Biofuel Production with Castor Bean: A Win–Win Strategy for Marginal Land

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Abstract: The urgency to reduce resource depletion and waste production is expected to lead to an economy based on renewable resources. Biofuels, for instance, are a great green alternative to fossil fuel, but they are currently derived from edible vegetable oils such as soybean, palm, and sunflower. Concerns have been raised about the social–economic implication and ecological impacts of biodiesel production. Cultivating new lands as biodiesel feedstock rather than food supply, with the consequent increase in food prices, leads to so-called indirect land-use change (ILUC). Establishing bioenergy crops with phytoremediation ability on contaminated soils offers multiple benefits such as improving soil properties and ecosystem services, decreasing soil erosion, and diminishing the dispersion of potentially toxic elements (PTEs) into the environment. Castor bean is an unpalatable, high-biomass plant, and it has been widely demonstrated to possess phytoremediation capability for several PTEs. Castor bean can grow on marginal lands not suitable for food crops, has multiple uses as a raw material, and is already used in biodiesel production. These characteristics make it perfect for sustainable biodiesel production. Linking biofuel production with environmental remediation can be considered a win–win strategy.

Keywords: *Ricinus communis*; heavy-metal contamination; biodiesel; indirect land-use change; circular economy

1. Introduction

Increasing industrialization, which follows the "take–make–dispose" plan, has led to the depletion of nonrenewable resources, producing waste and causing environmental impacts due to air, soil, and water contamination [1]. Currently, there is an increased use of renewables (e.g., biofuels) to replace the over-reliance on fossil fuels, as well as reduce resource consumption and waste production [2]. The most popular biodiesels are mainly produced from edible crops such as soybean, rapeseed, palm, mustard, and sunflower [3]. However, some concerns have recently been raised about the socioeconomic implications and ecological impacts of biofuel production [4]. To be sustainable, biofuels should not affect the quality, quantity, and use of water or soil, with unacceptable social consequences [5]. Consequently, a biofuel feedstock has to reduce the indirect land-use change, (e.g., the emission of more carbon dioxide as a consequence of the cultivation of new land in response to biofuel demand), which causes a subsequent deficit in food supply and an increase in food prices [6]. It is well known that many areas of the world are contaminated. As an example, the European Union (EU) has estimated the existence of around 2.8 million sites where land contamination exists or is taking place [7]. Hence, linking the production of renewable energy with phytoremediation may be considered a winning strategy to avoid land competition with traditional food crops, protecting human health by remediating land contamination and mitigating the energy crisis and climate change [8,9]. In particular, the establishment of bioenergy crops with phytoremediation potential on soil contaminated by potentially toxic elements

(PTEs) may offer multiple environmental benefits, such as improving soil properties and ecosystem services, decreasing soil erosion, and diminishing the mobility of PTEs through their adsorption and accumulation in roots or their precipitation within the root zone [10]. Phytoremediation involves the use of plants for the restoration of polluted environments being an in situ, solar-powered alternative to the conventional remediation procedure, with a very high public acceptance [11]. Fast-growing perennial crops with high tolerance to biotic and abiotic stress are able to lower soil-available PTEs (phytoextraction), thereby reducing their mobility/bioavailability (phytostabilization), being considered the best option for phytoremediation programs [10]. Additionally, while remediating a contaminated site, the plant biomass can be used for green fine chemistry, bioplastics, and renewable energy, and it can be considered an integral part of a sustainable economy [2]. However, uncertainties have been raised about the safe use of contaminated plant biomass for energy conversion. According to numerous studies, different thermal conversion methods, especially pyrolysis, are exploited to convert metal-contaminated biomass after phytoremediation [12,13]. Pyrolysis greatly reduces the weight and volume of the biomass, resulting in easier disposal, while concentrating the PTEs in the char/ash fraction, which can eventually undergo additional treatments or metal extraction before discarding [14]. The most contaminated plant part or the metal-enriched slags generated from energy conversion can be removed according to the safe disposal of heavy metals [15].

Bearing the above in mind, castor bean (CB) is an unpalatable, fast-growing plant with high biomass production that has been widely demonstrated to have phytoremediation potential for several PTEs (Table 1), as well as a high tolerance to salt and drought stress [16–20]. In this review, we evaluated the potential of using castor bean for phytoremediation programs linked to biofuel and byproduct production.

2. Botanical Aspects and Ecological Characteristics

2.1. Botanical Aspects

Castor bean (*Ricinus communis* L.) is a tropical plant with C3 metabolism belonging to the spurge family (Euphorbiaceae), genus *Ricinus* (Figure 1) [21], with numerous wild and semiwild types that differ genotypically and phenotypically [21,22]. Castor bean can be as short as two feet in height (1.5–2.4 m), especially in a temperate climate, or as tall as a moderate-sized tree in tropical and subtropical areas (10–13 m) [21,23]. In Ethiopia, where it is thought to have originated, plant size varies from a perennial tree or shrub to a small annual [23,24]. The leaves are palmate with 5–11 lobes and alternate; they are often dark glossy green, but the color can vary from light green to dark red, depending on the anthocyanin level and genotype [24,25]. The fruit is a spiny, greenish to reddish purple capsule with three locules containing one oval, shiny, and highly poisonous brownish seed with marble-gray marks and a light-brown caruncle [25,26]; at maturity, the capsules are dried and may have dehiscence, depending on the genotype [27]. Some castor bean varieties can produce capsules with rudimentary spines, whereas others produce soft, flexible, and nonirritant spiny capsules, and others produce spiny irritant capsules [25]. The seeds of castor bean grow inside capsules on raceme that develops progressively over the life of the plant. Seeds, exposed to different environmental conditions, end in an inhomogeneous maturity, with different developmental stages among the raceme and their order [27,28]. The seeds can differ in color, size, external markings, weight, and shape between cultivars [24,29–31]; however, they are of an oval form on average. The number of capsules per raceme depends on the number of female flowers on it. Male flowers are yellowish green with creamy stamens, while female flowers lie in undeveloped spiny capsules with prominent red stigmas. Castor bean plants can be "normal monoecious" with pistillate flowers on the upper part of the raceme and staminate flowers on the lower part or "interspersed monoecious" with pistillate and staminate flowers interspersed along the entire raceme axis [25–28]. Rarely, castor bean inflorescence can terminate with a hermaphrodite flower that regularly drops off before capsule setting [21]. The female and male flower proportion on the raceme can vary within and among genotypes [26], and it is extensively influenced

