

Review

Chemical and Bioenergetic Characterization of Biofuels from Plant Biomass: Perspectives for Southern Europe

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Featured Application: An overview of the characteristics of biofuels, their feedstock materials including energy crops, and of the techniques and processes for bioenergy production is provided in this review.

Abstract: The global demand for and, therefore, the production of primary energy is continuously increasing. Consequently, the need to intervene with appropriate measures has arisen in order to achieve sustainable economic, social, and environmental objectives. The reduction of fuel and electricity consumption, the containment of atmospheric emissions of greenhouse gases (like carbon dioxide, methane, other hydrocarbons, and nitrous oxide), and the improvement of environmental quality in urban centers can be considered to be among these objectives. The search for efficient measures for the overall improvement of the environment is directed towards the replacement of traditional fossil fuels with the production of bioenergy (also known as green energy) from different materials and biomasses obtained from specific agricultural activities and/or plant residues. These materials have physico-chemical and biological characteristics of interest regarding their use as sources of renewable energy. The purpose of this review was to provide an overview of the chemical and bioenergetic characteristics of biofuels, the main techniques and processes employed for their production, and the characteristics of the different feedstock materials, especially potential energy crops.

Keywords: energy crops; renewable energy; plant biomass

1. The Bioenergy Situation in Europe

The Directive 2009/28/EC established a series of legally binding targets for renewable energy production that has led to a considerable increase in the demand for and production of renewable energy in the European Union (EU). The EU as a whole is likely going to meet its 2020 goals, but some of the states within the EU may need additional efforts to meet their obligations regarding the share of energy derived from renewable sources in the gross final consumption of energy.

Two of the key objectives of the Europe 2020 strategy are a reduction in greenhouse gas emissions of at least 20% compared to 1990 levels and an increase in the share of renewable energy in the final energy consumption of 20%.

Consequently, it is thought that primary production of renewable energy will increase in the long-term (Figure 1). However, despite the growth of new and renewable energy sources, such as solar and wind power, most of the increase in the contribution of renewable energy could be attributable to biomass. In 2015, the production of primary renewable energy in the EU increased by 3.8%

compared to 2014 [1]. For example, electricity production from solid renewables (wood and other solid biomass) used in conventional thermal power stations increased from 3.5% to 7% in 2015. In addition, the production of liquid biofuels has increased significantly, with an average annual growth rate of 32% between 2000 and 2010 [2,3].

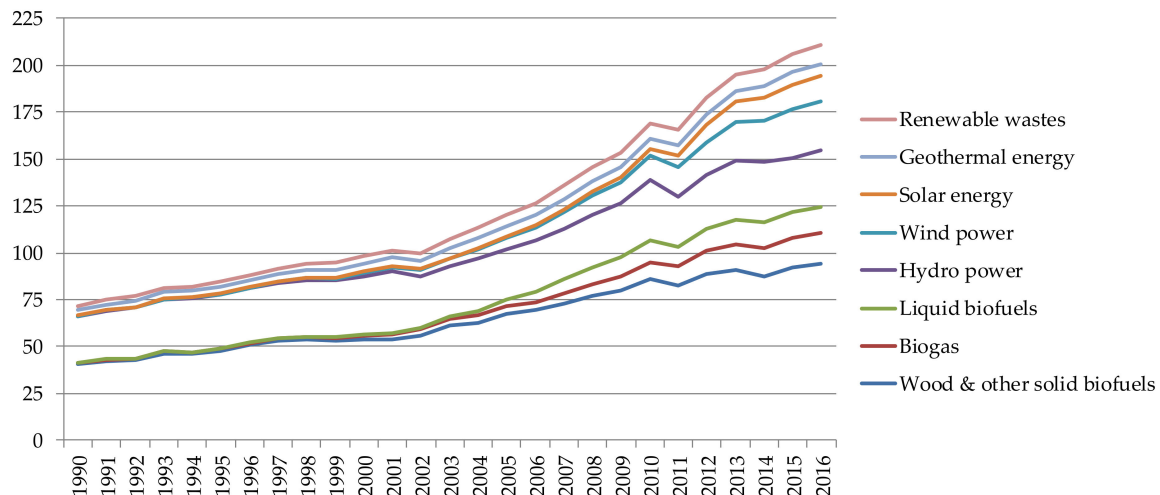


Figure 1. Primary production of energy (Mtoe) from renewable sources, EU—28, 1990–2016 [1].

The year 2018 was a key one for the renewable gas sector in Europe. Several legislative innovations were introduced and adopted by institutions of the Community in order to strengthen its role in the energy transition. New technologies such as power-to-gas and biomass gasification will also be protagonists of this transition. The number of biogas plants in Europe has grown exponentially in the last decade. Between 2009 and 2016, it almost tripled, going from 6200 to 17,662 units, and the growth was particularly intense from 2010 to 2012. A similar increase was observed in the number of farm-based plants, from 4797 units in 2009 to 12,496 in 2016; such plants are by far the most numerous in the EU, followed by plants that convert sewage sludge (2838), urban waste (1604), and other types of waste (688) [4].

According to Eurostat [1], the annual production of biogas in the EU was 181,565 GWh in 2015, with Germany, the United Kingdom, Italy, and France representing the main producing countries. In 2016, the most dynamic countries in the construction of new plants were France (+93) and the United Kingdom (+41). In parallel with the growing maturity of biogas technologies and industry, from 2016 there has been also a substantial increase in the quantity of biomethane produced in Europe. Biomethane is a gas that contains about 97% CH₄ (quality of natural gas) and is obtained from biogas (about 50%–75% CH₄) after purification (dehydration, desulfurization, removal of gaseous ammonia, mercaptans, dust) and upgrading (removal of carbon dioxide) [5,6]. Like biogas plants, biomethane plants (which currently number around 500 units in the EU; [4]) mainly use resources from the agricultural sector (380 plants), but also waste (115 plants) and sewage sludge (73). In 2016, EU production of biomethane amounted to 17,264 GWh, with development driven mainly by Germany (+900 GWh), France (+133 GWh), and Sweden (+78 GWh).

This growth will likely continue in the next few years, driven by the excellent environmental performance of biomethane and its use as vehicle fuel, and should be immediately achievable by exploiting the existing technologies. The countries that have a large potential for raw materials generation and have defined specific targets for the production of biomethane will consequently experience a significant development in this sector. This is the case, for example, of France, the Scandinavian peninsula, and Italy [4].

Renewable energy (understood as that coming exclusively from sources that replenish themselves naturally) available for final consumption increased by 68% between 2005 and 2015, and by 4.4% in 2015 compared to 2014 [1]. In the EU-28, the contribution of energy from renewable sources to the

gross final consumption of energy increased from 8.5% in 2004 to 16.7% in 2015. This is a clear index of progress towards the Europe 2020 target of 20%. With energy from renewable sources representing more than half (53.9%) of its gross final consumption of energy, in 2015 Sweden had by far the highest share, ahead of Finland (39.3%), Latvia (37.6%), Austria (33.0%), and Denmark (30.8%). Contrastingly, the lowest percentages of renewable energy were registered in Luxembourg and Malta (both 5.0%), the Netherlands (5.8%), Belgium (7.9%), and the United Kingdom (8.2%; [1]). The percentage of the total energy used for heating and cooling coming from renewable energy in the EU-28 increased from 10.2% in 2004 to 18.6% in 2015. In addition, renewable energy will continue to play a key role in helping the EU meet its energy needs beyond 2020, and member states have agreed on a new EU renewable energy target of at least 32% by 2030 and 55%–75% by 2050 [3].

