when it comes to Hg. A longer time for composting the material may be necessary, a factor that leads to the possible leaching of HMs contaminating the soil and groundwater [506].
	Fermentation	Many studies have confirmed the feasibility of using biomass when applied for phytoremediation in the fermentation of sugars for the formation of bioethanol. One of the main concerns of the enzymatic process (saccharification) is whether metals inhibit the process. However, metals such as Zn, Ni, and As do not inhibit the process [506] when compared to other metals. When studying 3 different types of pre-treatments such as alkaline (soda), organosolv, and acid to analyze biomass (willow wood) contaminated with HMs (Mn, Zn, and Fe) for the application of a	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils			
Treatment or Conversion Process		**Benefits**	**Constraints**
		fermentation process for the production of bioethanol, it was obtained that the best pre-treatment was acid (temperature of 170 °C and 2% w w^{-1} of H_2SO_4) as it allowed the efficient extraction of all metals being recovered in the residual water fluid forming a clean cellulosic pulp. In the enzymatic hydrolysis step, the 3 metals did not show any type of change in the hydrolysis of polysaccharides [373]. *Sorghum bicolor* L. Moench was evaluated in soil contaminated with different concentrations of Cd for bioethanol production. Sorghum proved to be an excellent candidate for bioenergy when soil Cd concentrations were less than 30 mg kg^{-1}, with another positive aspect being the fact that Cd is mainly concentrated in the roots and not in the shoots, therefore, it does not affect the biomass used for bioenergy production [517]. The potential of *Miscanthus* × *giganteus* in soils contaminated with Mn, strontium (Sr), zirconium (Zr), Zn, As, Pb, Fe, titanium (Ti), and Cu for bioethanol production was analyzed. The high concentration of these metals in the soil, mainly from Mn, Zr, Fe, and Ti, did not impede the development of the species, with the concentration of these metals being higher in the roots and then in the aerial part (stems and leaves), a factor that is advantageous for being the aboveground fraction of interest for bioenergy. Ti, Cu, Sr, Fe, Mn, and Zn storage was lower in shoots and the accumulation of Pb, As and Zr was also almost null [518].	In order to be able to produce bioethanol on a laboratory scale, a more rigorous control of the system is necessary, and the biomass (in some cases) must be subjected to several treatments to reduce the greatest amount of contaminants before the fermentation process. In the enzymatic process (saccharification), metals such as Pb are strong inhibitors, and Cd and Cu are considered to be moderately inhibitory [506]. Considering the study by Asad et al., 2017 [373] for the alkaline pre-treatment (soda) with the same temperature (170 °C) and 15% w w^{-1} of NaOH, a low extraction of HMs (Fe, Zn, and Mn being the recovery of metals in the same order), with the metals being mostly in the cellulosic pulp fraction, then in less proportion in the liquid waste fluid and finally, the lowest concentration was in lignin. For the case of organosolv pre-treatment, the recovery of metals in each fraction was followed in the same order as in the alkaline pre-treatment.
Chemical conversion	Oil transesterification	The use of biomass when applied for phytoremediation in the transesterification of oils for the formation of biodiesel has been shown to be viable in several studies [506].	
Post-treatment	Hot-gas filter	When contaminated biomass is used, there is an almost zero transfer of metals to the product of interest, which is bio-oil, being less than 1 mg kg^{-1} for Pb and Cd and less than 5 mg kg^{-1} for the Zn and Cu, all at a temperature of 350 °C. It can be said that the same results are obtained when uncontaminated (willow) biomass is used. There is a greater transfer of HMs to synthesis gas when using a hot gas filter than in the case of a cyclone [394].	
	Cyclone	In contaminated biomass with HMs, the best conditions for the application of the cyclone in pyrolysis systems is at a temperature of 650 °C in order to simultaneously obtain the recovery of metals and a liquid product (bio-oil) without the presence of these.	

Table 3. *Cont.*

Low ILUC Energy Crops Developed in Contaminated and Marginal Soils		
Treatment or Conversion Process	**Benefits**	**Constraints**
	In a gasifier coupled to a cyclone and operating at a temperature between 500 °C and 600 °C, solid-phase recovery of metals such as Ni, Zn, Cu, and Pb is possible, with the sole exception of Cd [394].	
Co-combustion	The application of co-combustion maintaining certain air conditions allows for the elimination of HMs. This can be seen in the following aspects: • High temperatures help volatile HMs based on the following order Pb > Cd > Zn. • When the incorporation of oxygen into the system was greater, elements such as Cd and Zn were stored in the bottom ash [394].	• In the presence of an oxidative-type atmosphere, Zn was found in the form of oxides of heavy materials and therefore they were not easily volatilized. • When the incorporation of oxygen into the system was greater, elements such as Pb initially increased in the bottom ash but then subsequently decreased [394].

Results presented in Table 3 show that the production of industrial crops in contaminated soils presents higher constraints than in marginal and degraded soils. Pre-treatments bring advantages to the processing of the contaminated biomass. Microbial treatment shows high potential and advantages: aerobic or anaerobic microorganisms can be used, the process presents low environmental impact and requires low amounts of energy, factors that increase their efficiency. However, this is also the pre-treatment with the most constraints because its application is only advisable when the amount of HMs present in the biomass is low, otherwise, it is a process that can lead to the formation of secondary contaminants, limiting its environmental sustainability.

Of the biochemical processes, fermentation presents several advantages, but also some constraints. In terms of advantages, it is possible to process a wide variety of biomasses harvested from a multitude of contaminants without the system being affected or inhibited. However, certain contaminants/concentrations can inhibit the system.

For thermochemical processes, pyrolysis presents the greatest advantages in the processing of contaminated biomass, with a wide variety of HMs such as Cu, Ni, Zn, and Pb, since they act as catalysts increasing the rate of pyrolytic reaction, favoring the conditions of the system. Another important factor is that in most cases and depending on the type of pyrolysis that is applied, metals are recovered in the solid phase resulting from the system, therefore, in coal, obtaining a bio-oil with a higher degree of purity for application as a biofuel. The thermochemical process that has the most limitations is combustion due to the oxidation that occurs in the contaminated biomass, a factor that causes the emission of components such as CO, HMs, and NOx, among many others through fly ash, generating a high risk of producing secondary contaminants, requiring greater control and care within the system.

Finally, from the described post-treatments (hot-gas filter, cyclone, and co-combustion), and in accordance with the behavior and conditions applied in the system, the three present several advantages for processing contaminated biomass, with only co-combustion presenting some limitations.

4. Conclusions

Herbaceous species or those that have a different classification than forest species are those that are of greater interest to be implemented as energy crops because their use occurs in the short term and a greater diversity of biofuels (bioenergy sector) and by-products can be produced considering its implementation in an industrial unit biorefinery-type. The common point between the 14 species is that all of them are currently present in Portugal, so their viability and development in the territory are known.

It can be said that *Sorghum bicolor* is the species that was tested in the largest variety of bioenergy technologies (eight) such as chemical (biodiesel), biochemical (biogas or biomethane, bioethanol, and biohydrogen), and thermochemical (combustion, gasification, pyrolysis, and HTL) for biofuels production. It also has the potential to grow in contaminated soils, managing to absorb certain HMs from the soil as well as growing in areas unsuitable for agriculture such as marginal soils. Oil extracted from *Sorghum bicolor* is a promising material for liquid fuel production such as biodiesel. Cardoon and microalgae are the other species that have been tested in a larger range of technological applications, namely, in seven conversion processes of biomass into biofuels. Jerusalem artichoke, miscanthu, and willow were tested in six different technologies, and in five conversion processes, four cultures were tested, hemp, switchgrass, maritime pine, and poplar.

Besides bioenergy, the species studied allows the production of a great diversity of by-products: animal feed; sources of functional compounds, production of paper pulp, biofertilizers free of synthetic chemical compounds that cause damage to the soil, bioplastics that allowed reducing the still latent dependence on fossil resources plastics, biolubricants, and biocomposites, among others. The products can be applied in different sectors such as construction, automotive, nutraceutical, and cosmetics, among others. Based on these data, it is confirmed that the energy crops described here not only allowed the recovery of soils with low ILUC risk, but they also allowed the development of a diversity of sectors through the production of materials/products with high commercial value, motivating the fulfillment of the measures implemented by the European Community through the circular economy.

Non-food energy crops deserve high expectations as the full commercial stage for bioenergy purposes still faces some constraints. The supply chain development for the majority of dedicated energy crops still needs development. Cost estimates are strongly affected by uncertainties derived from different crops, different crop yields, different crop locations, and different technologies chosen for bioenergy conversion.

The limitations that can still be found depend essentially on the processes of biomass conversion such as AD which, due to the complexity of the system, can take a long time, including years, to find the ideal conditions for the system, especially if the biomass has a high amount of contaminants; in alcoholic fermentation, which requires a pre-treatment phase that makes the process more expensive, and in most thermochemical processes, since, in all of these, the formation of a gaseous phase occurs when biomass with a high amount of nitrogen and chlorides are processed, the formation of contaminants can occur, and in the case of biochar (solid phase), if it presents a high amount of HMs, it cannot be applied as soils remediation, therefore, the limitations do not exist only by the type of material that is being processed, it also depends on the process itself.

As one of the main functions performed by energy crops with low ILUC risk is precisely the recovery of MDC soils, future studies should also focus on how the recovery of metals found in the roots or shoots of the species can be carried out or what can be found in the residual part of some processes, in order to recover these metals and thus comply with the principles that drive the circular economy, creating a new economic sector that allows the recycling of metals and thus avoid excessive exploitation of mining areas.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15124348/s1, Table S1: Microalgae raw material studied for chemical conversion (transesterification) pathways towards biofuels; Table S2: Microalgae feedstock applied for biochemical conversion (anaerobic digestion) pathways towards biofuels; Table S3: Microalgae feedstock studied for biochemical conversion (alcoholic fermentation) pathways towards biofuels; Table S4: Microalgae feedstock applied for biochemical conversion (biological H_2 production) pathways towards biofuels; Table S5: Microalgae raw material studied for thermochemical conversion (gasification) pathways towards biofuels; Table S6: Microalgae feedstock studied for thermochemical conversion (pyrolysis) pathways towards biofuels; Table S7: Microalgae raw material studied for thermochemical conversion (hydrothermal liquefaction) pathways towards biofuels.

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References

1. Briones, M.J.I.; Elias, D.M.O.; Grant, H.K.; McNamara, N.P. Plant identity control on soil food web structure and C transfers under perennial bioenergy plantations. *Soil Biol. Biochem.* **2019**, *138*, 107603. [CrossRef]
2. Zheng, Y.; Qiu, F. Bioenergy in the Canadian Prairies: Assessment of accessible biomass from agricultural crop residues and identification of potential biorefinery sites. *Biomass Bioenergy* **2020**, *140*, 105669. [CrossRef]
3. Traverso, L.; Colangeli, M.; Morese, M.; Pulighe, G.; Branca, G. Opportunities and constraints for implementation of cellulosic ethanol value chains in Europe. *Biomass Bioenergy* **2020**, *141*, 105692. [CrossRef]
4. Ferreira, S.; Monteiro, E.; Brito, P.; Vilarinho, C. Biomass resources in Portugal: Current status and prospects. *Renew. Sustain. Energy Rev.* **2017**, *78*, 1221–1235. [CrossRef]
5. Castillo, C.; Baranzelli, C.; Maes, J.; Zulian, G.; Barbosa, A.; Vandecasteele, I.; Mari-Rivero, I.; Vallecillo, S.; Batista e Silva, F.; Jacobs-Crisioni, C.; et al. An assessment of dedicated energy crops in Europe under the EU Energy Reference Scenario 2013. In *Application of the LUISA Modelling Platform—Updated Configuration 2014*; European Union: Brussels, Belgium, 2015.
6. Maucieri, C.; Camarotto, C.; Florio, G.; Albergo, R.; Ambrico, A.; Trupo, M.; Borin, M. Bioethanol and biomethane potential production of thirteen pluri-annual herbaceous species. *Ind. Crops Prod.* **2019**, *129*, 694–701. [CrossRef]
7. Pires, J.R.A.; Souza, V.G.L.; Fernando, A.L. Valorization of energy crops as a source for nanocellulose production—Current knowledge and future prospects. *Ind. Crops Prod.* **2019**, *140*, 111642. [CrossRef]
8. Papazoglou, E.G.; Fernando, A.L. Preliminary studies on the growth, tolerance and phytoremediation ability of sugarbeet (*Beta vulgaris* L.) grown on heavy metal contaminated soil. *Ind. Crops Prod.* **2017**, *107*, 463–471. [CrossRef]
9. Barbosa, B.; Fernando, A.L. Aided Phytostabilization of Mine Waste. In *Bio-Geotechnologies for Mine Site Rehabilitation*; Prasad, M., Fava, P., SK, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 147–157.
10. Hanzhenko, O. *Seemla: Sustainable Exploitation of Biomass for Bioenergy from Marginal Lands in Europe—Catalogue for Bioenergy Crops and Their Suitability in the Categories of MagLs*; Institute of Bioenergy Crops and Sugar Beet National Academy of Agrarian Sciences of Ukraine (IBCSB NAASU): Kiev, Ukraine, 2016.
11. Kulig, B.; Gacek, E.; Wojciechowski, R.; Oleksy, A.; Kołodziejczyk, M.; Szewczyk, W.; Klimek-Kopyra, A. Biomass yield and energy efficiency of willow depending on cultivar, harvesting frequency and planting density. *Plant Soil Environ.* **2019**, *65*, 377–386. [CrossRef]
12. Pulighe, G.; Bonati, G.; Colangeli, M.; Morese, M.M.; Traverso, L.; Lupia, F.; Khawaja, C.; Janssen, R.; Fava, F. Ongoing and emerging issues for sustainable bioenergy production on marginal lands in the Mediterranean regions. *Renew. Sustain. Energy Rev.* **2019**, *103*, 58–70. [CrossRef]

13. Cosentino, S.L.; Patanè, C.; Sanzone, E.; Copani, V.; Foti, S. Effects of soil water content and nitrogen supply on the productivity of *Miscanthus* × *giganteus* Greef et Deu. in a Mediterranean environment. *Ind. Crops Prod.* **2007**, *25*, 75–88. [CrossRef]
14. Zatta, A.; Clifton-Brown, J.; Robson, P.; Hastings, A.; Monti, A. Land use change from C3 grassland to C4 Miscanthus: Effects on soil carbon content and estimated mitigation benefit after six years. *GCB Bioenergy* **2014**, *6*, 360–370. [CrossRef]
15. Cosentino, S.L.; Copani, V.; Scalici, G.; Scordia, D.; Testa, G. Soil Erosion Mitigation by Perennial Species Under Mediterranean Environment. *BioEnergy Res.* **2015**, *8*, 1538–1547. [CrossRef]
16. Fernando, A.L.; Rettenmaier, N.; Soldatos, P.; Panoutsou, C. Sustainability of Perennial Crops Production for Bioenergy and Bioproducts. In *Perennial Grasses for Bioenergy and Bioproducts*; Alexopoulou, E., Ed.; Academic Press: Cambridge, MA, USA, 2018; pp. 245–283.
17. Pin, M.; Vecchiet, A.; Picco, D. Diffusion of a Sustainable EU Model to Produce 1st Generation Ethanol from Sweet Sorghum in Decentralised Plants. In Proceedings of the 19th European Biomass Conference and Exhibition (EUBCE 2011), Berlin, Germany, 6–10 June 2011; ETA-Florence Renewable Energies: Florence, Italy, 2011.
18. Fernando, A.L.; Oliveira, J.F. Caracterização do potencial da planta *Miscanthus* × *giganteus* em Portugal para fins energéticos e industriais. In *Biologia Vegetal e Agro-Industrial*; Robalo, M., Ed.; Edições Sílabo: Lisboa, Portugal, 2005; Volume 2, pp. 195–204.
19. Long, X.H.; Shao, H.B.; Liu, L.; Liu, L.P.; Liu, Z.P. Jerusalem artichoke: A sustainable biomass feedstock for biorefinery. *Renew. Sustain. Energy Rev.* **2016**, *54*, 1382–1388. [CrossRef]
20. Cumplido-Marin, L.; Graves, A.R.; Burgess, P.J.; Morhart, C.; Paris, P.; Jablonowsk, N.D.; Facciotto, G.; Bury, M.; Martens, R.; Nahm, M. Two Novel Energy Crops: *Sida hermaphrodita* (L.) Rusby and *Silphium perfoliatum* L.—State of Knowledge. *Agronomy* **2020**, *10*, 928. [CrossRef]
21. Bury, M.; Rusinowski, S.; Sitko, K.; Krzyżak, J.; Kitczak, T.; Możdżer, E.; Siwek, H.; Włodarczyk, M.; Zieleźnik-Rusinowska, P.; Szada-Borzyszkowska, A.; et al. Physiological status and biomass yield of *Sida hermaphrodita* (L.) Rusby cultivated on two distinct marginal lands in Southern and Northern Poland. *Ind. Crops Prod.* **2021**, *167*, 113502. [CrossRef]
22. Dębowski, M.; Zieliński, M.; Kisielewska, M.; Krzemieniewski, M. Anaerobic Co-digestion of the Energy Crop Sida hermaphrodita and Microalgae Biomass for Enhanced Biogas Production. *Int. J. Environ. Res.* **2017**, *11*, 243–250. [CrossRef]
23. Papamatthaiakis, N.; Laine, A.; Haapala, A.; Ikonen, R.; Kuittinen, S.; Pappinen, A.; Kolström, M.; Mola-Yudego, B. New energy crop alternatives for Northern Europe: Yield, chemical and physical properties of Giant knotweed (*Fallopia sachalinensis* var. 'Igniscum') and Virginia mallow (*Sida hermaphrodita*). *Fuel* **2021**, *304*, 121349. [CrossRef]
24. Kurucz, E.; Fári, M.G.; Antal, G.; Gabnai, Z.; Popp, J.; Bai, A. Opportunities for the production and economics of Virginia fanpetals (*Sida hermaphrodita*). *Renew. Sustain. Energy Rev.* **2018**, *90*, 824–834. [CrossRef]
25. Rooney, W.L.; Blumenthal, J.; Bean, B.; Mullet, J.E. Designing sorghum as a dedicated bioenergy feedstock. *Biofuels Bioprod. Biorefin.* **2007**, *1*, 147–157. [CrossRef]
26. Lourenço, A.; Neiva, D.M.; Gominho, J.; Curt, M.D.; Fernández, J.; Marques, A.V.; Pereira, H. Biomass production of four *Cynara cardunculus* clones and lignin composition analysis. *Biomass Bioenergy* **2015**, *76*, 86–95. [CrossRef]
27. Barracosa, P.; Barracosa, M.; Pires, E. Cardoon as a Sustainable Crop for Biomass and Bioactive Compounds Production. *Chem. Biodivers.* **2019**, *16*, e1900498. [CrossRef] [PubMed]
28. Oginni, O.; Singh, K. Pyrolysis characteristics of *Arundo donax* harvested from a reclaimed mine land. *Ind. Crops Prod.* **2019**, *133*, 44–53. [CrossRef]
29. Ge, X.; Xu, F.; Vasco-Correa, J.; Li, Y. Giant reed: A competitive energy crop in comparison with miscanthus. *Renew. Sustain. Energy Rev.* **2016**, *54*, 350–362. [CrossRef]
30. Ji, A.; Jia, L.; Kumar, D.; Yoo, C.G. Recent Advancements in Biological Conversion of Industrial Hemp for Biofuel and Value-Added Products. *Fermentation* **2021**, *7*, 6. [CrossRef]
31. Kim, S.; Park, J.M.; Kim, C.H. Ethanol production using whole plant biomass of jerusalem artichoke by Kluyveromyces marxianus CBS1555. *Appl. Biochem. Biotechnol.* **2013**, *169*, 1531–1545. [CrossRef]
32. Kim, S.; Kim, C.H. Evaluation of whole Jerusalem artichoke (*Helianthus tuberosus* L.) forconsolidated bioprocessing ethanol production. *Renew. Energy* **2014**, *65*, 83–91. [CrossRef]
33. Cabral, M.R.; Nakanishi, E.Y.; Mármol, G.; Palacios, J.; Godbout, S.; Lagacé, R.; Savastano, H.; Fiorelli, J. Potential of Jerusalem Artichoke (*Helianthus tuberosus* L.) stalks to produce cement-bonded particleboards. *Ind. Crops Prod.* **2018**, *122*, 214–222. [CrossRef]
34. Singh, D.; Sharma, D.; Soni, S.L.; Sharma, S.; Kumari, D. Chemical compositions, properties, and standards for different generation biodiesels: A review. *Fuel* **2019**, *253*, 60–71. [CrossRef]
35. Appiah-Nkansah, N.B.; Li, J.; Rooney, W.; Wang, D. A review of sweet sorghum as a viable renewable bioenergy crop and its techno-economic analysis. *Renew. Energy* **2019**, *143*, 1121–1132. [CrossRef]
36. Samson, R.; Mani, S.; Boddey, R.; Sokhansanj, S.; Quesada, D.; Urquiaga, S.; Reis, V.; Lem, C.H. The Potential of C 4 Perennial Grasses for Developing a Global BIOHEAT Industry. *CRC. Crit. Rev. Plant Sci.* **2005**, *24*, 461–495. [CrossRef]
37. Bonfiglio, F.; Cagno, M.; Rey, F.; Torres, M.; Böthig, S.; Menéndez, P.; Mussatto, S.I. Pretreatment of switchgrass by steam explosion in a semi-continuous pre-pilot reactor. *Biomass Bioenergy* **2019**, *121*, 41–47. [CrossRef]
38. Alcheikh, A. Advantages and Challenges of Hemp Biodiesel Production: A Comparison of Hemp vs. Other Crops Commonly Used for Biodiesel Production. Master's Thesis, University of Gävle, Gävle, Sweden, 2015.
39. Hashemzadeh Gargari, M.; Sadrameli, S.M. Investigating continuous biodiesel production from linseed oil in the presence of a Co-solvent and a heterogeneous based catalyst in a packed bed reactor. *Energy* **2018**, *148*, 888–895. [CrossRef]