by the environment. Racemes can have different shapes (conical, cylindrical, or oval) with different capsule arrangements, which can be compact, semi-compact, or loose [25]. According to the order of manifestation, the racemes are called primary, secondary, or tertiary, and their numbers increase geometrically with the number of branches [27]. The castor bean stem is round, sometimes covered with a waxy bloom, and it may be green, reddish, or purple [25]. The dark-purple stem and the sulfur-yellow colors are occasional [24].

Figure 1. *Ricinus communis* L. (CB).

2.2. Ecological Niche

Castor bean can grow well in a wide range of ecosystems, from temperate to tropical desert and wet forests [32], in a range of 250–4250 mm annual precipitation [23,33], and in a wide range (4.5–8.3) of soil pH [24]. Considered a wasteland colonizer plant, it is commonly found on landfills, railway tracks, roadsides, etc. Castor bean cultivation spreads to 40° north (N) and 40° south (S) latitudes, but some cultivars have been found at 52° N in Russia [26]. It can grow from sea level to more than 2000 m above sea level (a.s.l.) [21], but the optimal altitude is 300–1800 m a.s.l. [26].

Table 1. Studies on castor bean (CB; *Ricinus communis*) phytoremediation capability for potentially toxic elements (PTEs).

Contaminants	Aims of the Research	Reference	Genotype
As	Phytoremediation potential of CB and *Helianthus annus*	[34]	cv. Guarany
As, B, Cu, Fe, Mn, Zn	Phytoremediation potential	[35]	Not specified
As, Cd, Pb	Phytoremediation potential co-planting CB with *Pteris vitatta* with chitosan addition	[36]	Not specified
As, Cd, Pb, Zn	Phytoremediation potential of CB and *Z. mays* with chelates	[37]	Not specified
B, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Effects of organic matter addition	[38]	Not specified
Ba	Phytoremediation potential of CB, *B. juncea* and *H. annus*	[39]	Not specified
Cd	Cd accumulation and drought stress	[40]	Cv. Zibi 5
Cd	Phytoremediation potential	[41]	JX-22 and ZB-9
Cd	Phytoremediation potential	[42]	Zibo 5 and Zibo 8
Cd	Phytoremediation potential	[43]	Cv. Kalpi
Cd	Phytoremediation potential of CB and *Brassica juncea*	[44]	Cv. Kalpi
Cd	Phytoremediation potential of CB and *Brassica juncea* + salinity and drought stress	[17]	Cv. Kalpi
Cd	Phytoremediation potential of CB and *Brassicaa juncea* + Organic and Inorganic amendments	[45]	Cv. Kalpi
Cd, Cu, Mn, Ni, Pb, Zn	Crude oil and bioproducts	[46]	Plants established naturally on contaminated site
Cd, Cu, Mn, Pb, Zn	Phytoremediation potential	[47]	Plants established naturally on contaminated site
Cd, Cu, Ni, Pb, Zn	Phytoremediation potential of fly ash disposal site	[48]	Plants established naturally on contaminated site
Cd, DDT	Phytoremediation potential	[49]	Not specified
Cd, Ni	Phytoremediation potential with spent mushroom substrate	[50]	Not specified
Cd, PAHs, Pb, Zn	Phytoextraction and rhizoremediation by co-planting of *Sedum alfredii* with CB and *Lolium perenne*	[36]	Not specified
Cd, Pb	Phytoremediation potential	[51]	Cv. Guarany
Cd, Zn	Phytoremediation potential co-planting CB with *Medicago sativa*	[52]	Not specified
Cu	Effects of S on toxicity bioavailability of Cu	[53]	Plants established naturally on contaminated site
Cu	Influence of nitrogen forms and application rates on phytoextraction	[54]	Not specified
Cu	Phytoremediation potential	[55]	Not specified
Mineral oil	Phytoremediation potential of mineral oil	[56]	Plants in full production at the municipality of Rio Verde
Organochlorine pesticides	Phytoremediation potential of organochlorine pesticides	[57]	Not specified
Pb	Phytoremediation potential	[58]	Plants established naturally on contaminated site
Pb	Phytoremediation potential	[9]	Not specified
Pb	Phytoremediation assisted by mycorrhizal fungi	[59]	Ascession SF7 (previous study from plants established naturally)
Pb	Phytoremediation potential	[60]	Not specified
Pb	Phytoremediation potential	[61]	DCS-108
Pb	Enhanced phytoremediation with citric acid	[62]	Not specified