2. Biofuels Classification

The term “biofuel” refers to a fuel in the liquid or gaseous state obtained from biomass [7]. Traditionally, the use of biofuels has been linked to the transport sector, for motor vehicles, to replace fossil fuels. However, there has been a recent and rapid expansion of the production and application of biofuels for electrical and thermal energy generation, and in particular, for cogeneration. Therefore, the current concept of biofuel has outgrown the link with the transport sector, and more emphasis has been given to other applications. Based on the state of maturity of the production and use technologies, biofuels can be divided in two categories [8]:

1. First-generation biofuels: e.g., biodiesel from pure vegetable oils, bioethanol produced from cereals and sugary raw materials, bio-ETBE (ethyl tert-butyl ether) produced from bioethanol, and biogas from anaerobic digestion (AD) systems. Their production and application has already started, while the main margins for improvement being, at the moment, the reduction of production costs, the optimization of the energy balance, the increase in the energy yields of the engines, and the increase in the percentage of use in mixtures with fossil fuels;
2. Second-generation biofuels: e.g., bioethanol produced from lignocellulosic raw materials, biohydrogen, syngas, bio-oil, biomethanol, biodimethylether, bio-MTBE (methyl tert-butyl ether), biobutanol, and synthetic diesel, obtained through the Fischer–Tropsch reaction. Their production has not yet started on a commercial scale and is limited to experimental installations. The second-generation biofuels are linked by the possibility of being produced from lignocellulosic biomass at low or zero cost.

This differentiation between first- and second-generation biofuels is important as the former often stand in concurrence with or have undesired economic influences on food production, which implies a series of social/moral and economic consequences that have to be considered [9]. First-generation biofuels normally offer some advantages in terms of energy production potential, but they have some disadvantages such as raw materials supply, impact on biodiversity and land use, and competition with food crops, which provokes the increase in food prices resulting from increased production of these fuels [8].

However, the production of second-generation biofuels can imply benefits in terms of C-mitigation and ecosystem services, with a demonstrated lower impact on greenhouse gas emissions than the traditional fuels from fossil sources [9]. Therefore, second-generation biofuels, produced from plant biomass, one of the most abundant and underused biological resource systems on the planet, can be considered a viable alternative. Biomass, in fact, can be simply burned to produce heat and electricity, or used to produce liquid biofuels. But, as the production of biofuels from agricultural by-products could only meet part of the growing demand for liquid fuels, interest has shifted towards the use of dedicated crops. Second-generation biofuels could, therefore, significantly reduce CO₂ production, not compete with food crops, and in some cases offer better engine performance. If marketed, the cost of second-generation biofuels has the potential to be comparable to standard petrol or diesel and would be the cheapest route to low-carbon renewable energy for transport [8].

Comparing the higher heating value (HHV) and lower heating value (LHV) of biofuels with those of fossil fuels, it can be seen that they are normally lower than those presented, for example, by gasoline (HHV = 46.9 MJ kg⁻¹, LHV = 44.2 MJ kg⁻¹), fuel oil (HHV = 43.3 MJ kg⁻¹, LHV = 40.0 MJ kg⁻¹), and diesel fuel (HHV = 45.6, LHV = 42.6). However, the use of biomass provides many environmental benefits [10]. The production costs of biofuels are, at present, higher than those of fossil substitutes, even using the most advanced technologies. The cost of producing biogas varies greatly depending on the technology used and, above all, on the raw materials used, which are in most cases self-produced. For these reasons, the definition of the cost is problematic and subject to strong variability depending on the specific situation. In the EU, the optimization of the supply chains and the exploitation of new raw materials allowed a reduction in production costs from 2007 to 2010 of up to 30% [11].

Economic, social, and environmental impacts (including greenhouse gases (GHG) emissions and soil, water, and biodiversity impacts) have been evaluated by IEA (2010) [12]. The report indicated, through life cycle assessment (LCA) case studies, that bioethanol production from sugar cane significantly reduces the GHG emissions in comparison with fossil fuels, while the benefits are not clearly demonstrated for other biomass sources. However, clear reductions in GHG emissions were estimated for second-generation bioethanol and biodiesel production from lignocellulose biomass.

2.1. First generation Biofuels

- Biodiesel** consists of a mixture of methyl esters produced by the chemical conversion of animal and/or vegetable oils and fats and is characterized by a high energy density (37 MJ kg⁻¹; [8]). The materials used for the production of biodiesel are oilseed crops, such as sunflower and rapeseed. Other species, such as soybean or palm oil, are of less interest because their seeds have fairly modest oil contents or they pose problems of environmental and socioeconomic sustainability, respectively [11]. The production process includes the extraction of oils from the seeds, refining, and chemical conversion into biodiesel by transesterification reactions [13]. The process can be considered energetically efficient, with an output/input energy ratio between 1.25–3.67 for soybean (depending on the production conditions) and 2.29 for rapeseed oil [9], greater than 0.84 considered for diesel oil. Biodiesel is used in thermal motors for the direct production of electrical and thermal energy. However, the biodiesel production sector faces strong competition from the oil production sectors for human consumption of the same resources. Due to some of its properties (like a higher cetane number than gas), biodiesel performs better than diesel, as it shows a greater readiness to ignite and its higher flash point value, compared to diesel, ensures greater safety in handling [11].
- Bioethanol** is the ethyl alcohol produced by the fermentation of the sugars present in biomass in absence of oxygen and is characterized by a high energy content (27 MJ kg⁻¹) [14]. The raw materials are divided, according to their carbohydrates content, into saccharides (simple sugars), starch, and lignocellulose (cellulose and hemicellulose). Traditionally-used crops are sugar beet in Europe and sugar cane in Brazil as sugar crops [8], and maize as a starch crop [14]. The use of lignocellulosic biomass requires different pre-treatments followed by a hydrolysis (acid or enzymatic) step to obtain the monomeric sugars for microbial fermentation [14]. In the case of bioethanol production from starch or sugar crops (wheat grain or sugar beet), hydrolysis, fermentation, and distillation are the most energy demanding steps (64%–74% of total energy input) and involve the greatest GHG emissions, but the use of straw reduces the GHG emissions as this is a waste by-product of grain production [9]. Therefore, bioethanol production from by-products is a more environmentally friendly procedure than the production from grain. In terms of energy efficiency, the energy ratio ranges between 1.2 (for maize) to 2.78 for sugar beet [9]. But the efficiency depends on the conditions of the industrial process. However, clear advantages in terms of GHG emissions have been revealed by Rowe et al. [9], with values generally lower than 12 g C eq MJ⁻¹, in comparison with the range found for fuels from fossil sources (18–36.4 g C eq MJ⁻¹).

- **Bio-ETBE** (ethyl-tert-butyl-ether) is an organic compound derived from ethyl and isobutyl alcohols that can be used as an anti-detonator to increase the octane level in gasoline [15]. Bio-ETBE is produced from bioethanol and, therefore, shares its raw materials (cereals and sugary raw materials). It is produced through the chemical reaction between isobutanol and bioethanol, with acid catalysis, which takes place on the surface of an ion exchange resin [11].
- **Pure vegetable oils** are obtained by mechanical extraction from oil seeds. Some properties, such as the net calorific value (or lower heating value, LHV), are comparable to those of biodiesel [11].
- **Biogas** is a mixture of the gases carbon dioxide (CO₂) and methane (CH₄), produced as a result of the successive biochemical reactions that take place during the AD process—biomethanation (hydrolysis, acidogenesis, acetogenesis, methanogenesis). The presence of methane in the composition of biogas (50%–75%) [5] has a decisive influence on its energy capacity (average of 23 MJ Nm⁻³). Pure vegetable oils and biogas are mainly used for the production of electricity and thermal energy generation and cogeneration. Their use in the transport sector is currently limited [8].