40. Sambusiti, C.; Ficara, E.; Malpei, F.; Steyer, J.P.; Carrère, H. Influence of alkaline pre-treatment conditions on structural features and methane production from ensiled sorghum forage. *Chem. Eng. J.* **2012**, *211–212*, 488–492. [CrossRef]
41. Stamenković, O.S.; Siliveru, K.; Veljković, V.B.; Banković-Ilić, I.B.; Tasić, M.B.; Ciampitti, I.A.; Đalović, I.G.; Mitrović, P.M.; Sikora, V.; Prasad, P.V.V. Production of biofuels from sorghum. *Renew. Sustain. Energy Rev.* **2020**, *124*, 109769. [CrossRef]
42. Di Girolamo, G.; Grigatti, M.; Barbanti, L.; Angelidaki, I. Effects of hydrothermal pre-treatments on Giant reed (*Arundo donax*) methane yield. *Bioresour. Technol.* **2013**, *147*, 152–159. [CrossRef] [PubMed]
43. Sipos, B.; Kreuger, E.; Svensson, S.E.; Réczey, K.; Björnsson, L.; Zacchi, G. Steam pretreatment of dry and ensiled industrial hemp for ethanol production. *Biomass Bioenergy* **2010**, *34*, 1721–1731. [CrossRef]
44. Rossini, F.; Provenzano, M.E.; Kuzmanović, L.; Ruggeri, R. Jerusalem Artichoke (*Helianthus tuberosus* L.): A versatile and sustainable crop for renewable energy production in Europe. *Agronomy* **2019**, *9*, 528. [CrossRef]
45. Saratale, G.D.; Kshirsagar, S.D.; Saratale, R.G.; Govindwar, S.P.; Oh, M.-K. Fermentative hydrogen production using sorghum husk as a biomass feedstock and process optimization. *Biotechnol. Bioprocess Eng.* **2015**, *20*, 733–743. [CrossRef]
46. Lakshman, V.; Brassard, P.; Hamelin, L.; Raghavan, V.; Godbout, S. Pyrolysis of Miscanthus: Developing the mass balance of a biorefinery through experimental tests in an auger reactor. *Bioresour. Technol. Rep.* **2021**, *14*, 100687. [CrossRef]
47. Bi, Z.; Zhang, J.; Peterson, E.; Zhu, Z.; Xia, C.; Liang, Y.; Wiltowski, T. Biocrude from pretreated sorghum bagasse through catalytic hydrothermal liquefaction. *Fuel* **2017**, *188*, 112–120. [CrossRef]
48. Serrano, D.; Horvat, A.; Sobrino, C.; Sánchez-Delgado, S. Thermochemical conversion of *C. cardunculus* L. in nitrate molten salts. *Appl. Therm. Eng.* **2019**, *148*, 136–146. [CrossRef]
49. Wiklund, A. The genus *Cynara* L. (Asteraceae-Cardueae). *Bot. J. Linn. Soc.* **1992**, *109*, 75–123. [CrossRef]
50. Fernández, J.; Hidalgo, M.; Del Monte, J.P.; Curt, M.D. *Cynara cardunculus* L. as a perennial crop for non-irrigated lands: Yields and applications. *Acta Hortic.* **2005**, *681*, 109–116. [CrossRef]
51. Gominho, J.; Curt, M.D.; Lourenço, A.; Fernández, J.; Pereira, H. *Cynara cardunculus* L. as a biomass and multi-purpose crop: A review of 30 years of research. *Biomass Bioenergy J.* **2018**, *109*, 257–275. [CrossRef]
52. Zayed, A.; Farag, M.A. Valorization, extraction optimization and technology advancements of artichoke biowastes: Food and non-food applications. *LWT* **2020**, *132*, 109883. [CrossRef]
53. Barracosa, P.; Oliveira, J.; Barros, M.; Pires, E. Morphological evaluation of cardoon (*Cynara cardunculus* L.): Assessing biodiversity for applications based on tradition, innovation and sustainability. *Genet. Resour. Crop Evol.* **2018**, *65*, 17–28. [CrossRef]
54. Gominho, J.; Fernandez, J.; Pereira, H. *Cynara cardunculus* L.—A new fibre crop for pulp and paper production. *Ind. Crops Prod.* **2001**, *13*, 1–10. [CrossRef]
55. Neri, U.; Pennelli, B.; Simonetti, G.; Francaviglia, R. Biomass partition and productive aptitude of wild and cultivated cardoon genotypes (*Cynara cardunculus* L.) in a marginal land of Central Italy. *Ind. Crops Prod.* **2017**, *95*, 191–201. [CrossRef]
56. Pappalardo, H.D.; Toscano, V.; Puglia, G.D.; Genovese, C.; Raccuia, S.A. *Cynara cardunculus* L. as a Multipurpose Crop for Plant Secondary Metabolites Production in Marginal Stressed Lands. *Front. Plant Sci.* **2020**, *11*, 240. [CrossRef]
57. Sitepu, E.K.; Heimann, K.; Raston, C.L.; Zhang, W. Critical evaluation of process parameters for direct biodiesel production from diverse feedstock. *Renew. Sustain. Energy Rev.* **2020**, *123*, 109762. [CrossRef]
58. Ferrero, F.; Dinuccio, E.; Rollé, L.; Tabacco, E.; Borreani, G. Suitability of cardoon (*Cynara cardunculus* L.) harvested at two stages of maturity to ensiling and methane production. *Biomass Bioenergy* **2020**, *142*, 105776. [CrossRef]
59. Zabaniotou, A.; Bitou, P.; Kanellis, T.; Manara, P.; Stavropoulos, G. Investigating Cynara C. biomass gasification producer gas suitability for CHP, second generation biofuels, and H2 production. *Ind. Crops Prod.* **2014**, *61*, 308–316. [CrossRef]
60. Toscano, V.; Sollima, L.; Genovese, C.; Melilli, M.G.; Raccuia, S.A. Pilot plant system for biodiesel and pellet production from cardoon: Technical and economic feasibility. *Acta Hortic.* **2016**, *1147*, 429–442. [CrossRef]
61. Gutiérrez, J.; Galán, C.A.; Suárez, R.; Álvarez-Murillo, A.; González, J.F. Biofuels from cardoon pyrolysis: Extraction and application of biokerosene/kerosene mixtures in a self-manufactured jet engine. *Energy Convers. Manag.* **2018**, *157*, 246–256. [CrossRef]
62. Barbanera, M.; Castellini, M.; Tasselli, G.; Turchetti, B.; Cotana, F.; Buzzini, P. Prediction of the environmental impacts of yeast biodiesel production from cardoon stalks at industrial scale. *Fuel* **2021**, *283*, 118967. [CrossRef]
63. Nogales-Delgado, S.; Sánchez, N.; Encinar, J.M. Valorization of *Cynara cardunculus* L. Oil as the basis of a biorefinery for biodiesel and biolubricant production. *Energies* **2020**, *13*, 5085. [CrossRef]
64. Pesce, G.R.; Negri, M.; Bacenetti, J.; Mauromicale, G. The biomethane, silage and biomass yield obtainable from three accessions of *Cynara cardunculus*. *Ind. Crops Prod.* **2017**, *103*, 233–239. [CrossRef]
65. Espada, J.J.; Villalobos, H.; Rodríguez, R. Environmental assessment of different technologies for bioethanol production from *Cynara cardunculus*: A Life Cycle Assessment study. *Biomass Bioenergy* **2021**, *144*, 105910. [CrossRef]
66. Vergara, P.; Ladero, M.; García-Ochoa, F.; Villar, J.C. Valorization of *Cynara cardunculus* crops by ethanol-water treatment: Optimization of operating conditions. *Ind. Crops Prod.* **2018**, *124*, 856–862. [CrossRef]
67. Mancini, M.; Lanza Volpe, M.; Gatti, B.; Malik, Y.; Moreno, A.C.; Leskovar, D.; Cravero, V. Characterization of cardoon accessions as feedstock for biodiesel production. *Fuel* **2019**, *235*, 1287–1293. [CrossRef]
68. Fernandes, M.C.; Ferro, M.D.; Paulino, A.F.C.; Mendes, J.A.S.; Gravitis, J.; Evtuguin, D.V.; Xavier, A.M.R.B. Enzymatic saccharification and bioethanol production from *Cynara cardunculus* pretreated by steam explosion. *Bioresour. Technol.* **2015**, *186*, 309–315. [CrossRef] [PubMed]

69. Cotana, F.; Cavalaglio, G.; Gelosia, M.; Coccia, V.; Petrozzi, A.; Ingles, D.; Pompili, E. A comparison between SHF and SSSF processes from cardoon for ethanol production. *Ind. Crops Prod.* **2015**, *69*, 424–432. [CrossRef]
70. Mañas, P.; Castro, E.; de las Heras, J. Application of treated wastewater and digested sewage sludge to obtain biomass from *Cynara cardunculus* L. *J. Clean. Prod.* **2014**, *67*, 72–78. [CrossRef]
71. Abreu, M.; Reis, A.; Moura, P.; Fernando, A.L.; Luís, A.; Quental, L.; Patinha, P.; Gírio, F. Evaluation of the potential of biomass to energy in Portugal-conclusions from the CONVERTE project. *Energies* **2020**, *13*, 937. [CrossRef]
72. Duke, J.A. Handbook of Energy Crops. Available online: https://hort.purdue.edu/newcrop/duke_energy/Arundo_donax.html/hort.purdue.edu/newcrop/duke_energy/Arundo_donax.html (accessed on 17 January 2020).
73. Duke, J.; Wain, K. *Medicinal Plants of the World-Computer Index with More Than 85,000 Entries*; Plant genetics and germplasm Institute, Agriculture Research Services: Beltsville, MD, USA, 2008; pp. 231–239.
74. Raghu, S.; Anderson, R.C.; Daehler, C.C.; Davis, A.S.; Wiedenmann, R.N.; Simberloff, D.; Mack, R.N. Adding biofuels to the invasive species fire? *Science* **2006**, *313*, 1742. [CrossRef]
75. Low, T.; Carol, B. *The Weedy Truth About Biofuels*; Invasive Species Council: Melbourne, Australia, 2007.
76. Corno, L.; Pilu, R.; Adani, F. *Arundo donax* L.: A non-food crop for bioenergy and bio-compound production. *Biotechnol. Adv.* **2014**, *32*, 1535–1549. [CrossRef]
77. Dahl, J.; Obernberger, I. Evaluation of the combustion characteristics of four perennial energy crops (*Arundo donax*, *Cynara cardunculus*, *Miscanthus* × *giganteus* and *Panicum virgatum*). In Proceedings of the 2nd World Conference on Biomass for Energy, Industry and Climate Protection, Rome, Italy, 10–14 May 2004; pp. 1265–1270.
78. Ragaglini, G.; Dragoni, F.; Simone, M.; Bonari, E. Suitability of giant reed (*Arundo donax* L.) for anaerobic digestion: Effect of harvest time and frequency on the biomethane yield potential. *Bioresour. Technol.* **2014**, *152*, 107–115. [CrossRef]
79. Dell'Omo, P.P.; Spena, V.A. Mechanical pretreatment of lignocellulosic biomass to improve biogas production: Comparison of results for giant reed and wheat straw. *Energy* **2020**, *203*, 117798. [CrossRef]
80. Vasmara, C.; Cianchetta, S.; Marchetti, R.; Ceotto, E.; Galletti, S. Potassium Hydroxyde Pre-Treatment Enhances Methane Yield from Giant Reed (*Arundo donax* L.). *Energies* **2021**, *14*, 630. [CrossRef]
81. De Bari, I.; Liuzzi, F.; Ambrico, A.; Trupo, M. *Arundo donax* refining to second generation bioethanol and furfural. *Processes* **2020**, *8*, 1591. [CrossRef]
82. Lemons e Silva, C.F.; Schirmer, M.A.; Maeda, R.N.; Barcelos, C.A.; Pereira, N. Potential of giant reed (*Arundo donax* L.) for second generation ethanol production. *Electron. J. Biotechnol.* **2015**, *18*, 10–15. [CrossRef]
83. Jaradat, A.A. Genetic resources of energy crops: Biological systems to combat climate change. *Aust. J. Crop Sci.* **2010**, *4*, 309–323.
84. Jámbor, A.; Török, Á. The Economics of *Arundo donax*—A Systematic Literature Review. *Sustainability* **2019**, *11*, 4225. [CrossRef]
85. Muthuvelu, K.S.; Rajarathinam, R.; Kanagaraj, L.P.; Ranganathan, R.V.; Dhanasekaran, K.; Manickam, N.K. Evaluation and characterization of novel sources of sustainable lignocellulosic residues for bioethanol production using ultrasound-assisted alkaline pre-treatment. *Waste Manag.* **2019**, *87*, 368–374. [CrossRef]
86. Komolwanich, T.; Tatijarern, P.; Prasertwasu, S.; Khumsupan, D.; Chaisuwan, T.; Luengnaruemitchai, A.; Wongkasemjit, S. Comparative potentiality of Kans grass (*Saccharum spontaneum*) and Giant reed (*Arundo donax*) as lignocellulosic feedstocks for the release of monomeric sugars by microwave/chemical pretreatment. *Cellulose* **2014**, *21*, 1327–1340. [CrossRef]
87. Ba, Y.; Liu, F.; Wang, X.; Yang, J. Pyrolysis of C3 energy plant (arundo donax): Thermogravimetry, mechanism, and potential evaluation. *Ind. Crops Prod.* **2020**, *149*, 112337. [CrossRef]
88. Fernando, A.L.; Barbosa, B.; Costa, J.; Papazoglou, E.G. Giant Reed (*Arundo donax* L.): A Multipurpose Crop Bridging Phytoremediation with Sustainable Bioeconomy. In *Bioremediation and Bioeconomy*; Prasad, M.N.V., Ed.; Elsevier: Amsterdam, The Netherlands, 2016; pp. 77–95.
89. Zhao, J.; Xu, Y.; Wang, W.; Griffin, J.; Roozeboom, K.; Wang, D. Bioconversion of industrial hemp biomass for bioethanol production: A review. *Fuel* **2020**, *281*, 118725. [CrossRef]
90. Johnson, R. *Hemp as an Agricultural Commodity*; Congressional Research Service (CRS)—USA Government: Washington, DC, USA, 2018.
91. DGADR. Cânhamo. Available online: http://guiaexploracoes.dgadr.pt/index.php/producao-vegetal/outros-setores/canhamo (accessed on 17 January 2020).
92. *European Parliament Regulation (EU) No 1308/2013 of the European Parliament and of the Council of 17 December 2013 Establishing a Common Organisation of the Markets in Agricultural Products and Repealing Council Regulations (EEC) No 922/72, (EEC) No 234/79, (EC) No 1037/2001*; European Union: Brussels, Belgium, 2013; pp. 671–854.
93. Fike, J. Industrial Hemp: Renewed Opportunities for an Ancient Crop. *CRC. Crit. Rev. Plant Sci.* **2016**, *35*, 406–424. [CrossRef]
94. Duque Schumacher, A.G.; Pequito, S.; Pazour, J. Industrial hemp fiber: A sustainable and economical alternative to cotton. *J. Clean. Prod.* **2020**, *268*, 122180. [CrossRef]
95. Parvez, A.M.; Lewis, J.D.; Afzal, M.T. Potential of industrial hemp (*Cannabis sativa* L.) for bioenergy production in Canada: Status, challenges and outlook. *Renew. Sustain. Energy Rev.* **2021**, *141*, 110784. [CrossRef]
96. Ingrao, C.; Lo Giudice, A.; Bacenetti, J.; Tricase, C.; Dotelli, G.; Fiala, M.; Siracusa, V.; Mbohwa, C. Energy and environmental assessment of industrial hemp for building applications: A review. *Renew. Sustain. Energy Rev.* **2015**, *51*, 29–42. [CrossRef]
97. Kraszkiewicz, A.; Kachel, M.; Parafiniuk, S.; Zając, G.; Niedziółka, I.; Sprawka, M. Assessment of the Possibility of Using Hemp Biomass (*Cannabis sativa* L.) for Energy Purposes: A Case Study. *Appl. Sci.* **2019**, *9*, 4437. [CrossRef]