3. Tolerance to Abiotic Stress

3.1. Drought Resistance

Castor bean is well known to be tolerant to two main abiotic stresses, salinity and drought, making its cultivation possible in marginal lands that are not suitable for food crops [11,44]. The deep taproot and the extensive root system enable CB plants to take up water from deep soil layers, surviving in dry conditions under which other crops would be severely inhibited. Osmotic adjustment, the active accumulation of solutes in response to water deficit, has been reported to be a drought adaptation mechanism in several crop plants. Osmotic adjustment helps maintain turgor, providing more efficient extraction of water from the soil [63]. Osmotic adjustment capacity can vary greatly among CB genotypes; however, CB plants under water deficit accumulate proline (+12%), total soluble sugars (+61%), total free amino acids (+17%), and potassium (+2.8%), indicating that sugars are the main contributors to osmotic adjustment in CB leaves. This is in contrast with other crops in which potassium has been found to contribute the most [11]. Furthermore, prompt stomatal closure seems to be linked to drought resistance in CB plants, resulting in reduced photosynthesis (−59%) and minimal water loss via transpiration (−96%), while maintaining high net CO_2 fixation rates [18]. Water deficiency leads to reduced leaf area, lower leaf, root, and shoot biomass, and reduced height, with shoot elongation being affected very early after irrigation suspension [18,37,40]. This early growth response and the reduced size attained by water-stressed plants may contribute to plant survival, reducing the plant's water requirements [18]. Seed yield is significantly decreased by water stress, mainly in the primary racemes, since the reduction is less pronounced in secondary and compensated for in higher-order racemes [64]. Water deficiency stimulates CB plants to increase wax deposition, contributing to the maintenance of relative water content, since wax is an efficient obstacle of leaf transpiration [65]. Leaf expansion is detectable 30 min after rewatering, showing that, after 2 days of no expansion, there is still potential to develop [66], and, after 7 days of rewatering, proline and total soluble sugar accumulation decreases, albeit remaining higher than in control plants [11]. Drought stress increases K, Ca, and Na contents in CB plants as the drought severity intensifies and decreases Fe, Cu, Zn, and Mg contents according to genotype [67]. Castor bean's drought resistance makes its cultivation possible without irrigation, thus reducing its costs.

3.2. Salt Resistance

In addition to drought, land salinization represents an important environmental constraint that reduces crop growth and yield [20]. Castor bean can grow on marginal lands, which are mostly located in arid and semiarid regions where soil salinity is too high for most common food crops [68,69]. Castor bean's salt tolerance seems to be related to its roots marked ability to limit Na^+ uptake, being selective in K^+ uptake, excluding it from leaf blades and maintaining relatively high K^+ concentrations in leaves [19]. Furthermore, potassium is selectively translocated to young shoots, retaining Na^+ and Cl^- in older tissue. The stem and petiolar tissue can remove Na^+ from the xylem and phloem [19]. Castor bean cotyledons are less affected by saline stress than true leaves, enabling seedling survival in salty soils [70]. After 59 days under 30 mM NaCl, corresponding to 2 g NaCl·kg^{-1} soil, Pinheiro et al. [20] observed a recovery of leaf water potential, suggesting an ability of CB seedling to acclimatize to high salt conditions. The potential photosynthetic activity is augmented by salt stimulation, as reflected by the increased Fv/F_0 ratio, a very sensitive indicator of the potential photosynthetic activity, in CB plants grown under 100 mM·L^{-1} [71]. A certain level of NaCl stimulation may promote CB growth as suggested by the increase in chlorophyll in seedlings [71]. Salt stress effects on chlorophyll a and chlorophyll b contents can be seen only after 59 days [20]. Carotenoids increase, acting as a protective mechanism [71]. The salt tolerance of CB can be indicated by the maintenance of cellular integrity, as indicated by leaf electrolyte leakage, high photorespiratory activity, and nitrate assimilation [72]. The salinity threshold for seed emergence was identified by Zhou et al. [73] at 7.1 dS·m^{-1}; however, in some cultivars the emergence index can even increase at

10.3 dS·m^{-1} [69,73]. Serious plasma membrane lipid peroxidation may not occur, as indicated by the non-significant increase in malondialdehyde at 200 mM·L^{-1} and the proline increase in response to salt stress [74]. The effects of saline irrigation water on the oil content of the racemes are small and more pronounced in primary than in secondary racemes [75]. Castor bean growth parameters are affected by salt stress [20,69], but the sum of the distinct responses to salinity appears to be quite a successful strategy, well organized in the whole plant, allowing survival and reproduction even under adverse conditions of excessive external Na$^+$ and Cl$^-$ [19]. The deep-rooted perennial CB can be used to ameliorate seashore saline soils, increasing the soil porosity and, thus, facilitating the transfer of salts into deeper soil layers and improving soil organic matter content. Furthermore, CB plants positively influence microbial community activity and biodiversity, increasing functional bacteria such as halophilic, phosphate-solubilizing, potassium-solubilizing, cellulose-decomposing, ammonifying, and nitrogen-fixing bacteria, thus enhancing soil nutrient availability, and improving soil structure [76]. The application of nitrogen fertilizers such as monoammonium phosphate plus urea has been shown to increase root biomass and stem diameter on CB cv. BRS Energia, reducing the effect of salinity on CB growth [77]. Finally, arbuscular mycorrhizal fungi stimulate CB growth by alleviating salt stress, increasing the aboveground biomass, phosphorus, carotenoid and chlorophyll, soluble protein, and proline content, and decreasing malondialdehyde (MDA) [78,79].

4. Agronomic Features

4.1. Growth Requirements

Castor bean requires temperatures between 20 and 26 °C [80]; shoots die at temperatures below −1 °C and adult plants die at −3 °C [24]. Castor bean requires a frost-free period of 140–180 days and at least 140 days with mean temperature between 20° and 27 °C for satisfactory yields [21,23] (Table 2). Castor bean grows in all kinds of soils but prefers a well-drained moisture-retentive soil such as sandy loam [25]. Castor bean cultivation necessitates fertile, well-aerated soils with a pH of 6–7.3 and rainfall of 600–700 mm for optimum yield [25]. Castor bean is a long-day plant, but is adaptable to a wide range of photoperiods even if with reduced yields [25]. The optimal relative air humidity range falls between 30% and 60% [24], with low relative humidity in the growth phase to obtain maximum productivity; humid and cloudy days, despite the temperature, can be reflected in lower seed yield [80].