2.2. Second-Generation Biofuels

Innovative “second-generation” biofuels are obtained from lignocellulosic biomass and represent a promising technological improvement. These biofuels show better characteristics and performance than those of the first generation (Tables 1 and 2) but, at the same time, require more complex and improved technological and processing solutions.

- **Biohydrogen** is obtained from the biomass and/or the biodegradable fraction of organic wastes through two different processes: a thermochemical process, which involves gasification followed by a steam-reforming phase to increase the final hydrogen content; and microbial fermentation of sugars in the dark, under anaerobic conditions. Different microorganisms (*Enterobacter*, *Citrobacter*, *Bacillus*, and *Clostridium*) have been reported to produce hydrogen through dark fermentation [16]. This option is similar to AD but is reformulated to produce hydrogen directly instead of methane. While dark fermentation is a major light-independent process, other biological options for biohydrogen production are light-mediated processes, which include direct or indirect biophotolysis and photofermentation. Biophotolysis involves the light-driven decomposition of water in the presence of micro-algae or cyanobacteria, while in photofermentation, photosynthetic microorganisms convert organic acids, intermediate products of the microbial metabolic pathways, into biohydrogen in the presence of solar radiation [16].
- **Bio-oil** is the liquid product of lignocellulosic biomass pyrolysis, with similar characteristics to petroleum. The pyrolysis process is the initial stage of combustion and gasification processes. Pyrolysis is a thermochemical transformation process at a temperature of about 500 °C, generally carried out in an oxygen-free environment, which yields liquid (bio-oil), solid (biochar), and gas products. Fast pyrolysis is preferred to increase the bio-oil yield, while slow processes are used to obtain biochar [17]. In the fast pyrolysis process, the biomass is rapidly heated to a high temperature in the absence of oxygen, producing about 60%–75% oil products, 15%–25% solid products, and 10%–20% gaseous phase. The characteristics of the fast pyrolysis process are a high rate of heat transfer and heating, a very short residence time of the steam, and rapid cooling of the vapors and aerosol to give a high yield of bio-oil and precision in the control of the reaction temperature. This technology has been widely studied in the last decade because it shows several advantages, like: (i) the production of renewable fuels for boilers, engines, and turbines; (ii) low costs; (iii) low CO₂ production; (iv) the possibility of using second-generation bio-oil and waste materials (forest residues, urban and industrial waste, etc.); (v) ease of storage and transport of liquid fuels; (vi) high energy density compared to combustible gases; (vii) the possibility of separating the minerals, to be recycled as nutrients for the soil; (viii) the possibility of primary separation of sugars and lignin [17]. Bio-oil is one of the highest-quality combustible hydrocarbons, although it is currently burdened by unacceptable energy and economic costs [18,19].

- **Biomethanol** is obtained from lignocellulosic biomass, while traditional methanol is obtained by the catalytic conversion of a fossil fuel (usually natural gas). However, the most widespread process involves the gasification of the biomass and the catalytic conversion (with chromium oxide and zinc oxide) of the CO_2 and H_2 present in the syngas obtained into biomethanol. The reaction for the production of biomethanol generally occurs under conditions of high temperature ($400\text{ }^\circ\text{C}$) and pressure (40–80 atm; [11]). The main problem of biomethanol is linked to the safety of the storage, transport, and handling phases, as it burns without a visible flame and is toxic by inhalation, contact, and ingestion. Moreover, its low volatility (boiling temperature of $78.4\text{ }^\circ\text{C}$, higher than that of petrol, normally around $30\text{--}35\text{ }^\circ\text{C}$) leads to problems and higher costs associated with the distribution network [20].
- **Biodimethyl ether** (bio-DME) is dimethyl ether obtained from biomass. The production process is based on the gasification of lignocellulosic biomass to biomethanol and its subsequent conversion to bio-DME. The bio-DME is gaseous at room temperature and liquid at pressures above 5 bar, or if the temperature is below $-25\text{ }^\circ\text{C}$. In general, it can be used in the liquid state, operating at pressure values in the order of 5–10 bar [11]. DME and BioDME are most commonly used as substitutes for propane in liquid petroleum gas (LPG), especially in Asia, but can also be used as substitutes for diesel fuel in transportation. Besides being able to be produced from a number of renewable and sustainable resources, bio-DME also has the advantage of having a higher cetane number than traditional diesel and, therefore, better combustion quality than diesel fuel during compression ignition. As a result, an engine tailored to work with DME can achieve higher efficiencies, better mileage, and emissions reductions [20].
- **Bio-methyl tert-butyl ether** (bio-MTBE) is produced from biomethanol and has the effect of raising the octane number in gasoline, without reducing its energy density or increasing its volatility. Since isobutene from oil also participates in the synthesis reaction, bio-MTBE is considered a biofuel to the extent that biomethanol is present in its composition (36%). With the gradual elimination of lead, since the mid-1980s it has become one of the most used components for the formulation of gasoline. The lower cost and toxicity of bio-MTBE relative to tetraethyl lead and benzene have increased its use as an anti-knocking agent in all green gasolines. Nowadays, bio-MTBE is used in percentages ranging from 7% to 12% in volume [21].
- **Biobutanol** is a liquid biofuel produced, through the fermentation of sugars by the microorganism *Clostridium acetobutylicum*, from the same raw materials as bioethanol [22]. Biobutanol has some positive characteristics compared to bioethanol: it is less corrosive, its mixture with fossil fuels is more convenient because the mixtures do not undergo phase separation, and the storage and distribution of biobutanol are easier. Although biobutanol has a higher energy density than bioethanol, it has a lower octane number and, therefore, better performance [22].
- **Fischer–Tropsch diesel** (FT-diesel, FT-liquid, or synthetic biofuels) consists of synthetic hydrocarbons or mixtures of synthetic hydrocarbons derived from biomass. The best-known process for the conversion of energy from lignocellulosic biomass into liquid biofuels (biomass to liquid, BTL) is Fischer–Tropsch synthesis, which was used on a large scale in Germany during World War II [8]. The so-called Fischer–Tropsch process consists of the gasification of the lignocellulosic biomass, the purification and conditioning of the synthesis gas produced (a mixture of carbon monoxide (CO) and hydrogen (H_2)), and its subsequent conversion to liquid biofuels (FT-liquids). The liquid products consist of straight-chain hydrocarbons, do not contain sulfur compounds (which are eliminated in the purification process), and can be converted into fuels for automotive use [8]. FT-diesel has a behavior similar to that of fossil fuels, in terms of lower calorific value, density, and viscosity, but also a higher cetane number and lower aromatic content, which results in lower emissions of particulate matter and nitrogen oxides. The two fuels can be mixed in any proportion, without the need to make changes in the engine and the distribution infrastructures [11].

Table 1. Physico-chemical characteristics of first-generation biofuels (adapted from [11] LHV: lower heating value; Bio-ETBE: bioethyl tert-butyl ether.

Characteristics	Biodiesel	Vegetable Oils				Bioethanol	Bio-ETBE
		Sunflower	Rapeseed	Soybean	Palm		
LHV (MJ kg ⁻¹)	37	39.6	37.4	36.8	36.5	27	36
Oxygen content (% weight)	11	10	10.4	10.3	11.5	35	16
Iodine number	108.7	110–143	94–120	117–143	35–61	-	-
Cetane number	56	37	32–37.6	36–39	38–42	27	-
Octane number	-	-	-	-	-	113	110
Flash point (°C)	160	274	246	254	-	13	-
Cloud point (°C)	-2	7.2	-3.9	-3.9	-	-	-
Point of flow (°C)	-9	-15.0	-31.7	-12.2	-	-	-
Viscosity (cSt)	5.1 (20 °C)	37.1 (38 °C)	37 (38 °C)	28.5–32.6 (38 °C)	8.3 (38 °C)	0.5 (20 °C)	-
State	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Appearance	Limpid	Limpid	Limpid	Limpid	Limpid	Limpid	Limpid

Table 2. Physico-chemical characteristics of second-generation biofuels (modified from [11] LHV: lower heating value; Bio-DME: biodimethyl ether; Bio-MTBE: biomethyl tert-butyl ether; FT-Diesel: Fischer–Tropsch diesel.