98. Crini, G.; Lichtfouse, E.; Chanet, G.; Morin-Crini, N. Applications of hemp in textiles, paper industry, insulation and building materials, horticulture, animal nutrition, food and beverages, nutraceuticals, cosmetics and hygiene, medicine, agrochemistry, energy production and environment: A review. *Environ. Chem. Lett.* **2020**, *18*, 1451–1476. [CrossRef]
99. Pedrazzi, S.; Santunione, G.; Mustone, M.; Cannazza, G.; Citti, C.; Francia, E.; Allesina, G. Techno-economic study of a small scale gasifier applied to an indoor hemp farm: From energy savings to biochar effects on productivity. *Energy Convers. Manag.* **2021**, *228*, 113645. [CrossRef]
100. Salami, A.; Raninen, K.; Heikkinen, J.; Tomppo, L.; Vilppo, T.; Selenius, M.; Raatikainen, O.; Lappalainen, R.; Vepsäläinen, J. Complementary chemical characterization of distillates obtained from industrial hemp hurds by thermal processing. *Ind. Crops Prod.* **2020**, *155*, 112760. [CrossRef]
101. Peças, P.; Carvalho, H.; Salman, H.; Leite, M. Natural fibre composites and their applications: A review. *J. Compos. Sci.* **2018**, *2*, 66. [CrossRef]
102. Jami, T.; Karade, S.R.; Singh, L.P. A review of the properties of hemp concrete for green building applications. *J. Clean. Prod.* **2019**, *239*, 117852. [CrossRef]
103. Khan, B.A.; Chevali, V.S.; Na, H.; Zhu, J.; Warner, P.; Wang, H. Processing and properties of antibacterial silver nanoparticle-loaded hemp hurd/poly(lactic acid) biocomposites. *Compos. Part B Eng.* **2016**, *100*, 10–18. [CrossRef]
104. Viswanathan, M.B.; Cheng, M.H.; Clemente, T.E.; Dweikat, I.; Singh, V. Economic perspective of ethanol and biodiesel coproduction from industrial hemp. *J. Clean. Prod.* **2021**, *299*, 126875. [CrossRef]
105. Prade, T. *Industrial Hemp (Cannabis sativa L.)—A High-Yielding Energy Crop*; Swedish University of Agricultural Sciences: Uppsala, Sweden, 2011.
106. Li, S.Y.; Stuart, J.D.; Li, Y.; Parnas, R.S. The feasibility of converting *Cannabis sativa* L. oil into biodiesel. *Bioresour. Technol.* **2010**, *101*, 8457–8460. [CrossRef]
107. Ahmad, M.; Ullah, K.; Khan, M.A.; Zafar, M.; Tariq, M.; Ali, S.; Sultana, S. Physicochemical analysis of hemp oil biodiesel: A promising non edible new source for bioenergy. *Energy Sour. Part A Recover. Util. Environ. Eff.* **2011**, *33*, 1365–1374. [CrossRef]
108. Prade, T.; Svensson, S.E.; Mattsson, J.E. Energy balances for biogas and solid biofuel production from industrial hemp. *Biomass Bioenergy* **2012**, *40*, 36–52. [CrossRef]
109. Plöchl, M.; Heiermann, M.; Linke, B.; Schelle, H. Biogas Crops—Part II: Balance of Greenhouse Gas Emissions and Energy from Using Field Crops for Anaerobic Digestion. *Agric. Eng. Int. CIGR J.* **2009**, *XI*, 1–11.
110. Prade, T.; Svensson, S.E.; Andersson, A.; Mattsson, J.E. Biomass and energy yield of industrial hemp grown for biogas and solid fuel. *Biomass Bioenergy* **2011**, *35*, 3040–3049. [CrossRef]
111. Laghari, M.; Mirjat, M.S.; Hu, Z.; Fazal, S.; Xiao, B.; Hu, M.; Chen, Z.; Guo, D. Effects of biochar application rate on sandy desert soil properties and sorghum growth. *Catena* **2015**, *135*, 313–320. [CrossRef]
112. Pakarinen, A.; Maijala, P.; Stoddard, F.L.; Santanen, A.; Tuomainen, P.; Kymäläinen, M.; Viikari, L. Evaluation of annual bioenergy crops in the boreal zone for biogas and ethanol production. *Biomass Bioenergy* **2011**, *35*, 3071–3078. [CrossRef]
113. Kuglarz, M.; Gunnarsson, I.B.; Svensson, S.E.; Prade, T.; Johansson, E.; Angelidaki, I. Ethanol production from industrial hemp: Effect of combined dilute acid/steam pretreatment and economic aspects. *Bioresour. Technol.* **2014**, *163*, 236–243. [CrossRef]
114. Branca, C.; Di Blasi, C.; Galgano, A. Experimental analysis about the exploitation of industrial hemp (*Cannabis sativa*) in pyrolysis. *Fuel Process. Technol.* **2017**, *162*, 20–29. [CrossRef]
115. Viswanathan, M.B.; Park, K.; Cheng, M.H.; Cahoon, E.B.; Dweikat, I.; Clemente, T.; Singh, V. Variability in structural carbohydrates, lipid composition, and cellulosic sugar production from industrial hemp varieties. *Ind. Crops Prod.* **2020**, *157*, 112906. [CrossRef]
116. Matassa, S.; Esposito, G.; Pirozzi, F.; Papirio, S. Exploring the biomethane potential of different industrial hemp (*Cannabis sativa* L.) biomass residues. *Energies* **2020**, *13*, 3361. [CrossRef]
117. Kreuger, E.; Prade, T.; Escobar, F.; Svensson, S.E.; Englund, J.E.; Björnsson, L. Anaerobic digestion of industrial hemp-Effect of harvest time on methane energy yield per hectare. *Biomass Bioenergy* **2011**, *35*, 893–900. [CrossRef]
118. Kreuger, E.; Sipos, B.; Zacchi, G.; Svensson, S.E.; Björnsson, L. Bioconversion of industrial hemp to ethanol and methane: The benefits of steam pretreatment and co-production. *Bioresour. Technol.* **2011**, *102*, 3457–3465. [CrossRef] [PubMed]
119. Nykter, M.; Kymäläinen, H.R.; Thomsen, A.B.; Lilholt, H.; Koponen, H.; Sjöberg, A.M.; Thygesen, A. Effects of thermal and enzymatic treatments and harvesting time on the microbial quality and chemical composition of fibre hemp (*Cannabis sativa* L.). *Biomass Bioenergy* **2008**, *32*, 392–399. [CrossRef]
120. Das, L.; Liu, E.; Saeed, A.; Williams, D.W.; Hu, H.; Li, C.; Ray, A.E.; Shi, J. Industrial hemp as a potential bioenergy crop in comparison with kenaf, switchgrass and biomass sorghum. *Bioresour. Technol.* **2017**, *244*, 641–649. [CrossRef] [PubMed]
121. Zhao, J.; Xu, Y.; Wang, W.; Griffin, J.; Wang, D. Conversion of liquid hot water, acid and alkali pretreated industrial hemp biomasses to bioethanol. *Bioresour. Technol.* **2020**, *309*, 123383. [CrossRef]
122. Rheay, H.T.; Omondi, E.C.; Brewer, C.E. Potential of hemp (*Cannabis sativa* L.) for paired phytoremediation and bioenergy production. *GCB Bioenergy* **2021**, *13*, 525–536. [CrossRef]
123. Kays, S.J.; Nottingham, S.F. Biology and Chemistry of Jerusalem Artichoke. In *Biology and Chemistry of Jerusalem Artichoke*; CRC Press: Boca Raton, FL, USA; Taylor and Francis Group: Abingdon, UK, 2007; Volume 44, p. 478, ISBN 9781420044959.
124. Yang, L.; He, Q.S.; Corscadden, K.; Udenigwe, C.C. The prospects of Jerusalem artichoke in functional food ingredients and bioenergy production. *Biotechnol. Rep.* **2015**, *5*, 77–88. [CrossRef]

125. Barclay, T.; Ginic-Markovic, M.; Cooper, P.; Petrovsky, N. Inulin—A versatile polysaccharide with multiple pharmaceutical and food chemical uses. *J. Excip. Food Chem.* **2010**, *1*, 27–50.
126. Qiu, Y.; Lei, P.; Zhang, Y.; Sha, Y.; Zhan, Y.; Xu, Z.; Li, S.; Xu, H.; Ouyang, P. Recent advances in bio-based multi-products of agricultural Jerusalem artichoke resources. *Biotechnol. Biofuels* **2018**, *11*, 151. [CrossRef]
127. Johansson, E.; Prade, T.; Angelidaki, I.; Svensson, S.E.; Newson, W.R.; Gunnarsson, I.B.; Hovmalm, H.P. Economically viable components from jerusalem artichoke (*Helianthus tuberosus* L.) in a biorefinery concept. *Int. J. Mol. Sci.* **2015**, *16*, 8997–9016. [CrossRef]
128. Rakhimov, D.A.; Zhauynbaeva, K.S.; Mezhlumyan, L.G.; Salikhov, S.A. Carbohydrates and Proteins from *Helianthus tuberosus*. *Chem. Nat. Compd.* **2014**, *50*, 344–345. [CrossRef]
129. Baldini, M.; Danuso, F.; Turi, M.; Vannozzi, G.P. Evaluation of new clones of Jerusalem artichoke (*Helianthus tuberosus* L.) for inulin and sugar yield from stalks and tubers. *Ind. Crops Prod.* **2004**, *19*, 25–40. [CrossRef]
130. Li, L.; Li, L.; Wang, Y.; Du, Y.; Qin, S. Biorefinery products from the inulin-containing crop Jerusalem artichoke. *Biotechnol. Lett.* **2013**, *35*, 471–477. [CrossRef] [PubMed]
131. Gunnarsson, I.B.; Svensson, S.E.; Johansson, E.; Karakashev, D.; Angelidaki, I. Potential of Jerusalem artichoke (*Helianthus tuberosus* L.) as a biorefinery crop. *Ind. Crops Prod.* **2014**, *56*, 231–240. [CrossRef]
132. Bhagia, S.; Akinosho, H.; Ferreira, J.F.S.; Ragauskas, A.J. Biofuel production from Jerusalem artichoke tuber inulins: A review. *Biofuel Res. J.* **2017**, *4*, 587–599. [CrossRef]
133. Matei, G.; Vlăduț, V.; Isticioaia, S.; Pânzaru, R.L.; Popa, D. Potential of Jerusalem Artichoke (*Helianthus tuberosus* L.) as a Biomass Crop. *Agron. J.* **2020**, *LXIII*, 387–393.
134. Ge, X.Y.; Zhang, W.G. A shortcut to the production of high ethanol concentration from jerusalem artichoke tubers. *Food Technol. Biotechnol.* **2005**, *43*, 241–246.
135. Gao, J.; Yuan, W.; Kong, L.; Xiang, R.; Zhong, S. Efficient ethanol production from inulin by two-stage aerate strategy. *Biomass Bioenergy* **2015**, *80*, 10–16. [CrossRef]
136. Paixão, S.M.; Alves, L.; Pacheco, R.; Silva, C.M. Evaluation of Jerusalem artichoke as a sustainable energy crop to bioethanol: Energy and CO2eq emissions modeling for an industrial scenario. *Energy* **2018**, *150*, 468–481. [CrossRef]
137. Song, Y.; Wi, S.G.; Kim, H.M.; Bae, H.J. Cellulosic bioethanol production from Jerusalem artichoke (*Helianthus tuberosus* L.) using hydrogen peroxide-acetic acid (HPAC) pretreatment. *Bioresour. Technol.* **2016**, *214*, 30–36. [CrossRef]
138. Li, M.; Wang, J.; Yang, Y.; Xie, G. Alkali-based pretreatments distinctively extract lignin and pectin for enhancing biomass saccharification by altering cellulose features in sugar-rich Jerusalem artichoke stem. *Bioresour. Technol.* **2016**, *208*, 31–41. [CrossRef] [PubMed]
139. Zhang, C.; Wu, D.; Yang, H.; Ren, H. Production of ethanol from Jerusalem artichoke by mycelial pellets. *Sci. Rep.* **2019**, *9*, 18510. [CrossRef] [PubMed]
140. Sarchami, T.; Rehmann, L. Optimizing enzymatic hydrolysis of inulin from Jerusalem artichoke tubers for fermentative butanol production. *Biomass Bioenergy* **2014**, *69*, 175–182. [CrossRef]
141. Li, Z. Site Suitability Analysis for Biomass Energy Plants Using GIS. Available online: https://sites.tufts.edu/gis/files/2014/11/Li_Zhaohuan.pdf (accessed on 22 April 2021).
142. Celińska, E.; Grajek, W. Biotechnological production of 2,3-butanediol—Current state and prospects. *Biotechnol. Adv.* **2009**, *27*, 715–725. [CrossRef]
143. Wünsch, K.; Gruber, S.; Claupein, W. Profitability analysis of cropping systems for biogas production on marginal sites in southwestern Germany. *Renew. Energy* **2012**, *45*, 213–220. [CrossRef]
144. Lehtomäki, A.; Viinikainen, T.A.; Rintala, J.A. Screening boreal energy crops and crop residues for methane biofuel production. *Biomass Bioenergy* **2008**, *32*, 541–550. [CrossRef]
145. Emmerling, D.C.; Barton, J. Anaerobic co-digestion of topinambour (*Helianthus tuberosus* L.) and properties of the remaining biogas manure. *Arch. Agron. Soil Sci.* **2007**, *53*, 683–690. [CrossRef]
146. Cheng, Y.; Zhou, W.; Gao, C.; Lan, K.; Gao, Y.; Wu, Q. Biodiesel production from Jerusalem artichoke (*Helianthus tuberosus* L.) tuber by heterotrophic microalgae Chlorella protothecoides. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 777–781. [CrossRef]
147. Zhao, X.; Wu, S.; Hu, C.; Wang, Q.; Hua, Y.; Zhao, Z.K. Lipid production from Jerusalem artichoke by Rhodosporidium toruloides Y4. *J. Ind. Microbiol. Biotechnol.* **2010**, *37*, 581–585. [CrossRef]
148. Ciccoli, R.; Sperandei, M.; Petrazzuolo, F.; Broglia, M.; Chiarini, L.; Correnti, A.; Farneti, A.; Pignatelli, V.; Tabacchioni, S. Anaerobic digestion of the above ground biomass of Jerusalem Artichoke in a pilot plant: Impact of the preservation method on the biogas yield and microbial community. *Biomass Bioenergy* **2018**, *108*, 190–197. [CrossRef]
149. Gao, K.; Zhang, Z.; Zhu, T.; Coulter, J.A. The influence of flower removal on tuber yield and biomass characteristics of *Helianthus tuberosus* L. in a semi-arid area. *Ind. Crops Prod.* **2020**, *150*, 112374. [CrossRef]
150. Song, Y.; Oh, C.; Bae, H.J. Simultaneous production of bioethanol and value-added D-psicose from Jerusalem artichoke (*Helianthus tuberosus* L.) tubers. *Bioresour. Technol.* **2017**, *244*, 1068–1072. [CrossRef] [PubMed]
151. Mehmood, M.A.; Ahmad, M.S.; Liu, Q.; Liu, C.G.; Tahir, M.H.; Aloqbi, A.A.; Tarbiah, N.I.; Alsufiani, H.M.; Gull, M. *Helianthus tuberosus* as a promising feedstock for bioenergy and chemicals appraised through pyrolysis, kinetics, and TG-FTIR-MS based study. *Energy Convers. Manag.* **2019**, *194*, 37–45. [CrossRef]

152. Dixit, S.; Kanakraj, S.; Rehman, A. Linseed oil as a potential resource for bio-diesel: A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 4415–4421. [CrossRef]
153. Popa, V.-M.; Gruia, A.; Raba, D.-I.; Dumbrava, D.; Moldovan, C.; Bordean, D.; Mateescu, C. Fatty acids composition and oil characteristics of linseed (*Linum usitatissimum* L.) from Romania. *J. Agroaliment. Process. Technol.* **2012**, *18*, 136–140.
154. Saleem, M.H.; Ali, S.; Hussain, S.; Kamran, M.; Chattha, M.S.; Ahmad, S.; Aqeel, M.; Rizwan, M.; Aljarba, N.H.; Alkahtani, S.; et al. Flax (*Linum usitatissimum* L.): A Potential Candidate for Phytoremediation? Biological and Economical Points of View. *Plants* **2020**, *9*, 496. [CrossRef]
155. Zhang, J.; Xie, Y.; Dang, Z.; Wang, L.; Li, W.; Zhao, W.; Zhao, L.; Dang, Z. Oil content and fatty acid components of oilseed flax under different environments in China. *Agron. J.* **2016**, *108*, 365–372. [CrossRef]
156. Lafond, G.P.; Irvine, B.; Johnston, A.M.; May, W.E.; McAndrew, D.W.; Shirtliffe, S.J.; Stevenson, F.C. Impact of agronomic factors on seed yield formation and quality in flax. *Can. J. Plant Sci.* **2008**, *88*, 485–500. [CrossRef]
157. Blackshaw, R.E.; Johnson, E.N.; Gan, Y.; May, W.E.; McAndrew, D.W.; Barthet, V.; McDonald, T.; Wispinski, D. Alternative oilseed crops for biodiesel feedstock on the Canadian prairies. *Can. J. Plant Sci.* **2011**, *91*, 889–896. [CrossRef]
158. Athar, M.; Zaidi, S. A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production. *J. Environ. Chem. Eng.* **2020**, *8*, 104523. [CrossRef]
159. Tabatabaei, M.; Aghbashlo, M.; Dehhaghi, M.; Panahi, H.K.S.; Mollahosseini, A.; Hosseini, M.; Soufiyan, M.M. Reactor technologies for biodiesel production and processing: A review. *Prog. Energy Combust. Sci.* **2019**, *74*, 239–303. [CrossRef]
160. Moser, B.R. Fuel property enhancement of biodiesel fuels from common and alternative feedstocks via complementary blending. *Renew. Energy* **2016**, *85*, 819–825. [CrossRef]
161. Warkhade, G.S.; Babu, A.V. Combustion characteristics of linseed (*Linum usitatissimum*) methyl ester fuelled biodiesel blends in variable compression ratio diesel engine. *Aust. J. Mech. Eng.* **2019**, *17*, 38–51. [CrossRef]
162. Bacenetti, J.; Restuccia, A.; Schillaci, G.; Failla, S. Biodiesel production from unconventional oilseed crops (*Linum usitatissimum* L. and *Camelina sativa* L.) in Mediterranean conditions: Environmental sustainability assessment. *Renew. Energy* **2017**, *112*, 444–456. [CrossRef]
163. Taherkhani, M.; Sadrameli, S.M. An improvement and optimization study of biodiesel production from linseed via in-situ transesterification using a co-solvent. *Renew. Energy* **2018**, *119*, 787–794. [CrossRef]
164. Ahmad, T.; Danish, M.; Kale, P.; Geremew, B.; Adeloju, S.B.; Nizami, M.; Ayoub, M. Optimization of process variables for biodiesel production by transesterification of flaxseed oil and produced biodiesel characterizations. *Renew. Energy* **2019**, *139*, 1272–1280. [CrossRef]
165. Griga, M.; Bjelková, M. Flax (*Linum usitatissimum* L.) and Hemp (*Cannabis sativa* L.) as Fibre Crops for Phytoextraction of Heavy Metals: Biological, Agro-technological and Economical Point of View. In *Plant-Based Remediation Processes*; Gupta, D.K., Ed.; Springer: Berlin, Heidelberg, 2013; Volume 35, pp. 199–237.
166. Saleem, M.H.; Fahad, S.; Khan, S.U.; Din, M.; Ullah, A.; Sabagh, A.E.L.; Hossain, A.; Llanes, A.; Liu, L. Copper-induced oxidative stress, initiation of antioxidants and phytoremediation potential of flax (*Linum usitatissimum* L.) seedlings grown under the mixing of two different soils of China. *Environ. Sci. Pollut. Res.* **2019**, *27*, 5211–5221. [CrossRef]
167. Amna; Masood, S.; Syed, J.H.; Munis, M.F.H.; Chaudhary, H.J. Phyto-Extraction of Nickel by *Linum usitatissimum* in Association with Glomus intraradices. *Int. J. Phytoremed.* **2015**, *17*, 981–987.
168. Fernando, A.L.; Godovikova, V.; Oliveira, J.F.S. *Miscanthus* × *giganteus*: Contribution to a Sustainable Agriculture of a Future/Present—Oriented Biomaterial. *Mater. Sci. Forum Adv. Mater. Forum II* **2004**, *455–456*, 437–441. [CrossRef]
169. Oliveira, J.S.; Duarte, M.P.; Christian, D.G.; Eppel-Hotz, A.; Fernando, A.L. Environmental aspects of Miscanthus production. In *Miscanthus: For Energy and Fibre*; Jones, M.B., Walsh, M., Eds.; James & James (Science Publishers): London, UK, 2001; pp. 172–178, ISBN 9781849710978.
170. Lewandowski, I.; Clifton-Brown, J.; Kiesel, A.; Hastings, A.; Iqbal, Y. Miscanthus. In *Perennial Grasses for Bioenergy and Bioproducts*; Alexopoulou, E., Ed.; Academic Press: Cambridge, MA, USA, 2018; pp. 35–59, ISBN 9780128129012.
171. Clifton-Brown, J.; Hastings, A.; Mos, M.; McCalmont, J.P.; Ashman, C.; Awty-Carroll, D.; Cerazy, J.; Chiang, Y.-C.; Cosentino, S.; Cracroft-Eley, W.; et al. Progress in upscaling Miscanthus biomass production for the European bio-economy with seed-based hybrids. *GCB Bioenergy* **2017**, *9*, 6–17. [CrossRef]
172. Danielewicz, D.; Surma-Ślusarska, B. *Miscanthus* × *giganteus* stalks as a potential non-wood raw material for the pulp and paper industry. Influence of pulping and beating conditions on the fibre and paper properties. *Ind. Crops Prod.* **2019**, *141*, 111744. [CrossRef]
173. Girones, J.; Vo, L.; Arnoult, S.; Brancourt-Hulmel, M.; Navard, P. Miscanthus stem fragment—Reinforced polypropylene composites: Development of an optimized preparation procedure at small scale and its validation for differentiating genotypes. *Polym. Test.* **2016**, *55*, 166–172. [CrossRef]
174. Okeke, I.J.; Sahoo, K.; Kaliyan, N.; Mani, S. Life cycle assessment of renewable diesel production via anaerobic digestion and Fischer-Tropsch synthesis from miscanthus grown in strip-mined soils. *J. Clean. Prod.* **2020**, *249*, 119358. [CrossRef]
175. Scordia, D.; van den Berg, D.; van Sleen, P.; Alexopoulou, E.; Cosentino, S.L. Are herbaceous perennial grasses suitable feedstock for thermochemical conversion pathways? *Ind. Crops Prod.* **2016**, *91*, 350–357. [CrossRef]
176. Schmidt, T.; Fernando, A.L.; Monti, A.; Rettenmaier, N. Life Cycle Assessment of Bioenergy and Bio-Based Products from Perennial Grasses Cultivated on Marginal Land in the Mediterranean Region. *BioEnergy Res.* **2015**, *8*, 1548–1561. [CrossRef]