Table 2. Average seed and oil yield of castor bean in different countries under different treatments. USA, United States of America; n.s., not specified.

Country	Site	Seed Yield Mg·ha^{-1}	Oil Yield Mg·ha^{-1}	Genotype	Treatment	Reference
Ethiopia	Rift Valley	1.2–1.4	0.6–0.7	Hiruy	Planting density	[81]
Greece	Aliartos	3.0–3.8	n.s.	Kaima 93, C-853, C-855, C-856, C-864, C-1002, C-1008	Genotype evaluation (year 2014)	[82]
Italy	Cadriano	0.7–4.0	n.s.	C-855, C-856, C-857, C-864, C-1008	Genotype evaluation (year 2014)	[82]
Italy	Ragusa	0.7–7.3	0.3–3.3	Local 1, Local 2, Brazil, Tunisia	Autumnal sowings	[33]
Mexico	Texcoco	2.6–5.2	n.s.	Krishna, Rincon	Optimal soil moisture	[83]
Colombia	Cordoba	0.8–1.2	0.3–0.6	Monteira, Cienaga de Oro, Los Cordobas, BRS Nordestina	Planting density	[84]
USA	Florida, Citra	0.7–1.3	0.3–0.6	Birminghan, Hale	Plant growth regulator and harvest aid	[85]
USA	Florida, Jay	0.7–1.2	0.3–0.6	Birminghan, Hale	Plant growth regulator and harvest aid	[85]

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Country	Site	Seed Yield Mg·ha^{-1}	Oil Yield Mg·ha^{-1}	Genotype	Treatment	Reference
Italy	Sardinia	1.4–2.5	n.s.	Hazera 22, ISCIOR 101	Irrigation	[86]
USA	Texas	0.2–2.7	n.s.	BRS Nordestina	Irrigation	[87]
Brazil	Carnaubais	0.1–1.2	n.s.	BRS Nordestina	Fertilization	[88]
Pakistan	Bahawalpur	1.2–2.4	n.s.	DS-30	Fertilization	[89]

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Castor bean has a slow and cold-sensitive germination [80]. Seeds (Figure 2) may have a dormancy period of several months, depending on variety, while others can germinate from freshly harvested seeds without any treatment [87]. The base temperature for CB seed emergence was found to be 15 °C, optimum at 31 °C and maximum at 35–36 °C, requiring 464 degree-days after pollination to reach physiological maturity [24,90,91].

Figure 2. *Ricinus communis* L. seeds.

4.2. Planting Density

Plant arrangement is a simple low-cost technology that can affect yield [21,92], ranging from 4200 plants·ha^{-1} for tall cultivars to 70,000 plants·ha^{-1} for dwarf varieties [73]. Castor bean plants compensate for a low population density by producing a higher number of racemes [93,94] which, however, do not increase the seed yield considering the reduced number of plants per hectare [95]. Lower plant population increases basal stem diameter and survival rate [92,94,96]. Seed number, a highly hereditable characteristic, is hardly influenced by environmental or exogenous factors [92]. The raceme size is slightly influenced by plant density [92,94]. In all the aforementioned studies, oil content, oil yield, and oil quality were not influenced by plant density [84].

4.3. Irrigation

Castor bean is very sensitive to root hypoxia caused by soil flooding; irreversible damage occurs after just 3 days of flooding [90]. The deep taproots and extensive root systems enable the plant to take up water from deep soil layers and allow seed production with little or no irrigation. Obviously, despite the adaptability of CB to drought, the greatest yields are obtained with irrigation. There is almost a linear increase in seed yield with irrigation, nearly doubling when additional water is supplied [86,97]. In Brazil, a rainfed (376 mm) CB field produced 1774 kg·ha^{-1} of seeds, +24% with supplementary irrigation (1099 mm), and +139% with 1662 mm of water supplied [98]. The castor bean plant response in seed yield to water treatments differs between cultivars, but most of the variation can

be explained by the number of racemes, followed by seeds per raceme and seed weight [86,99]. The seed yield increase in irrigated CB fields is small compared with that of other common crops cultivated in the same area, suggesting that it is more suitable for low-input, arid environments [83,86,100]. Castor bean can also grow well with wastewater irrigation [3,24,101]. Wastewater is an alternative water source being recently exploited to irrigate biofuel crops without depleting the already scarce water resources. A study by Tsoutsos et al. [102] investigated the use of wastewater on the quality of castor bean oil and biodiesel production. Oil samples derived from wastewater irrigation provided a lower concentration of free fatty acids and a slight reduction in viscosity. According to Abbas et al. [103], irrigation with wastewater resulted in higher fresh and dry weights of castor bean roots, shoots, leaves, and seeds (g·plant^{-1}) than those irrigated with freshwater, due to nutritive element contents such as N, P, and K.

4.4. Fertilization

CB can doubtlessly grow on agriculturally marginal lands; however, it obviously benefits considerably from the addition of fertilizer. For example, nitrogen applications can increase seed yield by 114% compared to unfertilized plants [96,104]. Organic fertilization can increase productivity by 458 kg·ha^{-1}, mineral fertilization by 824 kg·ha^{-1}, and the combination of organic fertilization and mineral by 1009 kg·ha^{-1}. Mineral fertilization with N, P, and K, with the addition of organic material, contributed to an increase in productivity of 184 kg·ha^{-1} [88]. Unfertilized plants produced 46% less fruit compared to well-fertilized ones, with a 50% decrease in fruit dry weight [105]. However, CB plants selected to grow at a certain nutrient level have been adapted to produce the maximum at that level [104]; when cultivated in very fertile soils, they tend to produce large vegetative mass at the expense of seed production. The oil content in seeds seemed to increase only in response to P and was not influenced by other nutrients [104]. Among the organic fertilizers, poultry manure seemed to be most effective [106].