Characteristics	Biogas	Bio Hydrogen	Syngas			Bio-Oil	Biomethanol	Bio-DME	Bio-MTBE	Biobutanol	FT-Diesel
			Type of Gasifier								
			Air	Oxygen	Vapor						
LHV (MJ kg ⁻¹)	23.3	10.05	4.2	10	12	18.5	19.5	28.3	35	36	42.9
Oxygen (% weight)	traces			-		45	34.7	35	18	22	
Methane (% weight)	65		2–4	4–6	12.4	-	-	-	-	-	-
CO ₂ (% weight)	40		14–17	25–29	17–19	-	-	-	-	-	-
H ₂ S (% weight)	0.1			-		-	-	-	-	-	-
Cetane number	-	-	0.2–1	0.7	2.5	10	5	57	-	17	74
Octane number	-	130		-		-	104.3	-	110	87	
Boiling temperature (°C)		–252		-		-	65	–23	55	118	
Flash point (°C)	-	585		-		-	464	292	-	35	315
State	Gaseous	Gaseous		Gaseous		Liquid	Liquid	Gaseous	Liquid	Liquid	Liquid
Appearance	Gaseous	Gaseous		Gaseous		Limpid	Limpid	Gaseous	Limpid	Limpid	Limpid

3. Processes for Bioenergy Production

The methods of biomass conversion for the production of energy are classified as thermochemical, biological, or physical (Figure 2).

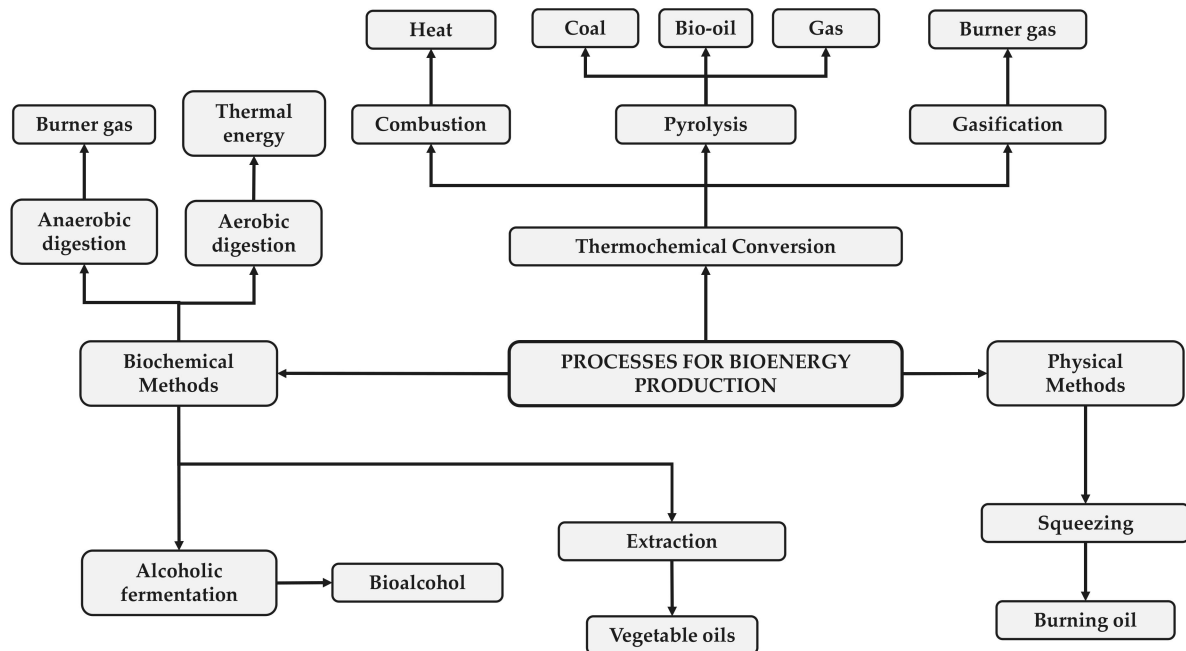


Figure 2. Processes for bioenergy production.

3.1. Methods of Biomass Thermochemical Conversion

Thermochemical biomass conversion involves drying, roasting, pyrolysis, and gasification. If the solid biomass is subjected to a progressive increase in temperature, in the partial or total absence of oxygen, several thermochemical processes take place, which originate other fuels in solid, liquid, or gaseous form [8]. Although these methods have been widely used in recent years, thermochemical conversion can be still considered the basis for the development of the second-generation biofuels.

Combustion is the most conventional process. Efficient combustion requires the reduction of the water content of the biomass, generally achieved by open-air drying. Combustion of wet material is less energy efficient as energy is used for evaporation of the water content [23,24]. For the combustion process to be effective (i.e., compensate the energy used for drying with the improvement in the efficiency of the process), the optimum moisture content of plant biomasses (wood chips, plant residues) has been set to be 10%–15% [25]. Pelletizing (the compression and mechanical pressing process) is an effective method to increase density and reduce moisture. Combustion is, from a thermodynamic point of view, a process of conversion of the chemical energy of the fuel (biomass) into heat. The heat is mostly generated by the oxidation of the carbon, in the presence of sufficient oxygen, to CO₂. The biomasses for the production of energy by combustion are generally wood processing residues, and cogeneration is used to produce heat and electricity [23]. A portion of the heat produced is used to produce steam for power turbines connected to electric generators. The remaining heat can be used by industrial or residential users. The efficiency of these plants is in the order of 20%–25% and, therefore, rather modest. Medium–large cogeneration plants can obtain energy efficiencies close to 25%, with about 10 MW of electric power. To generate these powers, the quantities of biomass to be burned become considerable, and complex and costly systems are needed for the elimination of the toxic substances present in the fumes [23].

According to the temperature reached, the thermochemical processes can be classified as:

- Drying, which occurs at temperatures of up to 150 °C, when water evaporates without substantial chemical modification of the raw material;
- Roasting, which arises between 150 °C and 280 °C, when in addition to water, some organic volatile compounds are released, including acetic acid, methanol, and carbon dioxide. The solid residue darkens, becomes very stable microbiologically, and reaches a high energy density;
- Pyrolysis (carbonization), which takes place when temperatures reach maximum values of 550–600 °C. During this process, the division of the C–C and C–O bonds (decarbonylation and decarboxylation) occurs with the production of gas (mainly carbon monoxide, hydrogen, carbon dioxide, and methane), hydrocarbons (also of high molecular weight, such as tars), phenols, esters, acetic acid, methanol, and water. The resulting solid residue is charcoal (or biochar), while the gas released, if properly cooled, can be divided in two types of product: the non-condensable part and the condensable part, which is liquid at room temperature and is called “pyrolytic juice” or “bio-oil” [8]. Biochar, with a carbon content greater than 95%, has an LHV of approximately 29.3 MJ kg^{−1}; the energetic value of bio-oil can range between 7 and 18 MJ kg^{−1} according to the water content, while the gas is characterized by an LHV of 4.8 MJ Nm^{−3} [11];
- Gasification, which takes place at temperatures between 600 and 1500 °C, with the total gasification of the biomass. Carbonaceous and organic compounds are converted into fuel gas, also known as syngas, a mixture of mainly carbon monoxide and hydrogen. The syngas can be further converted to hydrogen and CO₂. The high temperatures are obtained by burning aliquots of biomass in the reactor. Air or pure oxygen can be used as a gasification agent: in the first case, the gas produced will contain a high concentration of molecular nitrogen (N₂), while in the second case it will have a lower presence of N₂ but a higher LHV (up to 10.5 MJ Nm^{−3}; [11]).