177. Couto, N.D.; Silva, V.B.; Monteiro, E.; Rouboa, A.; Brito, P. An experimental and numerical study on the Miscanthus gasification by using a pilot scale gasifier. *Renew. Energy* **2017**, *109*, 248–261. [CrossRef]
178. Barbosa, B.; Costa, J.; Fernando, A.L. Production of Energy Crops in Heavy Metals Contaminated Land: Opportunities and Risks. In *Land Allocation for Biomass Crops*; Li, R., Monti, A., Eds.; Springer: Cham, Switzerland, 2018; pp. 83–102, ISBN 978-3-319-74536-7.
179. Wilk, M.; Magdziarz, A. Hydrothermal carbonization, torrefaction and slow pyrolysis of Miscanthus giganteus. *Energy* **2017**, *140*, 1292–1304. [CrossRef]
180. Kiesel, A.; Wagner, M.; Lewandowski, I. Environmental Performance of Miscanthus, Switchgrass and Maize: Can C4 Perennials Increase the Sustainability of Biogas Production? *Sustainalility* **2016**, *9*, 5. [CrossRef]
181. Dubis, B.; Bułkowska, K.; Lewandowska, M.; Szempliński, W.; Jankowski, K.J.; Idźkowski, J.; Kordala, N.; Szymańska, K. Effect of different nitrogen fertilizer treatments on the conversion of *Miscanthus* × *giganteus* to ethanol. *Bioresour. Technol.* **2017**, *243*, 731–737. [CrossRef]
182. Torrado, I.; Carvalheiro, F.; Duarte, L.C.; Raposo, S.; Gírio, F.M. Optimization of dilute acid hydrolysis for the selective recovery of hemicellulosic sugars from sorghum straw. In Proceedings of the 1-CIAB—1st Iberoamerican Congress on Biorefineries, Los Cabos, Mexico, 24–26 October 2012; pp. 557–563.
183. Sene, L.; Arruda, P.V.; Oliveira, S.M.M.; Felipe, M.G.A. Evaluation of sorghum straw hemicellulosic hydrolysate for biotechnological production of xylitol by Candida guilliermondii. *Braz. J. Microbiol.* **2011**, *42*, 1141–1146. [CrossRef]
184. Ledezma-Orozco, E.; Ruíz-Salazar, R.; Bustos-Vázquez, G.; Montes-García, N.; Roa-Cordero, V.; Rodríguez-Castillejos, G. Production of Xylitol from non-detoxified acid hydrolizates from Sorghum straw by Debaryomyces hansenii. *Agrociencia* **2018**, *52*, 1095–1106.
185. James, A.M.; Yuan, W.; Boyette, M.D.; Wang, D. The Effect of Air Flow Rate and Biomass Type on the Performance of an Updraft Biomass Gasifier. *BioResources* **2015**, *10*, 3615–3624. [CrossRef]
186. Qian, K.; Kumar, A.; Patil, K.; Bellmer, D.; Wang, D.; Yuan, W.; Huhnke, R.L. Effects of Biomass Feedstocks and Gasification Conditions on the Physiochemical Properties of Char. *Energies* **2013**, *6*, 3972–3986. [CrossRef]
187. Batog, J.; Frankowski, J.; Wawro, A.; Łacka, A. Bioethanol Production from Biomass of Selected Sorghum Varieties Cultivated as Main and Second Crop. *Energies* **2020**, *13*, 6291. [CrossRef]
188. Diallo, B.; Li, M.; Tang, C.; Ameen, A.; Zhang, W.; Xie, G.H. Biomass yield, chemical composition and theoretical ethanol yield for different genotypes of energy sorghum cultivated on marginal land in China. *Ind. Crops Prod.* **2019**, *137*, 221–230. [CrossRef]
189. Serra, P.; Giuntoli, J.; Agostini, A.; Colauzzi, M.; Amaducci, S. Coupling sorghum biomass and wheat straw to minimise the environmental impact of bioenergy production. *J. Clean. Prod.* **2017**, *154*, 242–254. [CrossRef]
190. Al Chami, Z.; Amer, N.; Smets, K.; Yperman, J.; Carleer, R.; Dumontet, S.; Vangronsveld, J. Evaluation of flash and slow pyrolysis applied on heavy metal contaminated *Sorghum bicolor* shoots resulting from phytoremediation. *Biomass Bioenergy* **2014**, *63*, 268–279. [CrossRef]
191. Kumar, V.; Kant, P. Study of Physical and Chemical Properties of Biodiesel from Sorghum Oil. *Res. J. Chem. Sci.* **2013**, *3*, 64–68.
192. Kumar, V.; Kant, P.; Nigam, G.D. Factor Affecting the Preparation of Biodiesel from Sorghum Oil. *Pet. Coal* **2013**, *55*, 6–11.
193. Kumar, V.; Kant, P. Differential Studies of Alkali Catalysed Production of Biodiesel from Sorghum Oil. *Res. J. Chem. Sci.* **2014**, *4*, 66–70.
194. Kumar, V.; Kant, P. Biodiesel Production from Sorghum Oil by Transesterification Using Zinc Oxide as Catalyst. *Pet. Coal* **2014**, *56*, 35–40.
195. Wyatt, V.T.; Jones, K.; Johnston, D.B.; Moreau, R.A. Production of Fatty-Acid Methyl Esters Via the In Situ Transesterification of Grain Sorghum Bran and Sorghum Distiller's Dried Grains and Solubles. *J. Am. Oil Chem. Soc.* **2018**, *95*, 743–752. [CrossRef]
196. Nazli, R.I. Evaluation of different sweet sorghum cultivars for bioethanol yield potential and bagasse combustion characteristics in a semiarid Mediterranean environment. *Biomass Bioenergy* **2020**, *139*, 105624. [CrossRef]
197. Mathur, S.; Umakanth, A.V.; Tonapi, V.A.; Sharma, R.; Sharma, M.K. Sweet sorghum as biofuel feedstock: Recent advances and available resources. *Biotechnol. Biofuels* **2017**, *10*, 146. [CrossRef] [PubMed]
198. Windpassinger, S.; Friedt, W.; Frauen, M.; Snowdon, R.; Wittkop, B. Designing adapted sorghum silage types with an enhanced energy density for biogas generation in temperate Europe. *Biomass Bioenergy* **2015**, *81*, 496–504. [CrossRef]
199. Gamawati Adinurani, P.; Rahayu, S.; Sulistiyo Budi, L.; Nindita, A.; Soni, P.; Mel, M. Biomass and Sugar Content of Some Varieties of Sorghum (*Sorghum bicolor* L. Moench) on Dry Land Forest as Feedstock Bioethanol. In Proceedings of the 3rd International Conference on Electrical Systems, Technology and Information (ICESTI 2017), Bali, Indonesia, 26–29 September 2017; EDP Sciences: Les Ulis, France, 2018; Volume 164, p. 01035.
200. Hu, Y.; Ma, H.; Shi, C.; Kobayashi, T.; Xu, K.Q. Nutrient augmentation enhances biogas production from sorghum mono-digestion. *Waste Manag.* **2021**, *119*, 63–71. [CrossRef] [PubMed]
201. Głąb, L.; Sowiński, J.; Chmielewska, J.; Prask, H.; Fugol, M.; Szlachta, J. Comparison of the energy efficiency of methane and ethanol production from sweet sorghum (*Sorghum bicolor* (L.) Moench) with a variety of feedstock management technologies. *Biomass Bioenergy* **2019**, *129*, 105332. [CrossRef]
202. Antonopoulou, G.; Gavala, H.N.; Skiadas, I.V.; Angelopoulos, K.; Lyberatos, G. Biofuels generation from sweet sorghum: Fermentative hydrogen production and anaerobic digestion of the remaining biomass. *Bioresour. Technol.* **2008**, *99*, 110–119. [CrossRef]

203. Sjöblom, M.; Matsakas, L.; Christakopoulos, P.; Rova, U. Production of butyric acid by Clostridium tyrobutyricum (ATCC25755) using sweet sorghum stalks and beet molasses. *Ind. Crops Prod.* **2015**, *74*, 535–544. [CrossRef]
204. Dweikat, I.; Weil, C.W.; Moose, S.; Kochian, L.; Mosier, N.; Ileleji, K.; Brown, P.; Peer, W.; Murphy, A.; Taheripour, F.; et al. Envisioning the transition to a next-generation biofuels industry in the US Midwest. *Biofuels, Bioprod. Biorefin.* **2012**, *6*, 376–386. [CrossRef]
205. Reddy, B.V.; Ramesh, S.; Reddy, P.S.; Ramaiah, B.; Salimath, M.; Kachapur, R. Sweet Sorghum—A Potential Alternate Raw Material for Bio-ethanol and Bio-energy. *Int. Crop. Res. Inst. Semi-Arid Trop.* **2005**, *46*, 79–86.
206. Soldatos, P.; Lychnaras, V.; Panoutsou, C.; Cosentino, S.L. Economic viability of energy crops in the EU: The farmer's point of view. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 637–657. [CrossRef]
207. Marx, S.; Ndaba, B.; Chiyanzu, I.; Schabort, C. Fuel ethanol production from sweet sorghum bagasse using microwave irradiation. *Biomass Bioenergy* **2014**, *65*, 145–150. [CrossRef]
208. Barcelos, C.A.; Maeda, R.N.; Santa Anna, L.M.M.; Pereira, N. Sweet sorghum as a whole-crop feedstock for ethanol production. *Biomass Bioenergy* **2016**, *94*, 46–56. [CrossRef]
209. Maw, M.J.W.; Houx, J.H.; Fritschi, F.B. Maize, sweet sorghum, and high biomass sorghum ethanol yield comparison on marginal soils in Midwest USA. *Biomass Bioenergy* **2017**, *107*, 164–171. [CrossRef]
210. Szambelan, K.; Nowak, J.; Frankowski, J.; Szwengiel, A.; Jeleń, H.; Burczyk, H. The comprehensive analysis of sorghum cultivated in Poland for energy purposes: Separate hydrolysis and fermentation and simultaneous saccharification and fermentation methods and their impact on bioethanol effectiveness and volatile by-products from the. *Bioresour. Technol.* **2018**, *250*, 750–757. [CrossRef]
211. Boboescu, I.Z.; Damay, J.; Chang, J.K.W.; Beigbeder, J.B.; Duret, X.; Beauchemin, S.; Lalonde, O.; Lavoie, J.M. Ethanol production from residual lignocellulosic fibers generated through the steam treatment of whole sorghum biomass. *Bioresour. Technol.* **2019**, *292*, 121975. [CrossRef]
212. Matsakas, L.; Rova, U.; Christakopoulos, P. Evaluation of dried sweet sorghum stalks as raw material for methane production. *Biomed Res. Int.* **2014**, *2014*, 731731. [CrossRef]
213. Zhang, Z.; Zhang, G.; Li, W.; Li, C.; Xu, G. Enhanced biogas production from sorghum stem by co-digestion with cow manure. *Int. J. Hydrogen Energy* **2016**, *41*, 9153–9158. [CrossRef]
214. Antonopoulou, G.; Lyberatos, G. Effect of Pretreatment of Sweet Sorghum Biomass on Methane Generation. *Waste Biomass Valorization* **2012**, *4*, 583–591. [CrossRef]
215. Laopaiboon, L.; Nuanpeng, S.; Srinophakun, P.; Klanrit, P.; Laopaiboon, P. Ethanol production from sweet sorghum juice using very high gravity technology: Effects of carbon and nitrogen supplementations. *Bioresour. Technol.* **2009**, *100*, 4176–4182. [CrossRef] [PubMed]
216. Castro, E.; Nieves, I.U.; Rondón, V.; Sagues, W.J.; Fernández-Sandoval, M.T.; Yomano, L.P.; York, S.W.; Erickson, J.; Vermerris, W. Potential for ethanol production from different sorghum cultivars. *Ind. Crops Prod.* **2017**, *109*, 367–373. [CrossRef]
217. Li, B.Z.; Balan, V.; Yuan, Y.J.; Dale, B.E. Process optimization to convert forage and sweet sorghum bagasse to ethanol based on ammonia fiber expansion (AFEX) pretreatment. *Bioresour. Technol.* **2010**, *101*, 1285–1292. [CrossRef] [PubMed]
218. Molaverdi, M.; Karimi, K.; Khanahmadi, M.; Goshadrou, A. Enhanced sweet sorghum stalk to ethanol by fungus Mucor indicus using solid state fermentation followed by simultaneous saccharification and fermentation. *Ind. Crops Prod.* **2013**, *49*, 580–585. [CrossRef]
219. Akanksha, K.; Sukumaran, R.K.; Pandey, A.; Rao, S.S.; Binod, P. Material balance studies for the conversion of sorghum stover to bioethanol. *Biomass Bioenergy* **2016**, *85*, 48–52. [CrossRef]
220. Barcelos, C.A.; Maeda, R.N.; Betancur, G.J.V.; Pereira, N., Jr. Ethanol production from sorghum grains [*Sorghum bicolor* (L.) Moench]: Evaluation of the enzymatic hydrolysis and the hydrolysate fermentability. *Braz. J. Chem. Eng.* **2011**, *28*, 597–604. [CrossRef]
221. Guigou, M.; Lareo, C.; Pérez, L.V.; Lluberas, M.E.; Vázquez, D.; Ferrari, M.D. Bioethanol production from sweet sorghum: Evaluation of post-harvest treatments on sugar extraction and fermentation. *Biomass Bioenergy* **2011**, *35*, 3058–3062. [CrossRef]
222. Su, M.Y.; Tzeng, W.S.; Shyu, Y.T. An analysis of feasibility of bioethanol production from Taiwan sorghum liquor waste. *Bioresour. Technol.* **2010**, *101*, 6669–6675. [CrossRef]
223. Antonopoulou, G.; Gavala, H.N.; Skiadas, I.V.; Lyberatos, G. Influence of pH on fermentative hydrogen production from sweet sorghum extract. *Int. J. Hydrogen Energy* **2010**, *35*, 1921–1928. [CrossRef]
224. Saraphirom, P.; Reungsang, A. Biological hydrogen production from sweet sorghum syrup by mixed cultures using an anaerobic sequencing batch reactor (ASBR). *Int. J. Hydrogen Energy* **2011**, *36*, 8765–8773. [CrossRef]
225. Shi, X.-X.; Song, H.-C.; Wang, C.-R.; Tang, R.-S.; Huang, Z.-X.; Gao, T.-R.; Xie, J. Enhanced bio-hydrogen production from sweet sorghum stalk with alkalization pretreatment by mixed anaerobic cultures. *Int. J. Energy Res.* **2010**, *34*, 662–672. [CrossRef]
226. Nagaiah, D.; Chiranjeevi, T.; Srinivas Rao, P.; Uma, A.; Prakasham, R.S. Fermentation of Pretreated High-Biomass Sorghum Hydrolysates to Biohydrogen by Mixed Consortia. *Sugar Tech* **2015**, *18*, 266–272. [CrossRef]
227. Rorke, D.; Gueguim Kana, E.B. Biohydrogen process development on waste sorghum (*Sorghum bicolor*) leaves: Optimization of saccharification, hydrogen production and preliminary scale up. *Int. J. Hydrogen Energy* **2016**, *41*, 12941–12952. [CrossRef]
228. Chen, D.E.S.; Liu, L. Analysis of pyrolysis characteristics and kinetics of sweet sorghum bagasse and cotton stalk. *J. Therm. Anal. Calorim.* **2017**, *131*, 1899–1909. [CrossRef]