5. Castor Bean Products

Castor bean has been used for a very long time and is one of the oldest commercial products [107], known in the traditional medicine of ancient Mediterranean and Asian cultures [108], being still used in traditional medicine worldwide (e.g., Chinese and Ayurveda) [21,108]. Long before "biobased" became a catchphrase, CB oil-derived products were used for centuries (e.g., in ancient Egypt lamps) [21,109]. Currently, CB oil has more than 700 industrial uses, and its global demand is increasing steadily by 3–5% per year [54]. It is a well-recognized commodity with a well-established market, costing 2–3 times more than soybean oil being cultivated only in a few countries [21]. Castor bean oil consists mainly of ricinoleic acid (85–90%), a hydroxylated fatty acid with one double bond, and some unique properties. Castor bean has an oil close to a technical grade of purity, a rare natural phenomenon [21,110]. It is more versatile than other vegetable oils and extensively used in a variety of industries, such as the cosmetic and pharmaceutical industries, as well as in paint, varnish, and lacquer production [111,112]. Because of its high viscosity, it is used as a lubricant in two-stroke engines, neat or blended, reducing smoke emissions by up to 50–70% [113,114]. It is a polyol that can readily form polymers making polyurethanes that find applications in adhesives and coatings, electrical insulators, and semirigid foams used in thermal insulation [115]; it was also suggested as a possible candidate biomaterial for wound dressings [116] and as a graft for bone defect treatments [117]. The so-called Turkey red oil, produced by CB oil sulfation, is widely used in textile industries in dyeing and in finishing cotton and linen [118]. The CB oil obtained mechanically by pressing results in CB cake, while CB meal derives from CB oil production through solvents. CB cake is a good organic fertilizer, containing about 5.5% nitrogen, 1.8–1.9% phosphorus, and 1.1% potassium [119,120]. It can be applied in moist soil 3 weeks before sowing the crops, allowing for toxicant degradation [121]. It has been used as a substrate for tomato seedlings and as a fertilizer for onion production [122,123]. Castor bean cake has also shown great potential for biogas production and was found to be a very interesting feedstock for the production of pyrolysis bio-oil [124,125]. According to Gonzalez-Chavez et al. [46], castor bean

cake derived from plants naturally established on polluted mine-tailings can be utilized as organic fertilizer due to the lower levels (e.g., Pb in cake: 2.6–8.8 mg·kg^{-1}) of metal contamination allowed by EU regulations (e.g., maximum limit values of Pb in organic fertilizer: 120 mg·kg^{-1} of dry matter) [126].

Castor bean meal may contain up to 55.8% crude protein and can be used as a protein source for animal feedstock [127]. Due to its ricin content, CB meal use necessitates caution. Different types of seed processing can reduce or eliminate this toxin [128,129]. For instance, it can be detoxified with calcium oxide replacing up to 50% of soybean meal in lambs' diet [127] and reducing the production costs in a beef cattle grazing system [130]. Furthermore, up to 15% non-detoxified CB meal can be used in goat feed [131]. Castor bean can also be considered an ecofriendly and economic alternative to synthetic insecticidal agents (e.g., against *Spodotpera frugiperda*, *Spodoptera littoralis*, *Musca domestica*, and *Phlebotomus duboscqi*, the *Leishmania* vector) [132–135]. Leaf extracts have also shown antimicrobial potential and antifungal activity [136–138]. Castor bean leaves are used, especially in India and Africa [139,140], as food for *Samia cynthia*, a moth used to produce silk; in Italy, the use of senescent leaves for the eri-silkworm artificial diet has provided a promising opportunity for valorizing residual biomass to good use after biorefinery [141]. Moreover, the reactive surface of CB leaf powder has been studied as a green adsorbent for the removal of heavy metals from natural river water [142]. In the eastern part of Nigeria, CB seeds are used as food seasoning called Ogiri, and CB can be used in honey production [80,112].

Castor Bean Biodiesel

Recently, castor bean biodiesel is receiving great attention [143]. Biodiesel is the alcoholic ester of vegetable oils obtained via transesterification. It presents many advantages over fuel, e.g., nontoxicity, biodegradability, renewability, and a decline in most exhaust emissions. For instance, the presence of oxygen in biodiesel makes it burn cleaner, and its higher viscosity cancels the need for added sulfur compounds in diesel, reducing SO_2 emissions [22,144]. Biodiesel production begins with vegetable oil extraction from the seeds, generally carried out with mechanical pressing, solvent extraction, or a combination of both technologies [144]. Supercritical fluids, ultrasound, and microwave are the newest technologies developed for oil extraction [144]. After oil extraction, some refining steps are carried out to improve biodiesel quality, such as filtration or discoloration [144]. Subsequently, biodiesel is obtained through the transformation of triglycerides into fatty acids (FA), which can be performed with ethanol (resulting in fatty acid ethyl esters, FAEEs) or methanol (fatty acid methyl esters, FAMEs), in the presence of catalysts that can be chemical (alkali or acid catalysts) or biological (enzymes) [145]. Afterward, separation by centrifugation or decantation is performed to decrease the impurities and recover all products (biodiesel, solvent, and glycerol) [144]. The fatty acid composition of the feedstock, its properties, and the production process employed are the parameters mainly affecting biodiesel quality [146]. The biodiesel obtained, used alone or blended with petrodiesel, has to conform to specific standards, e.g., ASTM D6751 or EN 14214 [144,147]. Some important biodiesel properties that need to conform to standards are kinetic viscosity, cetane number, cloud and pour point, and flashpoint.