3.2. Biochemical Methods

3.2.1. Alcoholic Fermentation

This process is based on the transformation of carbohydrates into ethanol by microorganisms (*Saccharomyces cerevisiae*). The optimal activity of the yeast occurs at 33–35 °C and pH 3–5. The maximum concentration of bioethanol in the growth medium must not exceed 11% by volume, since higher concentrations can inhibit the activity of the yeast [8]. During continuous fermentation, the concentration of bioethanol is maintained at levels close to the microorganisms’ tolerance values [11].

At the industrial level, fed-batch fermentation and semi-discontinuous fermentation are widely used to fulfill the dual purposes of maintaining the concentration of bioethanol below the threshold for inhibition of yeast and operating under variable volume conditions. In fed-batch fermentation, there is an initial batch phase followed by the fed-batch process once an adequate amount of microbial biomass is reached. This technique is ideal for processes in which either cell growth or product formation is sensitive to the concentration of the limiting substrate [26]. Finally, semi-discontinuous fermentation can be considered as a combination of the fed-batch and continuous processes. In this operation, the feed solution is fed at constant intervals, while the effluent is removed discontinuously. The advantage of this system is that the intermittent feeding of the substrate, which has an inhibitory effect on the production of the catabolites, keeps its concentration low, improving fermentation productivity. Both methods have the advantage that there is no non-productive idle time for cleaning and re-sterilization and not much control is required. However, there is a high risk of contamination and mutation due to the long periods of cultivation and handling, and since larger reactor volumes are required, investment costs are higher [26].

Several studies have focused on enhancing the digestibility of lignocellulosic biomass through physical, chemical, biological, and hybrid pretreatments in the production of liquid fuels (primarily ethanol) via biochemical pathways [27–29].

3.2.2. Transesterification

Transesterification is a chemical reaction in which the main result is the rupture of the triglyceride molecules, i.e., the fatty acids that characterize vegetable oil and are the basis of its high viscosity. The transesterification process takes place using an alcoholic reagent (methanol or ethanol), whose action is reinforced and accelerated by a catalyst (caustic soda). Alcohol, reacting with fatty acids, produces methyl esters (i.e., biodiesel), with a yield of 90% by weight, and glycerol (or glycerin), with a yield of 10% by weight [8,13]. The splitting of triglycerides, components of oils, into methyl esters has the effect of reducing their viscosity to values close to those of diesel fuel and, as a result, simplifies the interventions necessary for the preparation of the motors, especially for automotive applications. Transesterification can be carried out using different operational temperature and pressure conditions, which are selected in terms of the desired production capacities, the quality of the vegetable oils, and the economic investment that is envisaged [11].

3.2.3. Aerobic Digestion

This process involves the degradation of organic substances by microorganisms under aerobic conditions. The bacteria degrade complex organic substances into simple compounds, with the final production of CO_2 , H_2O , and heat, which is produced in proportion to the microbial metabolic activity [30], and can therefore be considered a bioenergy production process.

One example of bioenergy production through aerobic degradation is composting. Composting consists of a spontaneous biological decomposition of solid organic material in a predominantly aerobic environment, during which primarily bacteria, fungi, and other microorganisms transform organic materials into a stable product called compost, useful as a fertilizer or soil amendment [31]. Composting is an exothermic and spontaneous process in which the microbial activity releases energy as heat, increasing the temperature of the material, which can then be recovered for the production of renewable energy as bioenergy [32,33]. Although the ultimate energy available from a composting substrate is the same as that available from the combustion of the substrate, the actual amount of heat produced is determined by factors such as the feedstock energy content, biodegradability, duration of the composting process, and composting conditions [33]. In fact, composting does not lead to biofuel production, but it can be considered a source of renewable thermal energy. The heat produced from composting can be used directly as vapor for greenhouse heating, as hydronic heating through conduction of heat exchanges inside the pile for consumption of hot water, and by a condenser-type heat exchanger [33]. The last option is considered the most efficient for energy recovery. Different heat recoveries have been reported from the composting process: 1.9 MJ kg^{-1} of organic matter from tomato plant residues using a rotary drum bioreactor [34]; 6 MJ kg^{-1} of compost from kitchen and garden waste [35]; $17.7\text{--}32.9 \text{ MJ h}^{-1}$ during the composting of animal manure, animal bedding, and waste feed hay in a commercial-scale system with compost vapor temperatures of $51\text{--}66 \text{ }^\circ\text{C}$ [36].

3.2.4. Anaerobic Digestion

This biochemical conversion process takes place in the absence of oxygen and entails the microbial degradation of complex organic substances (lipids, proteins, carbohydrates) contained in plants and animal by-products, with the production of gas (biogas). The raw biogas is usually constituted mainly of methane (about 50%–75%), CO_2 (25%–50%), H_2O (1%–5%), and other minor volatile components, such as N_2 , H_2S , NH_3 and siloxanes or other organic hydrocarbons [5]. During AD, degradation and stabilization of complex organic matter are performed by microorganisms, leading to the production of an energy-rich biogas that can be used as renewable energy to replace fossil energy sources [37,38].

The digestion of the biomass takes place in four phases (Figure 3): hydrolysis, acidogenesis, acetogenesis, and methanogenesis, each one carried out by specific microorganisms [5]. In the hydrolysis phase, complex organic substrates, such as proteins, fats, and carbohydrates, are degraded by different bacterial groups, with the formation of simple compounds, such as amino acids, fatty

acids, monosaccharides, and alcohols. The acidogenic phase oxidates microbially the hydrolyzed simple organic substrates to low molecular weight intermediate compounds (e.g., lactic, propionic, butyric, formic, and acetic acids, ethanol, and H_2), which are converted into acetate in the subsequent acetogenic phase by acetogenic bacteria. Then, methanogenic archaea are responsible for the final degradation and the formation of CH_4 [37].

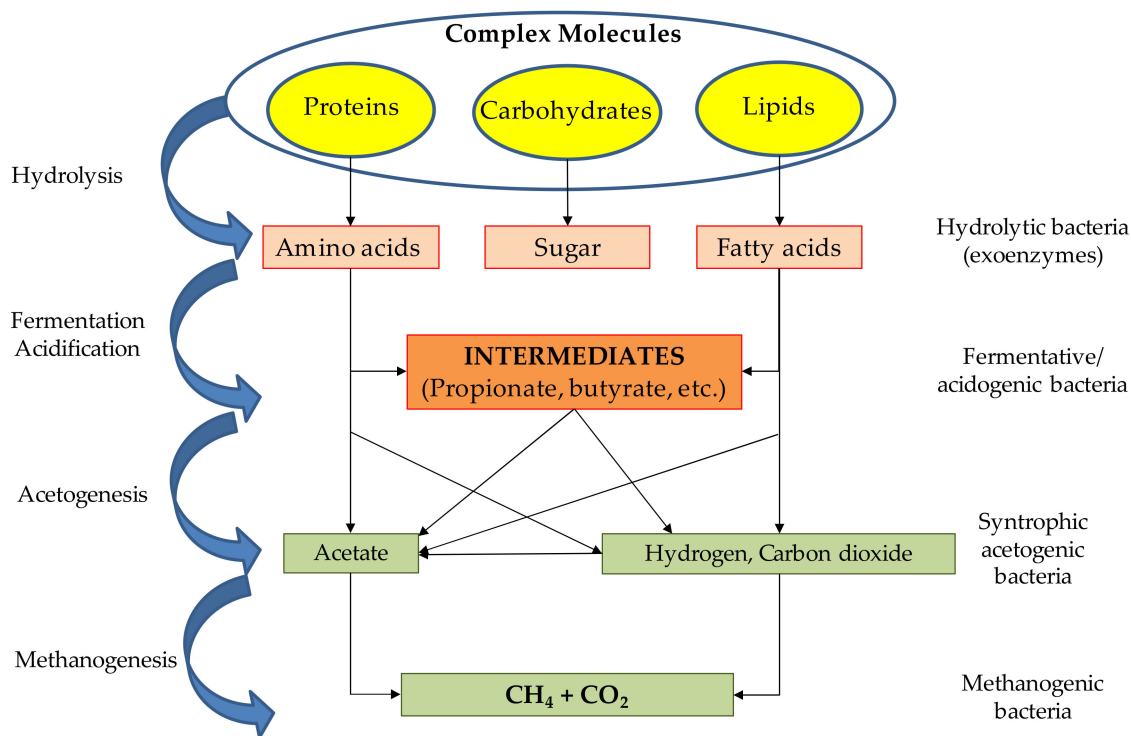


Figure 3. Phases of the anaerobic digestion process [8,11].