229. Carvalho, W.S.; Júnior, J.A.; de Oliveira, T.J.P.; Ataíde, C.H. Fast pyrolysis of sweet sorghum bagasse in a fluidized bed reactor: Product characterization and comparison with vapors generated in analytical pyrolysis. *Energy* **2017**, *131*, 186–197. [CrossRef]
230. Yin, R.; Liu, R.; Mei, Y.; Fei, W.; Sun, X. Characterization of bio-oil and bio-char obtained from sweet sorghum bagasse fast pyrolysis with fractional condensers. *Fuel* **2013**, *112*, 96–104. [CrossRef]
231. Carvalho, W.S.; Cunha, I.F.; Pereira, M.S.; Ataíde, C.H. Thermal decomposition profile and product selectivity of analytical pyrolysis of sweet sorghum bagasse: Effect of addition of inorganic salts. *Ind. Crops Prod.* **2015**, *74*, 372–380. [CrossRef]
232. Yue, Y.; Singh, H.; Singh, B.; Mani, S. Torrefaction of sorghum biomass to improve fuel properties. *Bioresour. Technol.* **2017**, *232*, 372–379. [CrossRef]
233. Yan, H.L.; Zong, Z.M.; Li, Z.K.; Kong, J.; Zheng, Q.X.; Li, Y.; Wei, X.Y. Sweet sorghum stalk liquefaction in supercritical methanol: Effects of operating conditions on product yields and molecular composition of soluble fraction. *Fuel Process. Technol.* **2017**, *155*, 42–50. [CrossRef]
234. Cordella, M.; Berrueco, C.; Santarelli, F.; Paterson, N.; Kandiyoti, R.; Millan, M. Yields and ageing of the liquids obtained by slow pyrolysis of sorghum, switchgrass and corn stalks. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 316–324. [CrossRef]
235. Kotaiah Naik, D.; Monika, K.; Prabhakar, S.; Parthasarathy, R.; Satyavathi, B. Pyrolysis of sorghum bagasse biomass into bio-char and bio-oil products. *J. Therm. Anal. Calorim.* **2017**, *127*, 1277–1289. [CrossRef]
236. Filipovici, A.; Tucu, D.; Bialowiec, A.; Bukowski, P.; Crisan, G.C.; Lica, S.; Pulka, J.; Dyjakon, A.; Debowski, M. Effect of temperature and heating rate on the char yield in sorghum and straw slow pyrolysis. *Rev. Chim.* **2017**, *68*, 576–580. [CrossRef]
237. Santos, B.S.; Capareda, S.C. Energy sorghum pyrolysis using a pressurized batch reactor. *Biomass Convers. Biorefinery* **2015**, *6*, 325–334. [CrossRef]
238. Li, B.; Duan, M.M.; Zeng, X.B.; Zhang, Q.; Xu, C.; Zhu, H.H.; Zhu, Q.H.; Huang, D.Y. Effects of composited organic mobilizing agents and their application periods on cadmium absorption of *Sorghum bicolor* L. in a Cd-contaminated soil. *Chemosphere* **2021**, *263*, 128136. [CrossRef] [PubMed]
239. Xiao, M.Z.; Sun, R.; Du, Z.Y.; Yang, W.B.; Sun, Z.; Yuan, T.Q. A sustainable agricultural strategy integrating Cd-contaminated soils remediation and bioethanol production using sorghum cultivars. *Ind. Crops Prod.* **2021**, *162*, 113299. [CrossRef]
240. Başar, A.; Kökdemir Ünşar, E.; Ünyay, H.; Perendeci, N.A. Ethanol, methane, or both? Enzyme dose impact on ethanol and methane production from untreated energy crop switchgrass varieties. *Renew. Energy* **2020**, *149*, 287–297. [CrossRef]
241. Cheng, F.; Bayat, H.; Jena, U.; Brewer, C.E. Impact of feedstock composition on pyrolysis of low-cost, protein- and lignin-rich biomass: A review. *J. Anal. Appl. Pyrolysis* **2020**, *147*, 104780. [CrossRef]
242. Schmer, M.R.; Vogel, K.P.; Mitchell, R.B.; Perrin, R.K.; Matson, P.A. Net energy of cellulosic ethanol from switchgrass. *PNAS* **2008**, *105*, 464–469. [CrossRef]
243. Kim, S.; Dale, B.E. Cumulative Energy and Global Warming Impact from the Production of Biomass for Biobased Products. *J. Ind. Ecol.* **2004**, *7*, 147–162. [CrossRef]
244. Bai, Y.; Luo, L.; Van Der Voet, E. Life cycle assessment of switchgrass-derived ethanol as transport fuel. *Int. J. Life Cycle Assess.* **2010**, *15*, 468–477. [CrossRef]
245. Monti, A.; Barbanti, L.; Zatta, A.; Zegada-Lizarazu, W. The contribution of switchgrass in reducing GHG emissions. *GCB Bioenergy* **2012**, *4*, 420–434. [CrossRef]
246. Bustamante-Silveira, M.; Siri-Prieto, G.; Carrasco-Letelier, L. Water footprints of bioethanol cropping systems in Uruguay. *Agric. Water Manag.* **2021**, *252*, 106870. [CrossRef]
247. Keshwani, D.R.; Cheng, J.J. Switchgrass for bioethanol and other value-added applications: A review. *Bioresour. Technol.* **2009**, *100*, 1515–1523. [CrossRef] [PubMed]
248. Alexopoulou, E.; Monti, A.; Elbersen, H.W.; Zegada-Lizarazu, W.; Millioni, D.; Scordia, D.; Zanetti, F.; Papazoglou, E.G.; Christou, M. 3—Switchgrass: From Production to End Use. In *Perennial Grasses for Bioenergy and Bioproducts*; Alexopoulou, E., Ed.; Elsevier Inc.: London, UK, 2018; pp. 61–105, ISBN 9780128129005.
249. Balch, M.L.; Chamberlain, M.B.; Worthen, R.S.; Holwerda, E.K.; Lynd, L.R. Fermentation with continuous ball milling: Effectiveness at enhancing solubilization for several cellulosic feedstocks and comparative tolerance of several microorganisms. *Biomass Bioenergy* **2020**, *134*, 105468. [CrossRef]
250. Larnaudie, V.; Ferrari, M.D.; Lareo, C. Techno-economic analysis of a liquid hot water pretreated switchgrass biorefinery: Effect of solids loading and enzyme dosage on enzymatic hydrolysis. *Biomass Bioenergy* **2019**, *130*, 105394. [CrossRef]
251. Mullen, C.A.; Boateng, A.A. Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops. *Energy Fuels* **2008**, *22*, 2104–2109. [CrossRef]
252. Pilon, G.; Lavoie, J.-M. Pyrolysis of Switchgrass (*Panicum virgatum* L.) at Low Temperatures within N 2 and CO 2 Environments: Product Yield Study. *ACS Sustain. Chem. Eng.* **2013**, *1*, 198–204. [CrossRef]
253. Sun, X.; Atiyeh, H.K.; Adesanya, Y.; Okonkwo, C.; Zhang, H.; Huhnke, R.L.; Ezeji, T. Feasibility of using biochar as buffer and mineral nutrients replacement for acetone-butanol-ethanol production from non-detoxified switchgrass hydrolysate. *Bioresour. Technol.* **2020**, *298*, 122569. [CrossRef]
254. Vega, D.J.; Dopazo, R.; Ortiz, L. *Manual de Cultivos Energéticos*; Vigo University: Vigo, Spain, 2010.
255. Nunes, L.J.R.; Raposo, M.A.M.; Meireles, C.I.R.; Pinto Gomes, C.J.; Almeida Ribeiro, N.M.C. Control of invasive forest species through the creation of a value chain: *Acacia dealbata* biomass recovery. *Environments* **2020**, *7*, 39. [CrossRef]

256. Stickler, C.M.; Nepstad, D.C.; Coe, M.T.; Mcgrath, D.G.; Rodrigues, H.O.; Walker, W.S.; Soares-Filho, B.S.; Davidson, E.A. The potential ecological costs and cobenefits of REDD: A critical review and case study from the Amazon region. *Glob. Chang. Biol.* **2009**, *15*, 2803–2824. [CrossRef]
257. Davis, J.M. Genetic Improvement of Poplar (*Populus* spp.) as a Bioenergy Crop. In *Genetic Improvement of Bioenergy Crops*; Vermerris, W., Ed.; Springer: New York, NY, USA, 2008; pp. 377–396.
258. Sannigrahi, P.; Ragauskas, A.; Tuskan, G. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 209–226. [CrossRef]
259. Stanton, B.; Eaton, J.; Johnson, J.; Rice, D.; Schuette, B.; Moser, B. Hybrid Poplar in the Pacific Northwest: The Effects of Market-Driven Management. *J. For.* **2002**, *100*, 28–33.
260. De Rigo, D.; Enescu, C.M.; Durrant, T.H.; Caudullo, G. Populus nigra. In *European Atlas of Forest Tree Species*; San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A., Eds.; Publication Office of the European Union: Luxembourg, 2016; pp. 136–137.
261. Ferrarini, A.; Fornasier, F.; Serra, P.; Ferrari, F.; Trevisan, M.; Amaducci, S. Impacts of willow and miscanthus bioenergy buffers on biogeochemical N removal processes along the soil–groundwater continuum. *GCB Bioenergy* **2017**, *9*, 246–261. [CrossRef]
262. Ehrenfeld, J.G. Ecosystem Consequences of Biological Invasions. *Annu. Rev. Ecol. Evol. Syst.* **2010**, *41*, 59–80. [CrossRef]
263. CABI. Invasive Species Compendium—Datasheet Report for Acacia dealbata (acacia bernier). Available online: https://www.cabi.org/ISC/datasheetreport/2207 (accessed on 18 December 2018).
264. Álvarez-Álvarez, P.; Pizarro, C.; Barrio-Anta, M.; Cámara-Obregón, A.; María Bueno, J.L.; Álvarez, A.; Gutiérrez, I.; Burslem, D.F.R.P. Evaluation of tree species for biomass energy production in Northwest Spain. *Forests* **2018**, *9*, 160. [CrossRef]
265. Pontes, R.; Romaní, A.; Michelin, M.; Domingues, L.; Teixeira, J.; Nunes, J. Comparative autohydrolysis study of two mixtures of forest and marginal land resources for co-production of biofuels and value-added compounds. *Renew. Energy* **2018**, *128*, 20–29. [CrossRef]
266. 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. Characterization and Cytotoxicity Assessment of the Lipophilic Fractions of Different Morphological Parts of *Acacia dealbata*. *Int. J. Mol. Sci.* **2020**, *21*, 1814. [CrossRef]
267. López-Hortas, L.; Rodríguez-González, I.; Díaz-Reinoso, B.; Torres, M.D.; Moure, A.; Domínguez, H. Tools for a multiproduct biorefinery of *Acacia dealbata* biomass. *Ind. Crops Prod.* **2021**, *169*, 113655. [CrossRef]
268. Mendes, C.V.T.; Moreira, R.; Portugal, A.; Carvalho, M.G.V.S. Biorefining of *Pinus pinaster* Stump Wood for Ethanol Production and Lignin Recovery. *Chem. Eng. Technol.* **2021**, *44*, 1043–1050. [CrossRef]
269. López, M.; Vila, C.; Santos, V.; Parajó, J.C. Manufacture of Platform Chemicals from Pine Wood Polysaccharides in Media Containing Acidic Ionic Liquids. *Polym.* **2020**, *12*, 1215. [CrossRef]
270. Rodríguez-Seoane, P.; Díaz-Reinoso, B.; Moure, A.; Domínguez, H. Potential of Paulownia sp. for biorefinery. *Ind. Crops Prod.* **2020**, *155*, 112739. [CrossRef]
271. D'Auria, M.; Mecca, M.; Todaro, L. High temperature treatment allows the detection of episesamin in paulownia wood extractives. *Nat. Prod. Res.* **2020**, *34*, 1326–1330. [CrossRef] [PubMed]
272. Radeva, G.; Valchev, I.; Petrin, S.; Valcheva, E.; Tsekova, P. Kinetic study of the enzyme conversion of steam exploded Paulownia tomentosa to glucose. *BioResources* **2021**, *7*, 412–421.
273. El-Showk, N.; El-Showk, S. The Paulownia Tree an Alternative for Sustainable Forestry. The Farm—Crop Development.org. 2003. Available online: https://cropdevelopment.org/docs/PaulowniaBooklet_print.pdf (accessed on 20 September 2021).
274. Domínguez, E.; Romaní, A.; Domingues, L.; Garrote, G. Evaluation of strategies for second generation bioethanol production from fast growing biomass Paulownia within a biorefinery scheme. *Appl. Energy* **2017**, *187*, 777–789. [CrossRef]
275. Santos, J.I.; Fillat, Ú.; Martín-Sampedro, R.; Ballesteros, I.; Manzanares, P.; Ballesteros, M.; Eugenio, M.E.; Ibarra, D. Lignin-enriched Fermentation Residues from Bioethanol Production of Fast-growing Poplar and Forage Sorghum. *BioResources* **2015**, *10*, 5215–5232. [CrossRef]
276. Szczukowski, S.; Tworkowski, J.; Klasa, A.; Stolarski, M. Productivity and chemical composition of wood tissues of short rotation willow coppice cultivated on arable land. *Plant, Soil Environ.* **2002**, *48*, 413–417. [CrossRef]
277. Alexandropoulou, M.; Antonopoulou, G.; Fragkou, E.; Ntaikou, I.; Lyberatos, G. Fungal pretreatment of willow sawdust and its combination with alkaline treatment for enhancing biogas production. *J. Environ. Manag.* **2017**, *203*, 704–713. [CrossRef] [PubMed]
278. Hashaikeh, R.; Fang, Z.; Butler, I.S.; Hawari, J.; Kozinski, J.A. Hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion. *Fuel* **2007**, *86*, 1614–1622. [CrossRef]
279. Stephenson, A.L.; Dupree, P.; Scott, S.A.; Dennis, J.S. The environmental and economic sustainability of potential bioethanol from willow in the UK. *Bioresour. Technol.* **2010**, *101*, 9612–9623. [CrossRef]
280. Łukajtis, R.; Rybarczyk, P.; Kucharska, K.; Konopacka-Łyskawa, D.; Słupek, E.; Wychodnik, K.; Kamiński, M. Optimization of Saccharification Conditions of Lignocellulosic Biomass under Alkaline Pre-Treatment and Enzymatic Hydrolysis. *Energies* **2018**, *11*, 886. [CrossRef]
281. Ziegler-Devin, I.; Menana, Z.; Chrusciel, L.; Chalot, M.; Bert, V.; Brosse, N. Steam explosion pretreatment of willow grown on phytomanaged soils for bioethanol production. *Ind. Crops Prod.* **2019**, *140*, 111722. [CrossRef]

282. Eklund, R.; Galbe, M.; Zacchi, G. The influence of SO2 and H2SO4 impregnation of willow prior to steam pretreatment. *Bioresour. Technol.* **1995**, *52*, 225–229. [CrossRef]
283. Yi, W.; Nadeem, F.; Xu, G.; Zhang, Q.; Joshee, N.; Tahir, N. Modifying crystallinity, and thermo-optical characteristics of Paulownia biomass through ultrafine grinding and evaluation of biohydrogen production potential. *J. Clean. Prod.* **2020**, *269*, 122386. [CrossRef]
284. Viana, H.F.; Rodrigues, A.M.; Godina, R.; Matias, J.C.D.O.; Nunes, L.J.R. Evaluation of the physical, chemical and thermal properties of Portuguese maritime pine biomass. *Sustainability* **2018**, *10*, 2877. [CrossRef]
285. Amutio, M.; Lopez, G.; Alvarez, J.; Moreira, R.; Duarte, G.; Nunes, J.; Olazar, M.; Bilbao, J. Flash pyrolysis of forestry residues from the Portuguese Central Inland Region within the framework of the BioREFINA-Ter project. *Bioresour. Technol.* **2013**, *129*, 512–518. [CrossRef] [PubMed]
286. Yorgun, S.; Yildiz, D. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *J. Anal. Appl. Pyrolysis* **2015**, *114*, 68–78. [CrossRef]
287. Fassinou, W.F.; Van de Steene, L.; Toure, S.; Volle, G.; Girard, P. Pyrolysis of *Pinus pinaster* in a two-stage gasifier: Influence of processing parameters and thermal cracking of tar. *Fuel Process. Technol.* **2009**, *90*, 75–90. [CrossRef]
288. Selvi Gökkaya, D.; Çokkuvvetli, T.; Sağlam, M.; Yüksel, M.; Ballice, L. Hydrothermal gasification of poplar wood chips with alkali, mineral, and metal impregnated activated carbon catalysts. *J. Supercrit. Fluids* **2019**, *152*, 104542. [CrossRef]
289. De Neergaard, A.; Saarnak, C.; Hill, T.; Khanyile, M.; Berzosa, A.M.; Birch-Thomsen, T. Australian wattle species in the Drakensberg region of South Africa—An invasive alien or a natural resource? *Agric. Syst.* **2005**, *85*, 216–233. [CrossRef]
290. Tejada, M.; Gómez, I.; Fernández-Boy, E.; Díaz, M.-J. Effects of Sewage Sludge and *Acacia dealbata* Composts on Soil Biochemical and Chemical Properties. *Commun. Soil Sci. Plant Anal.* **2014**, *45*, 570–580. [CrossRef]
291. Yañez, R.; Alonso, J.L.; Díaz, M.J. Influence of bulking agent on sewage sludge composting process. *Bioresour. Technol.* **2009**, *100*, 5827–5833. [CrossRef]
292. Pinto, P.C.R.; Oliveira, C.; Costa, C.A.; Gaspar, A.; Faria, T.; Ataíde, J.; Rodrigues, A.E. Kraft delignification of energy crops in view of pulp production and lignin valorization. *Ind. Crops Prod.* **2015**, *71*, 153–162. [CrossRef]
293. Yáñez, R.; Romaní, A.; Garrote, G.; Alonso, J.L.; Parajó, J.C. Experimental evaluation of alkaline treatment as a method for enhancing the enzymatic digestibility of autohydrolysed *Acacia dealbata*. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 1070–1077. [CrossRef]
294. Yáñez, R.; Gómez, B.; Martínez, M.; Gullón, B.; Alonso, J.L. Valorization of an invasive woody species, *Acacia dealbata*, by means of Ionic liquid pretreatment and enzymatic hydrolysis. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 1337–1343. [CrossRef]
295. Reid, D.G.; Bonnet, S.L.; Kemp, G.; Van Der Westhuizen, J.H. 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* **2013**, *94*, 243–248. [CrossRef]
296. Okoli, B.J.; Shilowa, P.M.; Anyanwu, G.O.; Modise, J.S. Removal of Pb2+ from Water by Synthesized Tannin Resins from Invasive South African Trees. *Water* **2018**, *10*, 648. [CrossRef]
297. Yildiz, S.; Gürgen, A.; Can, Z.; Tabbouche, S.A.; Kiliç, A.O. Some bioactive properties of *Acacia dealbata* extracts and their potential utilization in wood protection. *Drew. Prace Nauk. Doniesienia Komun.* **2018**, *61*, 81–97.
298. Neiva, D.M.; Luís, Â.; Gominho, J.; Domingues, F.; Duarte, A.P.; Pereira, H. Bark residues valorization potential regarding antioxidant and antimicrobial extracts. *Wood Sci. Technol.* **2020**, *54*, 559–585. [CrossRef]
299. Casas, M.P.; Conde, E.; Ribeiro, D.; Fernandes, E.; Domínguez, H.; Torres, M.D. Bioactive properties of *Acacia dealbata* flowers extracts. *Waste Biomass Valorization* **2019**, *11*, 2549–2557. [CrossRef]
300. López-Hortas, L.; Falqué, E.; Domínguez, H.; Torres, M.D. Microwave hydrodiffusion and gravity versus conventional distillation for *Acacia dealbata* flowers. Recovery of bioactive extracts for cosmetic purposes. *J. Clean. Prod.* **2020**, *274*, 123143. [CrossRef]
301. Lorenzo, P.; Reboredo-Durán, J.; Muñoz, L.; Freitas, H.; González, L. Herbicidal properties of the commercial formulation of methyl cinnamate, a natural compound in the invasive silver wattle (*Acacia dealbata*). *Weed Sci.* **2020**, *68*, 69–78. [CrossRef]
302. Borges, A.; José, H.; Homem, V.; Simões, M. Comparison of techniques and solvents on the antimicrobial and antioxidant potential of extracts from *Acacia dealbata* and *Olea europaea*. *Antibiotics* **2020**, *9*, 48. [CrossRef] [PubMed]
303. Meenakshisundaram, S.; Fayeulle, A.; Leonard, E.; Ceballos, C.; Pauss, A. Fiber degradation and carbohydrate production by combined biological and chemical/physicochemical pretreatment methods of lignocellulosic biomass—A review. *Bioresour. Technol.* **2021**, *331*, 125053. [CrossRef] [PubMed]
304. Domínguez, E.; Romaní, A.; Alonso, J.L.; Parajó, J.C.; Yáñez, R. A biorefinery approach based on fractionation with a cheap industrial by-product for getting value from an invasive woody species. *Bioresour. Technol.* **2014**, *173*, 301–308. [CrossRef] [PubMed]
305. Carneiro, M.; Moreira, R.; Gominho, J.; Fabião, A. Could control of invasive acacias be a source of biomass for energy under mediterranean conditions? *Chem. Eng. Trans.* **2014**, *37*, 187–192.
306. Correia, R.; Quintela, J.C.; Duarte, M.P.; Gonçalves, M. Insights for the Valorization of Biomass from Portuguese Invasive Acacia spp. in a Biorefinery Perspective. *Forests* **2020**, *11*, 1342. [CrossRef]
307. Muñoz, C.; Mendonça, R.; Baeza, J.; Berlin, A.; Saddler, J.; Freer, J. Bioethanol production from bio-organosolv pulps of Pinus radiata and *Acacia dealbata*. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 767–774. [CrossRef]