Castor bean oil is mainly composed of ricinoleic acid (85–90%). Castor bean has a very high percentage of seed oil content (40–55%), higher than other normally used oil crops such as soybean (15–20%), sunflower (25–35%), or rapeseed (38–46%), with a cultivation cost reduced by up to 50% compared to rapeseed (Table 3) [143]. Castor bean oil can be used in diesel engines with few modifications [148,149], lowering the level of pollutants, carcinogens, and greenhouse gasses [22,144]. According to Anjani [24], about 79,782 Mg of CO_2 emission can be saved if 10% of total castor bean seed oil produced is transesterified into biodiesel. The world average castor bean seed production is 1.1 Mg·ha^{-1}, corresponding to 460 kg of castor bean oil with a seed oil content of 47% and oil yield of 90%; however, a higher yield can be obtained, indicating promising oil productivity [110,149]. Castor bean oil FAMEs present an unacceptably high value of kinematic viscosity (which influences characteristics such as the amount of fuel that drips in the injection pump [145]) and low cetane number (which quantifies the time between injection and ignition of the fuel [22]) that do not allow it to achieve

standard specifications [146,149,150]. Blending castor bean biodiesel with diesel is currently the only way to use it in current diesel engines without complicating engine performance while meeting all the required specifications [149,150]. Castor bean biodiesel's high viscosity could improve diesel lubricity when blended, at a concentration of 2 g·kg^{-1}, while rapeseed needs to be added at a concentration above 7.5 g·kg^{-1} to achieve the equivalent effect [80]. Castor bean biodiesel presents a cetane number (CN; 43.7) lower than diesel CN (51). Nevertheless, the B5 blend gave a CN of 50.6 [143]. Moreover, castor bean biodiesel also presents a high cloud and pour point (which monitors the flow proprieties at low temperature [145]), making it suitable for extreme winter temperatures, alone and blended [143,150]. Castor bean biodiesel requires a negligible amount of catalyst to give a high biodiesel yield, reducing the production cost for large-scale operations [22,150]. Furthermore, castor bean biodiesel can be obtained at low temperatures [110,151]: for instance, Keera et al. [143] produced castor bean biodiesel through alkaline transesterification, with biodiesel yield obtained at 30 °C similar to that obtained at 60 °C. It is highly soluble in alcohol, due to the presence of hydroxyl groups, with great advantage during transesterification [80,144,151,152]. A study by Bateni et al. [110] demonstrated that the whole castor bean plant may be used in biodiesel production, with transesterification performed with ethanol obtained by saccharification and fermentation of plant residues; 1 kg of castor bean plant produced 149 g of biodiesel and 30.1 g of ethanol. Meneghetti et al. [153] performed a comparison of ethanolysis versus methanolysis on commercial castor bean oil, obtaining similar yields but a shorter reaction time for methanolysis. All the above-mentioned studies indicate that castor bean is a great feedstock for biodiesel production. Applying a mathematical experimental design and methodology, such as response surface methodology [151,154] or the Taguchi approach [155,156], can improve and optimize castor bean oil transesterification. New technological innovations, new diesel engines, and mathematical model applications could greatly increase castor bean biodiesel production and utilization. According to Amouri et al. [157], who studied the impact of castor bean biodiesel production on global warming, energy return-on-energy investment (EROEI), and ecosystem and human health, castor bean biodiesel showed a positive carbon balance, equivalent to a reduction in climate change emissions and an EROEI of 2.60. The abovementioned positive impacts of castor bean biodiesel can also be improved by reducing its indirect land-use change (ILUC); according to Gonzalez-Chavez et al. [46], oil produced by *Ricinus* shrubs grown on metal-polluted sites presents low levels of contamination (e.g., Cd: 0–1.26 mg·L^{-1}; Pb: 0–2.2 mg·L^{-1}) and could be used as a raw material.

Table 3. Comparison of the most common biodiesel feedstocks.

Feedstock	Seed oil Content	Advantages	Disadvantages	References
Castor bean oil	45–55%	Nonedible, high flash point. high pour and cloud point (useful in winter condition), can grow on marginal and PTEs contaminated soils, miscible in alcohol, easily undergoes transesterification	Low cetane number, high viscosity, ricin content	[110,143–146, 152,158–162]
Soybean	15–20%	Low viscosity, high thermal stability	High production cost, edible, high acid value	[144–146,152, 158,161,162]
Sunflower	25–35%	Low viscosity	Edible, high acid value, long-term cultivation unsustainable	[144–146,152, 158,163]
Palm	18–40%	Cheap feedstock, high flashpoint	High cloud point, edible, long-term cultivation unsustainable	[144–146,152, 158,164]
Mustard	28–32%	High cetane number, cheap feedstock, can grow on soils contaminated with PTEs	High viscosity, low heating value, high cloud point	[145,146,152, 165–168]
Rapeseed	38–46%	High flash point and low cloud point	Effective power and torque decrease at all engine loads, increased NO$_x$ emissions up to 15% in most experiments	[145,146,152, 158,169,170]