Normally, the biogas produced is used in an endothermic engine to produce electricity. The electricity produced can be directly fed into the distribution network and sold at a remunerative price as a renewable energy source. Frequently, the digested material is applied to agricultural soil as a source of nutrients (due to its high concentration of nutrients, mainly N as NH_4^+ that is directly available to plants), partially substituting mineral fertilizers [39]. The most widely used biomass is maize silage (about 10 m^3 of methane can be obtained from 1 t of maize silage; [23]). However, other organic materials are also used frequently as feedstocks for AD, like animal manure, crop residues, sewage sludge, industrial wastewater, food waste, and municipal solid waste [5,29].

The calorific value of the biogas obtained varies according to the methane content. A typical value can be about $23,000\text{ kJ Nm}^{-3}$ [11]. The biogas can be treated, accumulated, and used as fuel for gas boilers or internal combustion engines. However, it can also be purified (i.e., removal of CO_2 , H_2O , H_2S - or S-containing compounds (mercaptans), siloxanes, and other minor components) [5,40] and upgraded to produce biomethane (97% CH_4), with a quality equivalent to natural gas, which can be used as a biofuel for transport and for introduction into the natural gas network. Upgrading the biogas by removing CO_2 and increasing the CH_4 concentration increases the energy content of the biogas, but also the costs of biogas production. Some technologies for biogas upgrading are already available, and others are in the pilot or demonstration plant stage [41]. Four methods are in use for biogas upgrading through CO_2 removal: washing on a temperature or pressure swing, in which a liquid removes CO_2 ; cryogenic, based on cooling and compressing for removing liquid CO_2 ; vacuum pressure swing adsorption (VPSA), in which a packed bed absorbs CO_2 ; selective membranes, which permeate through the CO_2 or methane, depending on the applied membrane [42]. Anaerobic digestion is, therefore, considered a competitive source for the production of renewable energy in

terms of efficiency and cost [5,37]. Considering the energy requirement of the process (input) and the energy produced (output), the output/input ratio reveals a high efficiency for crop residues such as potatoes, fodder beet, and maize (4.6–5.1), with low efficiency for rye and rapeseed oil (1.4 and 2.1, respectively) [5].

More recently, lignocellulosic biomasses, namely agro-residues and energy crops, have been gaining much attention as candidate feedstocks for the generation of bioenergy and biobased products [5,43,44]. Unlike conventional biorenewable feedstocks (i.e., sugar- and starch-rich crops), lignocellulosic biomass does not directly compete with food or feed production [29]. The composition of lignocellulosic biomass, however, consists primarily of cellulose, hemicellulose, and lignin, and the combination of these components creates a highly resistant and recalcitrant biomass structure. Consequently, the hydrolysis of lignocellulose often becomes the rate-limiting step during traditional AD [45]. In any case, lignocellulosic biomass has a great potential to serve as a feedstock for CH₄ production. The complexity of the biomass structure and the lack of appropriate digesters designed for efficient handling of the high-solids biomass are major challenges in the digestion of lignocellulosic biomass. However, harvesting of the biomass at an appropriate stage of maturity and co-digesting it with other feedstocks significantly enhances the CH₄ yield [29].

A common alternative biological pretreatment of feedstocks is treating them with rumen microorganisms (RM), the microflora found in ruminant stomachs, which create an *in situ* cellulolytic ecosystem that has a high potential to degrade the complex carbohydrate structures of lignocellulosic biomass [46]. Anaerobic degradation using RM is a pH-dependent process. The highest efficiency in terms of substrate digestion was found at a pH between 6.8 and 7.3 [47].

To evaluate a specific organic substrate for biogas production through AD, the biochemical methane potential (BMP) test is commonly used [48]. The general principle is the anaerobic incubation of the organic substrate in an inoculum containing a suitable medium (water and minerals) with a variety of anaerobic microorganisms, at neutral pH and with specific temperature conditions (mesophilic or thermophilic). The substrate acts as a source of carbon and energy for the microorganisms. During the incubation, the production and composition of the biogas and the degradation rate of the substrate are evaluated and the conversion rate determined [37]. The determination of the BMP allows the definition of the potential of a material to produce biogas by AD on an industrial scale. However, the efficiency of the industrial process must be proven.

The factors that affect the biodegradability and, therefore, the production of biogas include: the characteristics of the input materials (composition of the organic matter, moisture, total solids and volatile solids contents, biodegradability, and even the crystallinity of the cellulose) and the inoculation and anaerobic conditions [37,43,44,49–51].

In general, AD is classified into three important groups based on the operating total solids (TS) content: liquid (L-AD), with TS < 10%; semi-solid (S-AD), with 10%–20% TS; and solid-state (SS-AD), with TS > 20% [52,53]. However, Brown et al. [54] referred to liquid and solid-state AD with TS content < or > 15%, respectively. SS-AD is ideal for high-solids organic feedstocks, which typically have a TS content between 10% and 50%, like energy crops, food wastes, livestock manure, agro-residues, etc. [49]. In recent years, there has been growing interest in SS-AD with agricultural and forest residues, and also with energy crops. The advantages of SS-AD, in comparison to L-AD, are: lower reactor volumes, higher organic loading rates (OLRs), less water for dilution, a lower mixing requirement, no floating substrates (in the bioreactor), lower costs for managing the digestate, and overall, a lower energy input for operation [52,55]. Typically, due to the higher OLR during SS-AD, the accumulation of volatile fatty acids (VFAs), organic acids, and ammonia leads to an overload of the reactor and the whole system is prone to fail, especially when energy crops are used as a mono-substrate. Thus, the high solids content in SS-AD, which is considered an advantage, can also produce dead zones in the reactor and can lead to reductions in CH₄ production efficiency, as well as causing an overload of the reactor. Therefore, in this regard, further research is needed on reactor configurations to eliminate the build-up of toxic and/or inhibitory compounds in SS-AD systems. The efficiency of SS-AD systems can

be further improved through different reactor operating strategies, adequate OLRs and retention times, maintenance of healthy and well-balanced microbial communities, and subsequent identification and quantification of the efficiency of lignocellulosic-biomass-digesting microbes [29]. A possible future path for SS-ADs could be the two-step co-digestion of energy crops and animal manure. This approach could improve the microbial hydrolysis of substrates, prevent VFA build-up, and provide the necessary nutrients and trace elements. It would also be interesting to study and understand how the maturity and composition of animal feed affect the digestibility of biomass [29].