308. Ferreira, S.; Gil, N.; Queiroz, J.A.; Duarte, A.P.; Domingues, F.C. An evaluation of the potential of *Acacia dealbata* as raw material for bioethanol production. *Bioresour. Technol.* **2011**, *102*, 4766–4773. [CrossRef]
309. Valero Gutiérrez del Olmo, E.; Picos Martín, J. Parcelas invadidas por *Acacia dealbata* Link. Evaluación de su potencial aprovechamiento incluyendo bioenergía. In Proceedings of the 5° Congresso Forestal Español—Montes y Sociedad: Saber qué Hacer, Centro Municipal de Congresos y Exposiciones de Ávila, Ávila, Spain, 21–25 September 2009; pp. 1–12.
310. Nunes, L.J.R.; Raposo, M.A.M.; Meireles, C.I.R.; Pinto Gomes, C.J.; Almeida Ribeiro, N.M.C. Carbon Sequestration Potential of Forest Invasive Species: A Case Study with *Acacia dealbata* Link. *Resources* **2021**, *10*, 51. [CrossRef]
311. Forján, R.; Asensio, V.; Rodríguez-Vila, A.; Covelo, E.F. Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing. *CATENA* **2016**, *137*, 120–125. [CrossRef]
312. Nunes, L.J.R.; Rodrigues, A.M.; Loureiro, L.M.E.F.; Sá, L.C.R.; Matias, J.C.O. Energy recovery from invasive species: Creation of value chains to promote control and eradication. *Recycling* **2021**, *6*, 21. [CrossRef]
313. Ferreira, T.; Tavares Marques, E.M.; Almeida, D.; Pereira, C.; Paiva, J.; Pinho, C. Monitoring fluidization quality and combustion efficiency of invasive species pellets. In Proceedings of the 15 th Brazilian Congress of Thermal Sciences and Engineering, Belém, Brazil, 10–13 November 2014; pp. 10–13.
314. Vicente, E.D.; Vicente, A.M.; Evtyugina, M.; Carvalho, R.; Tarelho, L.A.C.; Paniagua, S.; Nunes, T.; Otero, M.; Calvo, L.F.; Alves, C. Emissions from residential pellet combustion of an invasive acacia species. *Renew. Energy* **2019**, *140*, 319–329. [CrossRef]
315. Correia, A.; Oliveira, Â. *Principais Espécies Florestais com Interesse Para Portugal—Zonas de Influência Atlântica, N.º 322*; Direção-Geral das Florestas e Ministério da Agricultura—Desenvolvimento Rural e Pescas: Lisboa, Portugal, 2003.
316. Direção-Geral de Agricultura e Desenvolvimento Rural—DGADR Direcção-Geral dos Recursos Florestais—DGRF. *Plano Regional de Ordenamento Florestal—Baixo Alentejo*; DGADR and DGRF: Lisboa, Portugal, 2006.
317. Oliveira, Â.; Moura, P.; Providência, F.M. *Boas Práticas Florestais Para o Pinheiro Bravo—Manual*; Centro Pinus: Porto, Portugal, 1999.
318. Serralves Pinus pinaster Aiton. Available online: http://serralves.ubiprism.pt/species/show/883 (accessed on 20 December 2018).
319. Santos, A.; Carvalho, A.; Barbosa-Póvoa, A. An economic and environmental comparison between forest wood products—Uncoated woodfree paper, natural cork stoppers and particle boards. *J. Clean. Prod.* **2021**, *296*, 126469. [CrossRef]
320. Viñas, R.A.; Caudullo, G.; Oliveira, S.; De Rigo, D. Pinus pinaster. In *European Atlas of Forest Tree Species*; San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A., Eds.; Publication Office of the European Union: Luxembourg, 2016; pp. 128–129.
321. Jiang, W.; Adamopoulos, S.; Hosseinpourpia, R.; Žigon, J.; Petrič, M.; Šernek, M.; Medved, S. Utilization of partially liquefied bark for production of particleboards. *Appl. Sci.* **2020**, *10*, 5253. [CrossRef]
322. da Costa, T.P.; Quinteiro, P.; Arroja, L.; Dias, A.C. Environmental comparison of forest biomass residues application in Portugal: Electricity, heat and biofuel. *Renew. Sustain. Energy Rev.* **2020**, *134*, 110302. [CrossRef]
323. Quinteiro, P.; Tarelho, L.; Marques, P.; Martín-Gamboa, M.; Freire, F.; Arroja, L.; Dias, A.C. Life cycle assessment of wood pellets and wood split logs for residential heating. *Sci. Total Environ.* **2019**, *689*, 580–589. [CrossRef] [PubMed]
324. Martín-Gamboa, M.; Dias, L.C.; Quinteiro, P.; Freire, F.; Arroja, L.; Dias, A.C. Multi-criteria and life cycle assessment of wood-based bioenergy alternatives for residential heating: A sustainability analysis. *Energies* **2019**, *12*, 4391. [CrossRef]
325. Rivas, S.; Raspolli-Galletti, A.M.; Antonetti, C.; Santos, V.; Parajó, J.C. Sustainable conversion of *Pinus pinaster* wood into biofuel precursors: A biorefinery approach. *Fuel* **2016**, *164*, 51–58. [CrossRef]
326. Telmo, C.; Lousada, J. Heating values of wood pellets from different species. *Biomass Bioenergy* **2011**, *35*, 2634–2639. [CrossRef]
327. Azevedo, J.C.; Pinto, M.V.; Escalante, E.; Feliciano, M.; Aranha, J.; Castro, J.P. Potential forest biomass and energy production at the regional scale: The case of maritime pine (*Pinus pinaster* Ait.) in the district of Bragança, Northeastern Portugal. In Proceedings of the Recent Researches in Environment, Energy Systems and Sustainability—8th WSEAS International Conference on Energy, Environment, Ecosystems and Sustainable Development (EEESD'12), Faro, Portugal, 2–4 May 2012; Volume 1, pp. 226–231.
328. Nunes, L.J.R.; Godina, R.; Matias, J.C.O.; Catalão, J.P.S. Evaluation of the utilization of woodchips as fuel for industrial boilers. *J. Clean. Prod.* **2019**, *223*, 270–277. [CrossRef]
329. Lapuerta, M.; Hernández, J.J.; Pazo, A.; López, J. Gasification and co-gasification of biomass wastes: Effect of the biomass origin and the gasifier operating conditions. *Fuel Process. Technol.* **2008**, *89*, 828–837. [CrossRef]
330. Zhao-Hua, Z.; Ching-Ju, C.; Xin-Yu, L.; Yao Gao, X. *Paulownia in China: Cultivation and Utilization*; Chinese Academy of Forestry Staff, Ed.; Asian Network for Biological Sciences and International Development Research Centre: Singapore, 1986; ISBN 9971845466.
331. López, F.; Pérez, A.; Zamudio, M.A.M.; De Alva, H.E.; García, J.C. Paulownia as raw material for solid biofuel and cellulose pulp. *Biomass Bioenergy* **2012**, *45*, 77–86. [CrossRef]
332. Zamudio, M.A.M.; Alfaro, A.; de Alva, H.E.; García, J.C.; García-Morales, M.; López, F. Biorefinery of paulownia by autohydrolysis and soda-anthraquinone delignification process. Characterization and application of lignin. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 534–542. [CrossRef]
333. Kim, S.K.; Cho, S.B.; Moon, H.I. Neuroprotective effects of a sesquiterpene lactone and flavanones from *Paulownia tomentosa* Steud. against glutamate-induced neurotoxicity in primary cultured rat cortical cells. *Phyther. Res.* **2010**, *24*, 1898–1900. [CrossRef]
334. Jung, S.; Moon, H.I.; Ohk, J.; Lee, S.; Li, C.; Kim, S.K.; Lee, M.S. Inhibitory effect and mechanism on antiproliferation of isoatriplicolide tiglate (PCAC) from paulownia coreana. *Molecules* **2012**, *17*, 5945–5951. [CrossRef] [PubMed]

335. He, T.; Vaidya, B.; Perry, Z.; Parajuli, P.; Joshee, N. Paulownia as a Medicinal Tree: Traditional Uses and Current Advances. *Eur. J. Med. Plants* **2016**, *14*, 1. [CrossRef]
336. Hori, M.; Aoki, Y.; Shinoda, K.; Chiba, M.; Sasaki, R. Wood volatiles as attractants of the confused flour beetle, *Tribolium confusum* (Coleoptera: Tenebrionidae). *Sci. Rep.* **2019**, *9*, 11544. [CrossRef]
337. Yorgun, S.; Vural, N.; Demiral, H. Preparation of high-surface area activated carbons from Paulownia wood by ZnCl2 activation. *Microporous Mesoporous Mater.* **2009**, *122*, 189–194. [CrossRef]
338. Qi, Y.; Yang, C.; Hidayat, W.; Jang, J.H.; Kim, N.H. Solid bioenergy properties of *Paulownia tomentosa* grown in Korea. *J. Korean Wood Sci. Technol.* **2016**, *44*, 890–896. [CrossRef]
339. Gong, C.; Bujanovic, B.M. Impact of hot-water extraction on acetone-water oxygen delignification of Paulownia Spp. and lignin recovery. *Energies* **2014**, *7*, 857–873. [CrossRef]
340. Chang, J.; Gao, Z.; Wang, X.; Wu, D.; Xu, F.; Wang, X.; Guo, Y.; Jiang, K. Activated porous carbon prepared from paulownia flower for high performance supercapacitor electrodes. *Electrochim. Acta* **2015**, *157*, 290–298. [CrossRef]
341. Allwright, M.R.; Payne, A.; Emiliani, G.; Milner, S.; Viger, M.; Rouse, F.; Keurentjes, J.J.B.; Bérard, A.; Wildhagen, H.; Faivre-Rampant, P.; et al. Biomass traits and candidate genes for bioenergy revealed through association genetics in coppiced European *Populus nigra* (L.). *Biotechnol. Biofuels* **2016**, *9*, 195. [CrossRef] [PubMed]
342. Caudullo, G.; De Rigo, D. Populus alba. In *European Atlas of Forest Tree Species*; San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A., Eds.; Publication Office of the European Union: Luxembourg, 2016; pp. 134–135.
343. Griu, T.; Lunguleasa, A. The use of the white poplar (*Populus alba* L.) biomass as fuel. *J. For. Res.* **2016**, *27*, 719–725. [CrossRef]
344. CABI. Invasive Species Compendium—Datasheet Report for Populus Alba (Silver-Leaf Poplar). Available online: https://www.cabi.org/isc/datasheetreport/43426 (accessed on 2 September 2020).
345. Sim, S.J.; Yong, S.H.; Park, D.J.; Choi, E.; Seol, Y.; Song, H.J.; Jeong, M.J.; Kim, H.G.; Choi, M.S. Influence of inorganic salts on biomass production, biochemical composition, and bioethanol production of Populus alba. *IForest* **2020**, *13*, 566–574. [CrossRef]
346. González-García, S.; Dias, A.C.; Clermidy, S.; Benoist, A.; Bellon Maurel, V.; Gasol, C.M.; Gabarrell, X.; Arroja, L. Comparative environmental and energy profiles of potential bioenergy production chains in Southern Europe. *J. Clean. Prod.* **2014**, *76*, 42–54. [CrossRef]
347. Oliveira, N.; Pérez-Cruzado, C.; Cañellas, I.; Rodríguez-Soalleiro, R.; Sixto, H. Poplar short rotation coppice plantations under mediterranean conditions: The case of Spain. *Forests* **2020**, *11*, 1352. [CrossRef]
348. Porth, I.; El-Kassaby, Y.A. Using Populus as a lignocellulosic feedstock for bioethanol. *Biotechnol. J.* **2015**, *10*, 510–524. [CrossRef]
349. Raud, M.; Kikas, T.; Sippula, O.; Shurpali, N.J. Potentials and challenges in lignocellulosic biofuel production technology. *Renew. Sustain. Energy Rev.* **2019**, *111*, 44–56. [CrossRef]
350. Tharakan, P.J.; Volk, T.A.; Abrahamson, L.P.; White, E.H. Energy feedstock characteristics of willow and hybrid poplar clones at harvest age. *Biomass Bioenergy* **2003**, *25*, 571–580. [CrossRef]
351. Elder, T.; Groom, L.H. Pilot-scale gasification of woody biomass. *Biomass Bioenergy* **2011**, *35*, 3522–3528. [CrossRef]
352. Martinez, M.; Duret, X.; Minh, D.P.; Nzihou, A.; Lavoie, J.-M. Conversion of lignocellulosic biomass in biobutanol by a novel thermal process. *Int. J. Energy Prod. Manag.* **2019**, *4*, 298–310. [CrossRef]
353. Zhang, Y.; Xia, C.; Lu, M.; Tu, M. Effect of overliming and activated carbon detoxification on inhibitors removal and butanol fermentation of poplar prehydrolysates. *Biotechnol. Biofuels* **2018**, *11*, 178. [CrossRef] [PubMed]
354. Bryant, N.D.; Pu, Y.; Tschaplinski, T.J.; Tuskan, G.A.; Muchero, W.; Kalluri, U.C.; Yoo, C.G.; Ragauskas, A.J. Transgenic Poplar Designed for Biofuels. *Trends Plant Sci.* **2020**, *25*, 881–896. [CrossRef] [PubMed]
355. Krzyżaniak, M.; Stolarski, M.J.; Warmiński, K. Life cycle assessment of poplar production: Environmental impact of different soil enrichment methods. *J. Clean. Prod.* **2019**, *206*, 785–796. [CrossRef]
356. Wang, H.; Larson, R.A.; Runge, T. Impacts to hydrogen sulfide concentrations in biogas when poplar wood chips, steam treated wood chips, and biochar are added to manure-based anaerobic digestion systems. *Bioresour. Technol. Rep.* **2019**, *7*, 100232. [CrossRef]
357. Negro, M.J.; Manzanares, P.; Ballesteros, I.; Oliva, J.M.; Cabañas, A.; Ballesteros, M. Hydrothermal Pretreatment Conditions to Enhance Ethanol Production from Poplar Biomass. *Appl. Biochem. Biotechnol.* **2003**, *105*, 87–100. [CrossRef]
358. El Bassam, N. *Handbook of Bioenergy Crops: A Complete Reference to Species, Development and Applications*, 1st ed.; Earthcan Ltd.: London, UK, 2010; ISBN 9781138975712.
359. Rosso, L.; Facciotto, G.; Bergante, S.; Vietto, L.; Nervo, G. Selection and testing of Populus alba and Salix spp. as bioenergy feedstock: Preliminary results. *Appl. Energy* **2013**, *102*, 87–92. [CrossRef]
360. Bartoli, M.; Rosi, L.; Giovannelli, A.; Frediani, P.; Frediani, M. Bio-oil from residues of short rotation coppice of poplar using a microwave assisted pyrolysis. *J. Anal. Appl. Pyrolysis* **2016**, *119*, 224–232. [CrossRef]
361. Chen, D.; Li, Y.; Cen, K.; Luo, M.; Li, H.; Lu, B. Pyrolysis polygeneration of poplar wood: Effect of heating rate and pyrolysis temperature. *Bioresour. Technol.* **2016**, *218*, 780–788. [CrossRef]
362. Soares Dias, A.P.; Rego, F.; Fonseca, F.; Casquilho, M.; Rosa, F.; Rodrigues, A. Catalyzed pyrolysis of SRC poplar biomass. Alkaline carbonates and zeolites catalysts. *Energy* **2019**, *183*, 1114–1122. [CrossRef]
363. Echresh Zadeh, Z.; Abdulkhani, A.; Saha, B. A comparative production and characterisation of fast pyrolysis bio-oil from Populus and Spruce woods. *Energy* **2021**, *214*, 118930. [CrossRef]

364. Werner, C.; Haas, E.; Grote, R.; Gauder, M.; Graeff-Hönninger, S.; Claupein, W.; Butterbach-Bahl, K. Biomass production potential from Populus short rotation systems in Romania. *GCB Bioenergy* **2012**, *4*, 642–653. [CrossRef]
365. Krzyżaniak, M.; Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Bieniek, A.; Mleczek, M. Willow biomass obtained from different soils as a feedstock for energy. *Ind. Crops Prod.* **2015**, *75*, 114–121. [CrossRef]
366. Klasnja, B.; Kopitovic, S.; Orlovic, S. Wood and bark of some poplar and willow clones as fuelwood. *Biomass Bioenergy* **2002**, *23*, 427–432. [CrossRef]
367. Bartha, S.; Vajda, B.; Duarte, L.C.; Carvalheiro, F.; Antal, N. *Environmental and Economical Assessment Analysis of the Energy Willow*; Les Presses Agronomiques: Gembloux, Belgium, 2017; pp. 9–22.
368. Fijałkowska, D.; Styszko, L. Calorific value of willow biomass. *Rocz. Ochr. Sr.* **2011**, *13*, 875–890.
369. Palmqvist, E.; Hahn-Hägerdal, B.; Galbe, M.; Zacchi, G. The effect of water-soluble inhibitors from steam-pretreated willow on enzymatic hydrolysis and ethanol fermentation. *Enzym. Microb. Technol.* **1996**, *19*, 470–476. [CrossRef]
370. Budsberg, E.; Rastogi, M.; Puettmann, M.E.; Caputo, J.; Balogh, S.; Volk, T.A.; Gustafson, R.; Johnson, L. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. *For. Prod. J. Online* **2012**, *62*, 305–313. [CrossRef]
371. Sassner, P.; Zacchi, G. Integration options for high energy efficiency and improved economics in a wood-to-ethanol process. *Biotechnol. Biofuels* **2008**, *1*, 4. [CrossRef]
372. Von Sivers, M.; Zacchi, G.; Olsson, L.; Hahn-Hügerdal, B. Cost Analysis of Ethanol Production from Willow Using Recombinant Escherichia coli. *Biotechnol. Prog.* **1994**, *10*, 555–560. [CrossRef]
373. Asad, M.; Menana, Z.; Ziegler-Devin, I.; Bert, V.; Chalot, M.; Herzig, R.; Mench, M.; Brosse, N. Pretreatment of trace element-enriched biomasses grown on phytomanaged soils for bioethanol production. *Ind. Crops Prod.* **2017**, *107*, 63–72. [CrossRef]
374. Kakuk, B.; Bagi, Z.; Rákhely, G.; Maróti, G.; Dudits, D.; Kovács, K.L. Methane production from green and woody biomass using short rotation willow genotypes for bioenergy generation. *Bioresour. Technol.* **2021**, *333*, 125223. [CrossRef]
375. Han, S.H.; Cho, D.H.; Kim, Y.H.; Shin, S.J. Biobutanol production from 2-year-old willow biomass by acid hydrolysis and acetone-butanol-ethanol fermentation. *Energy* **2013**, *61*, 13–17. [CrossRef]
376. Vervaeke, P.; Tack, F.M.G.; Navez, F.; Martin, J.; Verloo, M.G.; Lust, N. Fate of heavy metals during fixed bed downdraft gasification of willow wood harvested from contaminated sites. *Biomass Bioenergy* **2006**, *30*, 58–65. [CrossRef]
377. Lievens, C.; Carleer, R.; Cornelissen, T.; Yperman, J. Fast pyrolysis of heavy metal contaminated willow: Influence of the plant part. *Fuel* **2009**, *88*, 1417–1425. [CrossRef]
378. Mayer, Z.A.; Apfelbacher, A.; Hornung, A. A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 196–202. [CrossRef]
379. Keller, C.; Ludwig, C.; Davoli, F.; Wochele, J. Thermal Treatment of Metal-Enriched Biomass Produced from Heavy Metal Phytoextraction. *Environ. Sci. Technol.* **2005**, *39*, 3359–3367. [CrossRef]
380. Delplanque, M.; Collet, S.; Del Gratta, F.; Schnuriger, B.; Gaucher, R.; Robinson, B.; Bert, V. Combustion of Salix used for phytoextraction: The fate of metals and viability of the processes. *Biomass Bioenergy* **2013**, *49*, 160–170. [CrossRef]
381. Bartha, S.; Moniz, P.; Carvalheiro, F.; Duarte, L. Hydrothermal Treatment of Energy Willow Biomass. In Proceedings of the 3rd Conference on "Smart Energy Systems in Cities and Regions", Dublin, Ireland, 9–12 April 2018.
382. Wang, K.; Jiang, J.; Liang, X. Design, synthesis and evaluation of novel glycosyl surfactant—Lignocellulosic hydrolysate esters from shrub willow. *Ind. Crops Prod.* **2016**, *92*, 127–135. [CrossRef]
383. Kammerer, B.; Kahlich, R.; Biegert, C.; Gleiter, C.H.; Heide, L. HPLC-MS/MS analysis of willow bark extracts contained in pharmaceutical preparations. *Phytochem. Anal.* **2005**, *16*, 470–478. [CrossRef]
384. Kenstavičienė, P.; Nenortienė, P.; Kiliuvienė, G.; Ževžikovas, A.; Lukošius, A.; Kazlauskienė, D. Application of high-performance liquid chromatography for research of salicin in bark of different varieties of Salix. *Medicina* **2009**, *45*, 644–651. [CrossRef]
385. Liu, Y.; Wang, Y.; Zhang, G.; Liu, W.; Wang, D.; Dong, Y. Preparation of activated carbon from willow leaves and evaluation in electric double-layer capacitors. *Mater. Lett.* **2016**, *176*, 60–63. [CrossRef]
386. Cheshire, E.; Granzow, S.G.; Makkonen, H.P. Kraft Pulp from Plantation Grown Biomass Willow. In Proceedings of the 3rd Biennial Conference, Short Rotation Woody Crops—Operations Working Group, Syracuse, NY, USA, 10–13 October 2000.
387. Eklund, R.; Zacchi, G. Simultaneous saccharification and fermentation of steam-pretreated willow. *Enzym. Microb. Technol.* **1995**, *17*, 255–259. [CrossRef]
388. Sassner, P.; Galbe, M.; Zacchi, G. Bioethanol production based on simultaneous saccharification and fermentation of steam-pretreated Salix at high dry-matter content. *Enzym. Microb. Technol.* **2006**, *39*, 756–762. [CrossRef]
389. Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corns Stover*; National Renewable Energy Laboratory (NREL): Golden, CO, USA, 2002.
390. Yoon, S.Y.; Kim, B.R.; Han, S.H.; Shin, S.J. Different response between woody core and bark of goat willow (*Salix caprea* L.) to concentrated phosphoric acid pretreatment followed by enzymatic saccharification. *Energy* **2015**, *81*, 21–26. [CrossRef]
391. Huijgen, W.J.J.; Smit, A.T.; Reith, J.H.; Uil, H. Den Catalytic organosolv fractionation of willow wood and wheat straw as pretreatment for enzymatic cellulose hydrolysis. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1428–1438. [CrossRef]
392. Šyc, M.; Pohořelý, M.; Kameníková, P.; Habart, J.; Svoboda, K.; Punčochář, M. Willow trees from heavy metals phytoextraction as energy crops. *Biomass Bioenergy* **2012**, *37*, 106–113. [CrossRef]