6. Phytoremediation Potential

Castor bean has a great potential for phytoremediation programs because it is a high-biomass fast-growing plant, unpalatable to stock, and a potential phytoaccumulator of several PTEs, such as As, Cd, Pb, and Zn [38,44,49,157,171]. Being a perennial plant, its vegetation cover can immobilize PTEs in the rhizosphere, reducing their wind dispersion and, thus, interrupting the exposure pathways (Figure 3).
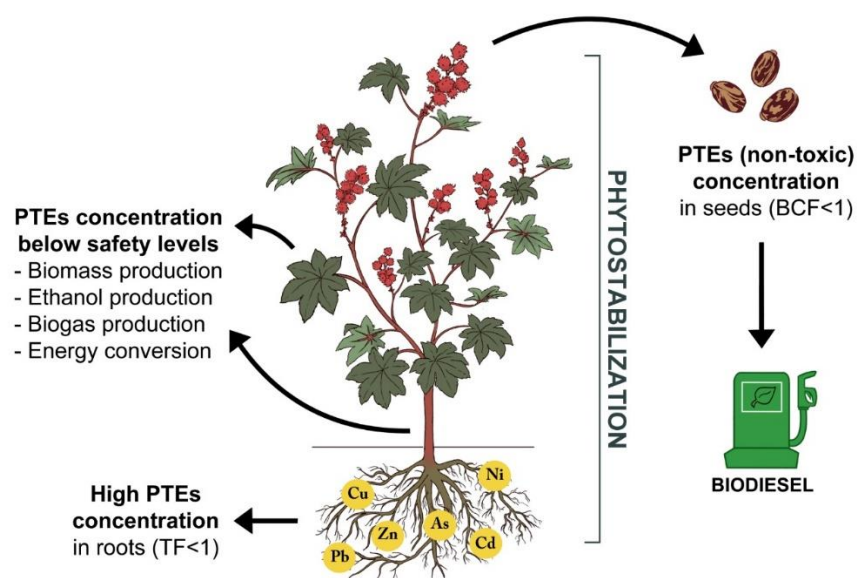

Figure 3. Castor bean phytostabilization scheme for biodiesel production. TF, translocation factor; BCF, bioconcentration factor; PTEs, potentially toxic elements.

In addition, its massive root growth can reduce PTE leaching into water [11,172], making it capable of adsorbing a high amount of contaminants [35,56]. Castor bean's low translocation factor demonstrates that it is highly suitable for phytostabilization of heavy metals and metalloids [35,37,173]. The phytoremediation potential of castor bean plant is of primary importance, given the increasing number of PTE-contaminated soils. According to Dastyar et al. [15], one-third of world resources are contaminated, mainly by heavy metals, although the real rate could be higher.

Copper accumulation, originating from the long-term use of Cu-based fungicides, carries an environmental risk of a progressive increase of Cu in agricultural soils [174]. Lead, considered one of the most hazardous PTEs, can have a geological origin in soils or be released into the environment by smelting, battery recycling, and mining [11]. Cadmium, by contrast, is less common in soils but exposure even to low concentrations can cause serious human health problems, with carcinogenic effects, cell injury, and endocrine destruction [175].

Copper toxicity results in growth cessation in plants, chlorosis and necrosis symptoms, and interference with many biological processes (e.g., cellular respiration) [49]. Castor bean plants exhibit a well-documented copper phytostabilization aptitude. Copper-contaminated soil seems to increase the biomass production of CB plants [35,55], without significant phytotoxic symptoms except for chlorosis in a few leaves, indicating its Cu-tolerant capacity [35,54]. Copper concentration in roots greatly exceeds the concentration in other tissue [53,175]. Depending on soil type, CB is able to remove 5900 g·ha^{-1} of Cu in Inceptisol and 3052 g·ha^{-1} in Mollisol, with root copper concentration 90 times higher than that in leaves and stems [55]. Castor bean plants exhibit a bioconcentration factor (BCF, a ratio of element concentration in the plant shoots to element concentration in the soil [172,174,176]) and translocation factor (TF, ratio of element concentration in shoots and roots [177,178]) <1, indicating that CB is not a Cu accumulator plant and is well suited for phytostabilization due its low metal transfer rate [35,55,179]. Copper accumulation in CB seems to be directly related to

phosphorous content in soils [35]. Accordingly, phosphorous fertilization at 300 mg P·kg^{-1} increased Cu root concentration by 68% while decreasing malondialdehyde (MDA) content [175]. Sulfur application decreases copper accumulation in roots by 30%, by reducing Cu bioavailability in soils [53]. Conversely, nitrogen fertilization increases Cu root content, while restricting Cu transport from the underground to the aboveground part, thus reducing the translocation factor [54].

Cadmium soil contamination events have been progressively increasing over the last few years, because of the excessive use of chemical fertilizers and pesticides, mining, smelting, and industrial wastewater irrigation [43]. Almost 5.6–38 × 10^6 kg·year^{-1} of Cd released into the environment is anthropogenic, e.g., from metallurgic works, wastes from the cement industry, municipal waste, sewage sludge, mining, and metal processing; Cd production worldwide in 2015 was estimated at 24,900 metric tons [180]. Castor bean has a strong ability for Cd accumulation in roots [43,44]. Eight month old CB plants grown in soil characterized by a total Cd concentration of 17.50 mg Cd·kg^{-1} showed no morphological differences with the controls, with only a 5% decrease in the number of capsules and seeds per plant [43]. After the harvest, in the same study, Bauddh et al. [43] observed a reduction of about 27% of soil cadmium. Cadmium tolerance and accumulation are dependent on the cultivar [41,42]. Compared with a well-known Cd hyperaccumulator, *Brassica juncea*, CB accumulates 17-fold higher Cd in roots, appearing more suitable for longer-term soil remediation in a single sowing, thus reducing operational costs [44,173]. Synthetic chelates, such as ethylenediaminetetraacetic acid (EDTA) or ethylenediamine disuccinic acid (EDDS), can increase the plant's ability to uptake cadmium [181]. EDDS was shown to be the most suitable chelate for phytoremediation of Cd in soil [182]. In addition to chelates, the application of water-soluble chitosan also enhances Cd uptake [36]. Moreover, crop co-planting with *Medicago sativa* can increase the cumulative amount of cadmium by 1.14 times [52]. Under saline conditions, Cd translocation from soil to CB roots is enhanced due to salt-induced Cd mobilization in the soil and Cl–Cd complex formation that increases Cd concentration in plants. On the other hand, it is reduced by drought [17]. Application of biostimulants, such as *Bacillus subtilis* and *Azotobacter chrocoocum*, and inorganic fertilizer (e.g., urea, diammonium phosphate) enhanced Cd accumulation, improved tolerance mechanism, and decreased MDA content [45]. Spent mushroom substrate (SMS) applied as an organic amendment increased plant Cd uptake and the total amount of Cd accumulation in CB by 28–152% [50].