The AD of N-rich substrates, such as animal manures, is also not recommended as it can result in digester instability caused by ammonia toxicity from the rapid degradation of organic nitrogen such as urea and protein [56]. In co-digestion processes, substrates from different origins (e.g., animal manures, agroindustrial wastes, crop residues, etc.) are mixed to increase their degradability and also to adjust the C/N ratio and, therefore, the efficiency of the process. The C/N ratio of feedstocks is critically important to facilitate the conversion of lignocellulosic biomass to CH₄ [57–59].

Thus, co-digestion of carbohydrate-rich lignocellulosic biomass with nitrogen-rich animal waste has significant implications for the maintenance of an optimal C/N ratio for commercial CH₄ production with renewable feedstocks [5,58]. Several studies to date have demonstrated the successful anaerobic co-digestion of livestock wastes and lignocelluloses. Ye et al. [59] reported the co-digestion of rice straw and swine manure in a series of batch experiments where co-digestion increased the CH₄ yield by an impressive 71% compared to the mono-digestion of rice straw, using a pig manure to rice straw ratio of 2:1 (on a vs. basis). The C/N ratios of the co-substrates (i.e., the mixture of swine manure and rice straw) and mono-substrate (i.e., rice straw) were 21.7 and 47, respectively.

3.3. Physical Methods

Physical conversion is essentially a process of mechanical pressing of crops with high oil content (like sunflower, rapeseed, and soybean). The vegetable oil obtained, which is a mixture of fatty acid esters, can be used directly as fuel for slightly modified diesel engines or can be chemically treated to make it similar to diesel fuel (biodiesel) [23]. The oils are normally extracted from the seeds of plants through cold or hot mechanical extraction methods, similar to those for producing oil for human consumption. They consist of a screening and press or centrifuge system, filtration (with carbon filters, plate filters, or centrifugal filters), and storage in tanks. The operational conditions can be continuous, taking place between the inner walls of a cylindrical chamber with a mechanical element (generally a screw) inside, in rotation on its longitudinal axis, or discontinuous, run with compression cycles [60]. During the extraction, the temperature can increase due to the friction occurring between the seeds and the press, but the temperature can also be controlled by a thermoregulation system. Average oil yields are 30%–33% by weight, but by optimizing the parameters that regulate the process, yields can reach 36% by weight. In fact, both the pressure and the temperature of the extraction significantly affect the yield; the influence of the pressure seems to be, however, more important than that of the temperature [60].

4. Characteristics of the Source Materials for Bioenergy Production

Among the different renewable energy sources, plant biomass is the most versatile from which to obtain solid, liquid, or gaseous fuels, and, in some cases, it can be directly used as a fuel [61]. It constitutes, therefore, a renewable and inexhaustible resource—if properly used—for the production of (bio)energy.

Conventionally, biomass can be classified into three sectors:

- Lignocellulosic materials, which include biomass crops and crop residues;
- Biofuel crops, which are subdivided into oilseed crops, such as rapeseed and sunflower, and sugary crops, such as sugar cane; and
- Organic materials, from which biogas can be obtained through fermentation or degradation [61].

The biomasses suitable for energy transformation, whether it takes place directly using the biomass or after its transformation into a solid, liquid, or gaseous fuel, can also be subdivided by category of origin into the following types:

- Forestry and agroforestry: residues from silvicultural or agroforestry activities, use of coppice woods, etc.;
- Agriculture: crop residues deriving from agricultural activity and dedicated crops of lignocellulosic species, oleaginous plants (for the extraction of oils and their transformation into biodiesel), and alcohol plants (for the production of bioethanol);
- Livestock waste: for the production of biogas;
- Industrial: waste from wood or wood products and the paper industry, as well as residues from the agri-food industry;
- Urban waste: residues from public gardens, maintenance operations, and the wet fraction of municipal solid waste.

Depending on the type of biomass used and the type of processing used, it is possible to classify biomass in two groups: that produced specifically for energy purposes (dedicated crops) and that recovered from the agricultural, forestry, and agroindustrial sectors (recovery biomass).

The dedicated crops can be classified in terms of the specialization of production or of the physico-chemical characteristics of the cultivated species to which the transformation process is inevitably linked (Table 3).

Table 3. Chemical composition of energy crops.

Crop	Carbohydrate (% d.m.)	Fat (% d.m.)	Protein (% d.m.)	Ash (% d.m.)	Dry Matter (t ha ⁻¹)	Moisture (%)
Oilseed crops						
Rapeseed	17.0 ^a	41–50 ^b	24.7 ^a	4.3 ^a	7.5 ^a	9–12 ^c
Sunflower	15.9 ^a	48–55 ^b	25.2 ^a	4.2 ^a	4.0 ^a	9 ^c
Soy	31.8 ^a	18–21 ^b	37.9 ^a	5.2 ^a	5.4 ^a	
Abyssinian mustard	30–38 ^q	30–39 ^b	38.9 ^q	5.2 ^q	-	8.9
Alcohol crops						
<i>Sugary</i>						
Sugar beet	Roots 18 ^b (sucrose, glucose, fructose)	Leaves 2.7 ^e Pulp 0.2 ^e	Leaves 16 ^e Pulp 1.00 ^e	Leaves 32 ^e Pulp 0.50 ^e	30–40 ^d	-
Sugar sorghum	Stems 15 ^b (sucrose, glucose, fructose)	2.0–2.4 ^f	8.6–9.4 ^f	Panicle 7.85 ^g Leaf 9.44 ^g Stalk 4.38 ^g Bagasse 3.41 ^g	25.29 ^g	Panicle 36.43 ^g Leaf 60.58 ^g Stalk 66.40 ^g Bagasse 47–56.62 ^g
<i>Starchy</i>						
Triticale	13 (Starch) ^e	3.23 ^e	8.6 ^e	6.01 ^e	16.5 ^d	50 ^c
Forage sorghum Grains	11 ^b (cellulose) 18 ^b (hemicellulose) 30 ^b (starch)	1.7–2.3 ^f	8.2–9.9 ^f	Panicle 4.19 ^g Leaf 9.22 ^g Stalk 7.19 ^g	21.37 ^g	Panicle 49.80 ^g Leaf 60.45 ^g Stalk 71.26 ^g Bagasse 46.50 ^g
Maize	Grains 70 ^b (starch)	1.9–2.6 ^f	6.6–8.6 ^f	Bagasse 1.1 ^r	21.5 ^d	27.7–33.9 ^f

Table 3. Cont.

Crop	Carbohydrate (% d.m.)	Fat (% d.m.)	Protein (% d.m.)	Ash (% d.m.)	Dry Matter (t ha ⁻¹)	Moisture (%)
<i>Lignocellulosic</i>						
Biomass sorghum	—	1.6–3.3 ^f	7.8–10.2 ^f	Panicle 4.34 ^g Leaf 6.30 ^g Stalk 4.77 ^g	42.33 ^g	Panicle 52.79 ^g Leaf 47.90 ^g Stalk 66.22 ^g
Common cane	31 ^b cellulose 22 hemicellulose	0.8–1	1.3–3.7 ^h	Leaves 11.3 ^d Stems 3.2 ^d	37.7 ^d	
Miscanthus	41 ^l cellulose 24 ^l hemicellulose	—	1.0–2.2 ^h	Leaves 6.2 ^d Stems 2.9 ^d	15–30 ^d	31 ⁱ average of two years
Cardoon	41 ^m cellulose 23.6 ^m hemicellulose	0.1	2.9–3.7 ^h	6.8–8.2 ^h	0.4–24.8 ^h	19.1–55.5 ^h
Switchgrass	63.2 ⁿ	4.0 ⁿ	12.8 ^p	Leaves 7–7.6 ^d Stems 2.3–2.6 ^d	10–25 ^o	35–45 ^o

^a [62]; ^b [11]; ^c [63]; ^d [64]; ^e [65]; ^f [66]; ^g (average of 2 sorghum cultivars, modified from [65]); ^h ([67]; ⁱ [68]; ^l [69]; ^m [70]; ⁿ [71]; ^o [72]; ^p [73]; ^q (average of 4 *Brassica carinata* cultivars from [74]); ^r [75].