393. Sas, E.; Hennequin, L.M.; Frémont, A.; Jerbi, A.; Legault, N.; Lamontagne, J.; Fagoaga, N.; Sarrazin, M.; Hallett, J.P.; Fennell, P.S.; et al. Biorefinery potential of sustainable municipal wastewater treatment using fast-growing willow. *Sci. Total Environ.* **2021**, *792*, 148146. [CrossRef]
394. Dastyar, W.; Raheem, A.; He, J.; Zhao, M. Biofuel Production Using Thermochemical Conversion of Heavy Metal-Contaminated Biomass (HMCB) Harvested from Phytoextraction Process. *Chem. Eng. J.* **2019**, *358*, 759–785. [CrossRef]
395. Stals, M.; Thijssen, E.; Vangronsveld, J.; Carleer, R.; Schreurs, S.; Yperman, J. Flash pyrolysis of heavy metal contaminated biomass from phytoremediation: Influence of temperature, entrained flow and wood/leaves blended pyrolysis on the behaviour of heavy metals. *J. Anal. Appl. Pyrolysis* **2010**, *87*, 1–7. [CrossRef]
396. Kuppens, T.; Van Dael, M.; Vanreppelen, K.; Thewys, T.; Yperman, J.; Carleer, R.; Schreurs, S.; Van Passel, S. Techno-economic assessment of fast pyrolysis for the valorization of short rotation coppice cultivated for phytoextraction. *J. Clean. Prod.* **2015**, *88*, 336–344. [CrossRef]
397. Grigoras, I.F.; Stroe, R.E.; Sintamarean, I.M.; Rosendahl, L.A. Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow. *Bioresour. Technol.* **2017**, *231*, 116–123. [CrossRef]
398. Raheem, A.; Wan Azlina, W.A.K.G.; Taufiq Yap, Y.H.; Danquah, M.K.; Harun, R. Thermochemical conversion of microalgal biomass for biofuel production. *Renew. Sustain. Energy Rev.* **2015**, *49*, 990–999. [CrossRef]
399. Campenni', L.; Nobre, B.P.; Santos, C.A.; Oliveira, A.C.; Aires-Barros, M.R.; Palavra, A.M.F.; Gouveia, L. Carotenoid and lipid production by the autotrophic microalga Chlorella protothecoides under nutritional, salinity, and luminosity stress conditions. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 1383–1393. [CrossRef] [PubMed]
400. Brennan, L.; Owende, P. Biofuels from microalgae-A review of technologies for production, processing, and extractions of biofuels and co-products. *Renew. Sustain. Energy Rev.* **2010**, *14*, 557–577. [CrossRef]
401. Gouveia, L.; Marques, A.E.; Da Silva, T.L.; Reis, A. Neochloris oleabundans UTEX #1185: A suitable renewable lipid source for biofuel production. *J. Ind. Microbiol. Biotechnol.* **2009**, *36*, 821–826.
402. Rawat, I.; Ranjith Kumar, R.; Mutanda, T.; Bux, F. Biodiesel from microalgae: A critical evaluation from laboratory to large scale production. *Appl. Energy* **2013**, *103*, 444–467. [CrossRef]
403. Miao, X.; Wu, Q. Biodiesel production from heterotrophic microalgal oil. *Bioresour. Technol.* **2006**, *97*, 841–846. [CrossRef]
404. Johnson, M.B.; Wen, Z. Production of biodiesel fuel from the microalga schizochytrium limacinum by direct transesterification of algal biomass. *Energy Fuels* **2009**, *23*, 5179–5183. [CrossRef]
405. Umdu, E.S.; Tuncer, M.; Seker, E. Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al2O3 supported CaO and MgO catalysts. *Bioresour. Technol.* **2009**, *100*, 2828–2831. [CrossRef]
406. Ma, Y.; Liu, S.; Wang, Y.; Adhikari, S.; Dempster, T.A.; Wang, Y. Direct biodiesel production from wet microalgae assisted by radio frequency heating. *Fuel* **2019**, *256*, 115994. [CrossRef]
407. Li, P.; Miao, X.; Li, R.; Zhong, J. In situ biodiesel production from fast-growing and high oil content chlorella pyrenoidosa in rice straw hydrolysate. *J. Biomed. Biotechnol.* **2011**, *2011*, 141207. [CrossRef]
408. Jazzar, S.; Olivares-Carrillo, P.; Pérez de los Ríos, A.; Marzouki, M.N.; Acién-Fernández, F.G.; Fernández-Sevilla, J.M.; Molina-Grima, E.; Smaali, I.; Quesada-Medina, J. Direct supercritical methanolysis of wet and dry unwashed marine microalgae (Nannochloropsis gaditana) to biodiesel. *Appl. Energy* **2015**, *148*, 210–219. [CrossRef]
409. Malekghasemi, S.; Kariminia, H.R.; Plechkova, N.K.; Ward, V.C.A. Direct transesterification of wet microalgae to biodiesel using phosphonium carboxylate ionic liquid catalysts. *Biomass Bioenergy* **2021**, *150*, 106126. [CrossRef]
410. Zamalloa, C.; Boon, N.; Verstraete, W. Anaerobic digestibility of Scenedesmus obliquus and Phaeodactylum tricornutum under mesophilic and thermophilic conditions. *Appl. Energy* **2012**, *92*, 733–738. [CrossRef]
411. Frigon, J.C.; Matteau-Lebrun, F.; Hamani Abdou, R.; McGinn, P.J.; O'Leary, S.J.B.; Guiot, S.R. Screening microalgae strains for their productivity in methane following anaerobic digestion. *Appl. Energy* **2013**, *108*, 100–107. [CrossRef]
412. Du, X.; Tao, Y.; Liu, Y.; Li, H. Stimulating methane production from microalgae by alkaline pretreatment and co-digestion with sludge. *Environ. Technol.* **2018**, *41*, 1546–1553. [CrossRef]
413. Nguyen, M.T.; Choi, S.P.; Lee, J.; Lee, J.H.; Sim, S.J. Hydrothermal acid pretreatment of Chlamydomonas reinhardtii biomass for ethanol production. *J. Microbiol. Biotechnol.* **2009**, *19*, 161–166.
414. Harun, R.; Danquah, M.K.; Forde, G.M. Microalgal biomass as a fermentation feedstock for bioethanol production. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 199–203. [CrossRef]
415. Lee, S.; Oh, Y.; Kim, D.; Kwon, D.; Lee, C.; Lee, J. Converting carbohydrates extracted from marine algae into ethanol using various ethanolic escherichia coli strains. *Appl. Biochem. Biotechnol.* **2011**, *164*, 878–888. [CrossRef]
416. Miranda, J.R.; Passarinho, P.C.; Gouveia, L. Bioethanol production from Scenedesmus obliquus sugars: The influence of photobioreactors and culture conditions on biomass production. *Appl. Microbiol. Biotechnol.* **2012**, *96*, 555–564. [CrossRef]
417. Rempel, A.; de Souza Sossella, F.; Margarites, A.C.; Astolfi, A.L.; Steinmetz, R.L.R.; Kunz, A.; Treichel, H.; Colla, L.M. Bioethanol from Spirulina platensis biomass and the use of residuals to produce biomethane: An energy efficient approach. *Bioresour. Technol.* **2019**, *288*, 121588. [CrossRef]
418. Cardias, B.B.; Trevisol, T.C.; Bertuol, G.G.; Costa, J.A.V.; Santos, L.O. Hydrolyzed Spirulina Biomass and Molasses as Substrate in Alcoholic Fermentation with Application of Magnetic Fields. *Waste Biomass Valorization* **2020**, *12*, 175–183. [CrossRef]

419. Kim, J.K.; Um, B.H.; Kim, T.H. Bioethanol production from micro-algae, Schizocytrium sp., using hydrothermal treatment and biological conversion. *Korean J. Chem. Eng.* **2012**, *29*, 209–214. [CrossRef]
420. Luiza Astolfi, A.; Rempel, A.; Cavanhi, V.A.F.; Alves, M.; Deamici, K.M.; Colla, L.M.; Costa, J.A.V. Simultaneous saccharification and fermentation of Spirulina sp. and corn starch for the production of bioethanol and obtaining biopeptides with high antioxidant activity. *Bioresour. Technol.* **2020**, *301*, 122698. [CrossRef]
421. Zhang, L.; Happe, T.; Melis, A. Biochemical and morphological characterization of sulfur-deprived and H2-producing Chlamydomonas reinhardtii (green alga). *Planta* **2002**, *214*, 552–561. [CrossRef]
422. Chader, S.; Hacene, H.; Agathos, S.N. Study of hydrogen production by three strains of Chlorella isolated from the soil in the Algerian Sahara. *Int. J. Hydrogen Energy* **2009**, *34*, 4941–4946. [CrossRef]
423. Tamburic, B.; Zemichael, F.W.; Maitland, G.C.; Hellgardt, K. Parameters affecting the growth and hydrogen production of the green alga Chlamydomonas reinhardtii. *Int. J. Hydrogen Energy* **2011**, *36*, 7872–7876. [CrossRef]
424. Rashid, N.; Lee, K.; Mahmood, Q. Bio-hydrogen production by Chlorella vulgaris under diverse photoperiods. *Bioresour. Technol.* **2011**, *102*, 2101–2104. [CrossRef]
425. Ruiz-Marin, A.; Canedo-López, Y.; Chávez-Fuentes, P. Biohydrogen production by Chlorella vulgaris and Scenedesmus obliquus immobilized cultivated in artificial wastewater under different light quality. *AMB Express* **2020**, *10*, 191. [CrossRef]
426. Liu, C.; Chang, C.; Cheng, C.; Lee, D. Fermentative hydrogen production by Clostridium butyricum CGS5 using carbohydrate-rich microalgal biomass as feedstock. *Int. J. Hydrogen Energy* **2012**, *37*, 15458–15464. [CrossRef]
427. Nobre, B.P.; Villalobos, F.; Barragán, B.E.; Oliveira, A.C.; Batista, A.P.; Marques, P.A.S.S.; Mendes, R.L.; Sovová, H.; Palavra, A.F.; Gouveia, L. A biorefinery from Nannochloropsis sp. microalga—Extraction of oils and pigments. Production of biohydrogen from the leftover biomass. *Bioresour. Technol.* **2013**, *135*, 128–136. [CrossRef]
428. Xia, A.; Cheng, J.; Ding, L.; Lin, R.; Huang, R.; Zhou, J.; Cen, K. Improvement of the energy conversion efficiency of Chlorella pyrenoidosa biomass by a three-stage process comprising dark fermentation, photofermentation, and methanogenesis. *Bioresour. Technol.* **2013**, *146*, 436–443. [CrossRef]
429. Batista, A.P.; Moura, P.; Marques, P.A.S.S.; Ortigueira, J.; Alves, L.; Gouveia, L. Scenedesmus obliquus as feedstock for biohydrogen production by Enterobacter aerogenes and Clostridium butyricum. *Fuel* **2014**, *117*, 537–543. [CrossRef]
430. Ortigueira, J.; Alves, L.; Gouveia, L.; Moura, P. Third generation biohydrogen production by Clostridium butyricum and adapted mixed cultures from Scenedesmus obliquus microalga biomass. *Fuel* **2015**, *153*, 128–134. [CrossRef]
431. Pacheco, R.; Ferreira, A.F.; Pinto, T.; Nobre, B.P.; Loureiro, D.; Moura, P.; Gouveia, L.; Silva, C.M. The production of pigments & hydrogen through a Spirogyra sp. biorefinery. *Energy Convers. Manag.* **2015**, *89*, 789–797.
432. Ortigueira, J.; Pinto, T.; Gouveia, L.; Moura, P. Production and storage of biohydrogen during sequential batch fermentation of Spirogyra hydrolyzate by Clostridium butyricum. *Energy* **2015**, *88*, 528–536. [CrossRef]
433. Usmanbaha, N.; Jariyaboon, R.; Reungsang, A.; Kongjan, P.; Chu, C.-Y. Optimization of Batch Dark Fermentation of Chlorella sp. Using Mixed-Cultures for Simultaneous Hydrogen and Butyric Acid Production. *Energies* **2019**, *12*, 2529. [CrossRef]
434. Caputo, G.; Dispenza, M.; Rubio, P.; Scargiali, F.; Marotta, G.; Brucato, A. Supercritical water gasification of microalgae and their constituents in a continuous reactor. *J. Supercrit. Fluids* **2016**, *118*, 163–170. [CrossRef]
435. Duman, G.; Uddin, M.A.; Yanik, J. Hydrogen production from algal biomass via steam gasification. *Bioresour. Technol.* **2014**, *166*, 24–30. [CrossRef]
436. Liu, G.; Liao, Y.; Wu, Y.; Ma, X.; Chen, L. Characteristics of microalgae gasification through chemical looping in the presence of steam. *Int. J. Hydrogen Energy* **2017**, *42*, 22730–22742. [CrossRef]
437. Raheem, A.; Cui, X.; Mangi, F.H.; Memon, A.A.; Ji, G.; Cheng, B.; Dong, W.; Zhao, M. Hydrogen-rich energy recovery from microalgae (lipid-extracted) via steam catalytic gasification. *Algal Res.* **2020**, *52*, 102102. [CrossRef]
438. Guan, Q.; Wei, C.; Ning, P.; Tian, S.; Gu, J. Catalytic Gasification of Algae Nannochloropsis sp. in Sub/Supercritical Water. *Procedia Environ. Sci.* **2013**, *18*, 844–848. [CrossRef]
439. Onwudili, J.A.; Lea-Langton, A.R.; Ross, A.B.; Williams, P.T. Catalytic hydrothermal gasification of algae for hydrogen production: Composition of reaction products and potential for nutrient recycling. *Bioresour. Technol.* **2013**, *127*, 72–80. [CrossRef] [PubMed]
440. Tiong, L.; Komiyama, M. Supercritical water gasification of microalga Chlorella vulgaris over supported Ru. *J. Supercrit. Fluids* **2019**, *144*, 1–7. [CrossRef]
441. Babich, I.V.; van der Hulst, M.; Lefferts, L.; Moulijn, J.A.; O'Connor, P.; Seshan, K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. *Biomass Bioenergy* **2011**, *35*, 3199–3207. [CrossRef]
442. Miao, X.; Wu, Q. High yield bio-oil production from fast pyrolysis by metabolic controlling of Chlorella protothecoides. *J. Biotechnol.* **2004**, *110*, 85–93. [CrossRef] [PubMed]
443. Peng, W.; Wu, Q.; Tu, P. Effects of temperature and holding time on production of renewable fuels from pyrolysis of Chlorella protothecoides. *J. Appl. Phycol.* **2000**, *12*, 147–152. [CrossRef]
444. Pan, P.; Hu, C.; Yang, W.; Li, Y.; Dong, L.; Zhu, L.; Tong, D.; Qing, R.; Fan, Y. The direct pyrolysis and catalytic pyrolysis of Nannochloropsis sp. residue for renewable bio-oils. *Bioresour. Technol.* **2010**, *101*, 4593–4599. [CrossRef]
445. Silva, C.M.; Ferreira, A.F.; Dias, A.P.; Costa, M. A comparison between microalgae virtual biorefinery arrangements for bio-oil production based on lab-scale results. *J. Clean. Prod.* **2016**, *130*, 58–67. [CrossRef]
446. Jamilatun, S.; Budhijanto, B.; Rochmadi, R.; Yuliestyan, A.; Hadiyanto, H.; Budiman, A. Comparative analysis between pyrolysis products of Spirulina platensis biomass and its residues. *Int. J. Renew. Energy Dev.* **2019**, *8*, 133–140. [CrossRef]