Lead accumulation in soils and, subsequently, in plant tissue can reduce biomass and photosynthetic activity, as well as root and shoot elongation, and increase the generation of reactive oxygen species (ROS) [58]. Castor bean was able to accumulate high amounts of Pb in roots, tolerating above phytotoxic levels of Pb without any symptom of toxicity [58,60]. Fungi are well known for their ability to detoxify potentially toxic elements through precipitation or valence transformation, via passive and active uptake [181,183]. According to this, arbuscular mycorrhizal fungal treatments significantly influenced rhizosphere soil pH, Pb bioavailability, and CB shoot Pb concentration [46]. Amendments, such as biochar or rice husk ash, can be used in mitigating Pb toxicity, improving plant growth, and decreasing Pb accumulation in roots up to 59% by immobilizing Pb [61]. Among the chelates, citric acid can remove 17-fold more Pb than untreated plants [37], while improving photosynthesis and plant growth [62]. EDTA is the most effective for Pb phytoextraction; however, due to environmental persistence, it is not the best option for field use [182]. Castor bean seems to defend itself against lead toxicity by increasing its production of proline and carotenoids, as well as via the upregulation of the ATP-binding cassette (ABC) transporter transcript, which are likely responsible for Pb detoxification in roots [58]. According to Costa-Souza, CB growth was not affected by lead [51].

Among the other PTEs, CB also emerged as a Zn phytostabilizer [35,46,47] and as being As- and Ba-tolerant [34,39]. Only B and Mn were translocated more intensely into the shoots, showing a TF greater than 1 [35,38,47]. Furthermore, CB has also been used for phytostabilization and revegetation of fly ash disposal, derived from coal-fired power plants, showing a BCF in roots greater than 1 and a TF lower than 1 [48]. Castor bean can also provide other benefits such as carbon sequestration and an esthetically pleasant landscape [48].

Organochlorine pesticides such as dichlorodipheno-xytrichloroethane (DDT) and organic pollutants are widely known for their toxicity, persistence in the environment, and biosolubility in fatty tissue [57]. Accumulation of organic pollutants in plant roots can be the result of two processes: (1) uptake and translocation, for pollutants with low hydrophobicity, and (2) adsorption in root tissue [57]. However, it is well known that the presence of arbuscular mycorrhizal fungi, which increase the contact surface and interact with roots and rhizosphere, can modify the bioavailability of organic contaminants and enhance plant adsorption [57,59]. Moreover, microbe-assisted phytoremediation, i.e., rhizoremediation, the degradation of pollutant in the rhizosphere, is affected by root characteristics and exudate compounds, which influence soil properties and organic pollutant mobilization [184]. Studies have proven that CB can be used in the phytoremediation of soils contaminated with these kinds of pollutant [49,57]. For example, co-planting CB with *Sedum alfredii* enhances the degradation of pyrene and anthracene, two polycyclic aromatic hydrocarbons (PAHs) [36]. Moreover, CB plants grown on soil contaminated with mineral oil can remove up to 81% of soil hydrocarbons, manifesting visual toxic effects only after 45 days of treatment [56]. Remediation of soils contaminated by organic pollutants with CB is a potential biotechnological approach with the side effects of erosion control, site restoration, carbon sequestration, and feedstock production for biofuel [57].

7. Conclusions

The multiple uses of CB oil clearly show that it is one of the most promising sources of renewable raw material for many industries. Being a nonedible plant, its use as an energy source does not compete with food production, and, unlike other industrial plants, CB can grow on marginal and PTE-polluted lands not suitable for food crops. It can survive in conditions under which other crops would be severely damaged, allowing seed production with little or no irrigation. Castor bean's fast growth and high biomass production can reduce the time required for phytoremediation programs, which is considered the real weakness of phytoextraction/phytostabilization. Furthermore, it has a higher oil yield potential, compared to other bioenergy crops.

According to the life-cycle analysis of the whole production system, CB cultivation has a major impact on the environment. Thus, exploiting metal-contaminated lands for bioenergy production might decrease CB cultivation impacts, reduce the ILUC of biodiesel production, and convert contaminated soils into fully utilized and productive sites. Moreover, oil produced from CB plants grown in PTE-polluted mine-tailings had higher linoleic acid content, which enriches fuel properties (ignition quality, cloud point), and nontoxic concentrations of Cd, Pb, Zn, Ni, and Mn. Furthermore, CB plant residues of biodiesel production could be used in biogas and ethanol production, when the PTE concentration allows it. Among thermal conversion methods, pyrolysis reduces the weight and volume of the contaminated biomass while concentrating the PTEs in the char/ash fraction, which can be removed according to the safe disposal of heavy metals.

Despite its high adaptability to different climates, CB oil is produced mainly in India, China, and Brazil, but one-quarter of its transformation is done by the EU oleochemical industry, which is completely dependent on imports. Using CB in different countries such as Europe to remediate contaminated sites and produce biofuel and byproducts could result in a great opportunity for the environment and a bio-based economy, leading to new job creation and opportunity. Moreover, the biodiesel produced from CB grown on marginal lands and contaminated soils would be able to eliminate the indirect land-use change, making the production of biofuels truly sustainable.

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