447. Aswie, V.; Qadariyah, L.; Mahfud, M. Pyrolysis of Microalgae Chlorella sp. using Activated Carbon as Catalyst for Biofuel Production. *Bull. Chem. React. Eng. Catal.* **2021**, *16*, 205–213. [CrossRef]
448. Wang, K.; Brown, R.C.; Homsy, S.; Martinez, L.; Sidhu, S.S. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. *Bioresour. Technol.* **2013**, *127*, 494–499. [CrossRef] [PubMed]
449. Couto, E.A.; Pinto, F.; Varela, F.; Reis, A.; Costa, P.; Calijuri, M.L. Hydrothermal liquefaction of biomass produced from domestic sewage treatment in high-rate ponds. *Renew. Energy* **2018**, *118*, 644–653. [CrossRef]
450. Dote, Y.; Sawayama, S.; Inoue, S.; Minowa, T.; Yokoyama, S. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. *Fuel* **1994**, *73*, 1855–1857. [CrossRef]
451. Minowa, T.; Yokoyama, S.; Kishimoto, M.; Okakura, T. Oil production from algal cells of Dunaliella tertiolecta by direct thermochemical liquefaction. *Fuel* **1995**, *12*, 1735–1738. [CrossRef]
452. Brown, T.M.; Duan, P.; Savage, P.E. Hydrothermal liquefaction and gasification of Nannochloropsis sp. *Energy Fuels* **2010**, *24*, 3639–3646. [CrossRef]
453. Duan, P.; Savage, P.E. Hydrothermal liquefaction of a microalga with heterogeneous catalysts. *Ind. Eng. Chem. Res.* **2011**, *50*, 52–61. [CrossRef]
454. Biller, P.; Ross, A.B. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresour. Technol.* **2011**, *102*, 215–225. [CrossRef]
455. Garcia Alba, L.; Torri, C.; Samorì, C.; Van Der Spek, J.; Fabbri, D.; Kersten, S.R.A.; Brilman, D.W.F. Hydrothermal treatment (HTT) of microalgae: Evaluation of the process as conversion method in an algae biorefinery concept. *Energy Fuels* **2012**, *26*, 642–657. [CrossRef]
456. Biller, P.; Sharma, B.K.; Kunwar, B.; Ross, A.B. Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae. *Fuel* **2015**, *159*, 197–205. [CrossRef]
457. Han, Y.; Hoekman, S.K.; Cui, Z.; Jena, U.; Das, P. Hydrothermal liquefaction of marine microalgae biomass using co-solvents. *Algal Res.* **2019**, *38*, 101421. [CrossRef]
458. Faeth, J.L.; Valdez, P.J.; Savage, P.E. Fast hydrothermal liquefaction of nannochloropsis sp. to produce biocrude. *Energy Fuels* **2013**, *27*, 1391–1398. [CrossRef]
459. Barbosa, B.; Boléo, S.; Sidella, S.; Costa, J.; Duarte, M.P.; Mendes, B.; Cosentino, S.L.; Fernando, A.L. Phytoremediation of Heavy Metal-Contaminated Soils Using the Perennial Energy Crops *Miscanthus* spp. and *Arundo donax* L. *Bioenergy Res.* **2015**, *8*, 1500–1511. [CrossRef]
460. Mehmood, M.A.; Ibrahim, M.; Rashid, U.; Nawaz, M.; Ali, S.; Hussain, A.; Gull, M. Biomass production for bioenergy using marginal lands | Elsevier Enhanced Reader. *Sustain. Prod. Consum.* **2017**, *9*, 3–21. [CrossRef]
461. Gerwin, W.; Repmann, F.; Galatsidas, S.; Vlachaki, D.; Gounaris, N.; Baumgarten, W.; Volkmann, C.; Keramitzis, D.; Kiourtsis, F.; Freese, D. Assessment and quantification of marginal lands for biomass production in Europe using soil-quality indicators. *SOIL* **2018**, *4*, 267–290. [CrossRef]
462. Fernando, A.L.; Costa, J.; Barbosa, B.; Monti, A.; Rettenmaier, N. Environmental impact assessment of perennial crops cultivation on marginal soils in the Mediterranean Region. *Biomass Bioenergy* **2018**, *111*, 174–186. [CrossRef]
463. Sameena, P.; Puthur, J.T. Heavy Metal Phytoremediation by Bioenergy Plants and Associated Tolerance Mechanisms. *Soil Sediment Contam.* **2021**, *30*, 253–274.
464. Ierna, A.; Sortino, O.; Mauromicale, G. Biomass, seed and energy yield of *Cynara cardunculus* L. as affected by environment and season. *Agronomy* **2020**, *10*, 1548. [CrossRef]
465. Garau, M.; Castaldi, P.; Patteri, G.; Roggero, P.P.; Garau, G. Evaluation of *Cynara cardunculus* L. and municipal solid waste compost for aided phytoremediation of multi potentially toxic element–contaminated soils. *Environ. Sci. Pollut. Res.* **2021**, *28*, 3253–3265. [CrossRef]
466. Madejón, P.; Domínguez, M.T.; Fernández-Boy, E.; Paneque, P.; Girón, I.; Madejón, E. Soil hydraulic properties as the main driver in the establishment of biomass crops in contaminated soils. *J. Environ. Manag.* **2019**, *233*, 812–822. [CrossRef]
467. Llugany, M.; Miralles, R.; Corrales, I.; Barceló, J.; Poschenrieder, C. *Cynara cardunculus* a potentially useful plant for remediation of soils polluted with cadmium or arsenic. *J. Geochem. Explor.* **2012**, *123*, 122–127. [CrossRef]
468. Sánchez-Pardo, B.; Cantero, C.; Zornoza, P. Alleviation of arsenic stress in cardoon plants via the supply of a low cadmium concentration. *Environ. Exp. Bot.* **2015**, *109*, 229–234. [CrossRef]
469. Sidella, S.; Consentino, S.L.; Fernando, A.L.; Costa, J.; Barbosa, B. Phytoremediation of soils contaminated with lead by *arundo donax* L. In *WASTES–Solutions, Treatments and Opportunities II*; CRC Press: Boca Raton, FL, USA, 2018.
470. Liu, Y.N.; Xiao, X.Y.; Guo, Z.H. Identification of indicators of giant reed (*Arundo donax* L.) ecotypes for phytoremediation of metal-contaminated soil in a non-ferrous mining and smelting area in southern China. *Ecol. Indic.* **2019**, *101*, 249–260. [CrossRef]
471. Praspaliauskas, M.; Žaltauskaitė, J.; Pedišius, N.; Striūgas, N. Comprehensive evaluation of sewage sludge and sewage sludge char soil amendment impact on the industrial hemp growth performance and heavy metal accumulation. *Ind. Crops Prod.* **2020**, *150*, 112396. [CrossRef]
472. Heuzé, V.; Tran, G.; Chapoutot, P.; Bastianelli, D.; Lebas, F. Feedipedia. Available online: https://agritrop.cirad.fr/582540/1/ID582540.pdf (accessed on 1 January 2020).
473. Fang, Y.R.; Liu, J.A.; Steinberger, Y.; Xie, G.H. Energy use efficiency and economic feasibility of Jerusalem artichoke production on arid and coastal saline lands. *Ind. Crops Prod.* **2018**, *117*, 131–139. [CrossRef]

474. Negro, M.; Ballesteros, I.; Manzanares, P.; Oliva, J.; Saez, F.; Ballesteros, M. Inulin containing biomass for ethanol production. *Appl. Biochem. Biotechnol.* **2006**, *129–132*, 922–932. [CrossRef]
475. Gengmao, Z.; Mehta, S.K.; Zhaopu, L. Use of saline aquaculture wastewater to irrigate salt-tolerant Jerusalem artichoke and sunflower in semiarid coastal zones of China. *Agric. Water Manag.* **2010**, *97*, 1987–1993. [CrossRef]
476. Zhang, T.; Chi, Z.; Zhao, C.H.; Chi, Z.M.; Gong, F. Bioethanol production from hydrolysates of inulin and the tuber meal of Jerusalem artichoke by Saccharomyces sp. W0. *Bioresour. Technol.* **2010**, *101*, 8166–8170. [CrossRef]
477. Hu, N.; Yuan, B.; Sun, J.; Wang, S.A.; Li, F.L. Thermotolerant Kluyveromyces marxianus and Saccharomyces cerevisiae strains representing potentials for bioethanol production from Jerusalem artichoke by consolidated bioprocessing. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 1359–1368. [CrossRef]
478. Monti, A.; Amaducci, M.T.; Venturi, G. Growth response, leaf gas exchange and fructans accumulation of Jerusalem artichoke (*Helianthus tuberosus* L.) as affected by different water regimes. *Eur. J. Agron.* **2005**, *23*, 136–145. [CrossRef]
479. Xue, S.; Lewandowski, I.; Wang, X.; Yi, Z. Assessment of the production potentials of Miscanthus on marginal land in China. *Renew. Sustain. Energy Rev.* **2016**, *54*, 932–943. [CrossRef]
480. Usmani, R.A. Potential for energy and biofuel from biomass in India. *Renew. Energy* **2020**, *155*, 921–930. [CrossRef]
481. Zheng, C.; Iqbal, Y.; Labonte, N.; Sun, G.; Feng, H.; Yi, Z.; Xiao, L. Performance of switchgrass and Miscanthus genotypes on marginal land in the Yellow River Delta. *Ind. Crops Prod.* **2019**, *141*, 111773. [CrossRef]
482. Rusinowski, S.; Krzyżak, J.; Sitko, K.; Kalaji, H.M.; Jensen, E.; Pogrzeba, M. Cultivation of C4 perennial energy grasses on heavy metal contaminated arable land: Impact on soil, biomass, and photosynthetic traits. *Environ. Pollut.* **2019**, *250*, 300–311. [CrossRef] [PubMed]
483. Dauber, J.; Brown, C.; Fernando, A.L.; Finnan, J.; Krasuska, E.; Ponitka, J.; Styles, D.; Thrän, D.; Van Groenigen, K.J.; Weih, M.; et al. Bioenergy from "surplus" land: Environmental and socio-economic implications. *BioRisk* **2012**, *7*, 5. [CrossRef]
484. Fernando, A.L.; Boléo, S.; Barbosa, B.; Costa, J.; Duarte, M.P.; Monti, A. Perennial Grass Production Opportunities on Marginal Mediterranean Land. *Bioenergy Res.* **2015**, *8*, 1523–1537. [CrossRef]
485. Von Cossel, M.; Wagner, M.; Lask, J.; Magenau, E.; Bauerle, A.; Cossel, V.; Warrach-Sagi, K.; Elbersen, B.; Staritsky, I.; Van Eupen, M.; et al. Prospects of Bioenergy Cropping Systems for A More Social-Ecologically Sound Bioeconomy. *Agronomy* **2019**, *9*, 605. [CrossRef]
486. Fijalkowski, K.; Rosikon, K.; Grobelak, A.; Hutchison, D.; Kacprzak, M.J. Modification of properties of energy crops under Polish condition as an effect of sewage sludge application onto degraded soil. *J. Environ. Manag.* **2018**, *217*, 509–519. [CrossRef]
487. Von Cossel, M.; Lewandowski, I.; Elbersen, B.; Staritsky, I.; Van Eupen, M.; Iqbal, Y.; Mantel, S.; Scordia, D.; Testa, G.; Cosentino, S.L.; et al. Marginal agricultural land low-input systems for biomass production. *Energies* **2019**, *12*, 3123. [CrossRef]
488. Patel, B.; Patel, A.; Gami, B.; Patel, P. Energy balance, GHG emission and economy for cultivation of high biomass verities of bamboo, sorghum and pearl millet as energy crops at marginal ecologies of Gujarat state in India. *Renew. Energy* **2020**, *148*, 816–823. [CrossRef]
489. Rodrigues de Sousa, E.M. Pinheiro-Bravo: A Conífera Mais Abundante em Portugal. Available online: https://florestas.pt/conhecer/pinheiro-bravo-a-conifera-mais-abundante-em-portugal/ (accessed on 8 July 2021).
490. Direção Nacional das Fileiras Florestais Culturas Energéticas Florestais—Primeira Abordagem do Levantamento da Situação Actual. Available online: http://www2.icnf.pt/portal/florestas/fileiras/resource/doc/biom/biomass-gtce-jun10 (accessed on 16 November 2018).
491. Tzvetkova, N.; Miladinova, K.; Ivanova, K.; Georgieva, T.; Geneva, M.; Markovska, Y. Possibility for using of two Paulownia lines as a tool for remediation of heavy metal contaminated soil—PubMed. *J. Environ. Biol.* **2015**, *36*, 145–151.
492. Kiser, L.C.; Fox, T.R. Short-rotation Woody Crop Biomass Production for Bioenergy. In *Biofuel Crop Sustainability*; Singh, B.P., Ed.; John Wiley & Sons, Ltd.: Oxford, UK, 2013; pp. 205–238, ISBN 9781118635797.
493. Blanco-Canqui, H. Energy Crops and Their Implications on Soil and Environment. *Agron. J.* **2010**, *102*, 403–419. [CrossRef]
494. Dimitriou, I.; Aronsson, P. Willows for energy and phytoremediation in Sweden. *Unasylva* **2005**, *56*, 47–50.
495. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Krzyżaniak, M. Extensive willow biomass production on marginal land. *Pol. J. Environ. Stud.* **2019**, *28*, 4359–4367. [CrossRef]
496. Bart, S.; Motelica Heino, M.; Miard, F.; Joussein, E.; Soubrand, M.; Bourgerie, S.; Morabito, D. Phytostabilization of As, Sb and Pb by two willow species (*S. viminalis* and *S. purpurea*) on former mine technosols. *CATENA* **2016**, *136*, 44–52.
497. Janssen, J.; Weyens, N.; Croes, S.; Beckers, B.; Meiresonne, L.; Van Peteghem, P.; Carleer, R.; Vangronsveld, J. Phytoremediation of Metal Contaminated Soil Using Willow: Exploiting Plant-Associated Bacteria to Improve Biomass Production and Metal Uptake. *Int. J. Phytoremed.* **2015**, *17*, 1123–1136. [CrossRef]
498. Dimitriou, I.; Mola-Yudego, B.; Aronsson, P.; Eriksson, J. Changes in Organic Carbon and Trace Elements in the Soil of Willow Short-Rotation Coppice Plantations. *Bioenergy Res.* **2012**, *5*, 563–572. [CrossRef]
499. Salam, M.M.A.; Mohsin, M.; Pulkkinen, P.; Pelkonen, P.; Pappinen, A. Effects of soil amendments on the growth response and phytoextraction capability of a willow variety (*S. viminalis* × *S. schwerinii* × *S. dasyclados*) grown in contaminated soils. *Ecotoxicol. Environ. Saf.* **2019**, *171*, 753–770. [CrossRef]
500. Chaganti, V.N.; Ganjegunte, G.; Niu, G.; Ulery, A.; Flynn, R.; Enciso, J.M.; Meki, M.N.; Kiniry, J.R. Effects of treated urban wastewater irrigation on bioenergy sorghum and soil quality. *Agric. Water Manag.* **2020**, *228*, 105894. [CrossRef]

501. Maucieri, C.; Cavallaro, V.; Caruso, C.; Borin, M.; Milani, M.; Barbera, A.C. Sorghum biomass production for energy purpose using treated urban wastewater and different fertilization in a mediterranean environment. *Agriculture* **2016**, *6*, 67. [CrossRef]
502. Invasoras Acacia Dealbata (Mimosa). Available online: http://invasoras.pt/wp-content/uploads/2012/10/Acacia-dealbata.pdf (accessed on 23 October 2017).
503. Dickmann, D.I. Silviculture and biology of short-rotation woody crops in temperate regions: Then and now. *Biomass Bioenergy* **2006**, *30*, 696–705. [CrossRef]
504. Djomo, S.N.; Kasmioui, O.E.; Ceulemans, R. Energy and greenhouse gas balance of bioenergy production from poplar and willow: A review. *GCB Bioenergy* **2011**, *3*, 181–197. [CrossRef]
505. Williams, P.R.D.; Inman, D.; Aden, A.; Heath, G.A. Environmental and sustainability factors associated with next-generation biofuels in the U.S.: What do we really know? *Environ. Sci. Technol.* **2009**, *43*, 4763–4775. [CrossRef] [PubMed]
506. Vázquez Núñez, E.; Fernández-Luqueño, F.; Peña-Castro, J.M.; Vera-Reyes, I. Coupling Plant Biomass Derived from Phytoremediation of Potential Toxic-Metal-Polluted Soils to Bioenergy Production and High-Value by-Products—A Review. *Appl. Sci.* **2021**, *11*, 2982.
507. Liu, Z.; Tran, K.Q. A review on disposal and utilization of phytoremediation plants containing heavy metals. *Ecotoxicol. Environ. Saf.* **2021**, *226*, 112821. [CrossRef]
508. Laval-Gilly, P.; Henry, S.; Mazziotti, M.; Bonnefoy, A.; Comel, A.; Falla, J. *Miscanthus* × *giganteus* Composition in Metals and Potassium After Culture on Polluted Soil and Its Use as Biofuel. *Bioenergy Res.* **2017**, *10*, 846–852. [CrossRef]
509. Danelli, T.; Sepulcri, A.; Masetti, G.; Colombo, F.; Sangiorgio, S.; Cassani, E.; Anelli, S.; Adani, F.; Pilu, R. *Arundo donax* L. Biomass Production in a Polluted Area: Effects of Two Harvest Timings on Heavy Metals Uptake. *Appl. Sci.* **2021**, *11*, 1147. [CrossRef]
510. Raikova, S.; Piccini, M.; Surman, M.K.; Allen, M.J.; Chuck, C.J. Making light work of heavy metal contamination: The potential for coupling bioremediation with bioenergy production. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 3064–3072. [CrossRef]
511. Uchman, W.; Skorek-Osikowska, A.; Werle, S. Evaluation of the potential of the production of electricity and heat using energy crops with phytoremediation features. *Appl. Therm. Eng.* **2017**, *126*, 194–203. [CrossRef]
512. Liu, W.J.; Li, W.W.; Jiang, H.; Yu, H.Q. Fates of Chemical Elements in Biomass during Its Pyrolysis. *Chem. Rev.* **2017**, *117*, 6367–6398. [CrossRef]
513. Dilks, R.T.; Monette, F.; Glaus, M. The major parameters on biomass pyrolysis for hyperaccumulative plants—A review. *Chemosphere* **2016**, *146*, 385–395. [CrossRef]
514. Grottola, C.M.; Giudicianni, P.; Pindozzi, S.; Stanzione, F.; Faugno, S.; Fagnano, M.; Fiorentino, N.; Ragucci, R. Steam assisted slow pyrolysis of contaminated biomasses: Effect of plant parts and process temperature on heavy metals fate. *Waste Manag.* **2019**, *85*, 232–241. [CrossRef] [PubMed]
515. Balsamo, R.A.; Kelly, W.J.; Satrio, J.A.; Ruiz-Felix, M.N.; Fetterman, M.; Wynn, R.; Hagel, K. Utilization of Grasses for Potential Biofuel Production and Phytoremediation of Heavy Metal Contaminated Soils. *Int. J. Phytoremed.* **2014**, *17*, 448–455. [CrossRef] [PubMed]
516. Liu, Y.; Guo, Z.; Sun, Y.; Shi, W.; Han, Z.; Xiao, X.; Zeng, P. Stabilization of heavy metals in biochar pyrolyzed from phytoremediated giant reed (*Arundo donax*) biomass. *Trans. Nonferrous Met. Soc. China* **2017**, *27*, 656–665. [CrossRef]
517. Tian, Y.L.; Zhang, H.Y.; Guo, W.; Wei, X.F. Morphological Responses, Biomass Yield, and Bioenergy Potential of Sweet Sorghum Cultivated in Cadmium-Contaminated Soil for Biofuel. *Int. J. Green Energy* **2014**, *12*, 577–584. [CrossRef]
518. Pidlisnyuk, V.; Trögl, J.; Stefanovska, T.; Shapoval, P.; Erickson, L. Preliminary Results on Growing Second Generation Biofuel Crop *Miscanthus* × *giganteus* at The Polluted Military Site in Ukraine. *Nov. Biotechnol. Chim.* **2016**, *15*, 77–84. [CrossRef]