In fact, dedicated crops can be divided into three main categories: lignocellulosic biomass crops, oil crops, and alcohol crops [76].

Studies carried out to date have shown that the efficacy of the different processes of energetic transformation, such as direct combustion, conversion into bioethanol, and the gasification of lignocellulosic crops, depends not only on the physico-chemical properties of the different plant species but also on the different parts of the plant (stems, leaves) used. For example, for direct combustion the biomass at harvest must have low water and ash content and a high amount of raw lignin; whereas, in the production of ethanol or in gasification systems, the lignocellulose components (such as cellulose and hemicellulose) are important [69]. In AD, if traditionally the materials used were mainly animal manure or slurry, today co-digestion processes are favored [56–59]. Co-digestion can achieve a significant enhancement of the biogas yields and, therefore, of the energy produced, as well as greater stability of the digestion process [11,77]. Silage maize is the most widely used material, both for its high energy and crop yield (at least in particularly suitable areas) and for its low market value. Currently, great interest has also been aroused by some crops, such as sugary sorghum and triticale, also with a view to crop rotation, which allows greater management flexibility and enhances the availability of substrates throughout the year [11].

Sorghum is a promising alternative in the bioenergy sector, thanks to its agronomic characteristics and adaptability to limiting soil and climatic conditions. Compared to eucalyptus, for example, the production of sorghum dry matter is 40 t ha⁻¹ in five months against the 20 t ha⁻¹ in about seven years of the former [78]. There are three agronomic types of sorghum: (i) biomass sorghum, whose crops have a high yield (about 30 t ha⁻¹ of dry stem) and for this reason are more suitable for the generation of solid biofuels (i.e., direct combustion); (ii) forage sorghum, whose biomass has a lower lignin content in the stems than other crops and, therefore, is more suitable for the generation of liquid biofuels; and (iii) sugar sorghum, from which second-generation bioethanol is produced in yields similar to those of other biomass crops like sugar beet, maize, or sugar cane (Table 4). Therefore, sorghum has several potential uses that can be exploited by the bioenergy sector, according to the agronomic group and the part of the plant used [78].

Table 4. Average yields of biodiesel, pure vegetable oil, bioethanol, and bio-ETBE, and the lower anaerobic biogasification potential (ABP), biomethane production (BMP), and higher heating value (HHV) of the principal energy crops.

Crops	Biodiesel (t ha ⁻¹)	Pure Vegetable Oil (t ha ⁻¹)	Bio-Ethanol (L ha ⁻¹)	Bio-ETBE (t ha ⁻¹)	ABP (Nm ³ t ⁻¹ DM)	BMP (Nm ³ CH ₄ ha ⁻¹)	HHV (MJ kg ⁻¹)
Rapeseed	0.9 ^a	0.8 ^a	-	-	-	-	-
Sunflower	1.1 ^a	1.0 ^a	-	-	-	832–4695 ^{b,c}	-
Soy	0.6 ^a	0.5 ^a	-	-	-	-	-
Abyssinian mustard	1.0 ^a	0.9 ^a	-	-	-	-	-
Sugar beet roots	-	-	5000–6000 ^{d,e,f}	9.6 ^a	-	1954–6309 ^c	-
Sugar sorghum stems	-	-	2800–6000 ^{h,m,n,f}	8.3 ^a	423 ^g	2124–8370 ^{c,i,l}	-
Maize	-	-	grains starch stover	700–3232 ^{h,m,n,q} 2010–4000 ^{d,r} 700–2000 ^{q,r}	7.2 ^a	5453–7768 ^{o,p} 5300–9000 ^b 5862–12,150 ^{b,c,i}	stover 18.4 ^g
Common cane	-	-	11,000 ^s		524 ^g	9580– 19,440 ^{t,u}	18.7 ^g
Triticale	-	-	2843 ^v		677 ^g	1000–5944 ^{c,i,z}	-
Miscanthus	-	-	8812 ^q		-	-	18.7 ^g
Sugar cane	-	-	3000–8000 ^{e,f,h,n,m}		-	-	16.8 ^g

^a [11]; ^b [43]; ^c [79]; ^d [80]; ^e [81]; ^f [82]; ^g [64]; ^h [83]; ⁱ [84]; ^l [85]; ^m [86]; ⁿ [87]; ^o [88]; ^p [44]; ^q [89]; ^r [90]; ^s [91]; ^t [92]; ^u [64]; ^v [93]; ^z [94].

For ethanol (first and second generation) and bioelectricity production, as well as direct combustion, only the stalk is used. The other parts (panicle and leaves) are used as agroindustrial waste, for animal feed production, or for production of energy through pyrolysis. By comparison, the production of cellulose from eucalyptus has high costs because of its high lignin content and because the forest cycle is about seven years. The use of sorghum is therefore competitive since the bagasse of sugar sorghum contains, on average, 30% cellulose, against 34% for wheat straw, 40% for sugar cane bagasse, 32% for maize cob, and 46% for *Eucalyptus globulus* wood [95]. The amount of lignin, which has a more complex structure compared to cellulose and hemicellulose, can positively influence the thermal degradation of biomass. The component that has the highest percentage of lignin is the stalk of biomass sorghum (18.7%).

Forage sorghum cultivars have a low concentration of lignin in the stalk (5.75%; Table 3). This makes them good candidates for hydrolysis, which yields sugars for the production of second-generation ethanol and, consequently, for the production of liquid biofuels. The ash content ranges from 3.41% to 9.44% (Table 3), values close to those of the maize cob (1.1% DW) and sugar cane bagasse (11.3% FW; [75]). Plant ashes contain reasonable quantities of micro- and macro-nutrients and are effective for reducing soil acidity, increasing the pH of the soil and its soluble concentrations of Mg, P, and K, and, therefore, can be used as fertilizers. However, in the bioenergy industries that use pyrolysis, the production of a great amount of ashes represents a disadvantage due to the need for their continuous removal from the furnace.

Arundo donax, or common cane, is an herbaceous perennial plant with a long, hollow, and robust stem that grows even in relatively poor soils. From its area of origin in the Mediterranean Basin and the Middle East, its distribution has expanded to temperate and subtropical regions of both hemispheres. It is a hydrophytic plant capable of growing in soils rich in water. Studies have shown that hereditary phenotypic differences exist among the clones of *A. donax* as regards, for example, the number, diameter, and height of the culms [96,97]. Therefore, the genetic improvement of the species could lead to an improvement in the production of biomass. The use of *A. donax* for the production of bioenergy is justified not only by its high biomass yields (37.7 t ha⁻¹; Table 3) but also because it has proven application in the production of bioenergy/biofuels, both through AD for the production of biogas and through direct combustion of its biomass (Table 4). Its anaerobic biogasification potential (ABP; 524 Nm³ t⁻¹ DM) is about 75%, 77%, and 124% of those of maize (694 Nm³ t⁻¹ DM), triticale (677 Nm³ t⁻¹ DM), and sorghum (423 Nm³ t⁻¹ DM), respectively, in terms of productivity per unit area (40 t ha⁻¹). The average production of biomethane from these plants (12,618 ± 3588 Nm³ t⁻¹ DM) varies according to the agronomic environment but is still higher than that of traditional energy crops (Table 4). With regard to the production of bioethanol, *A. donax* produces about 10,000 L ha⁻¹, at least 50% more than sugar cane (3000–6756 L ha⁻¹) and sugar beet (5000–6000 L ha⁻¹), and about 20% more than Miscanthus (8812 L ha⁻¹). The use of *A. donax* for direct combustion is promising as its higher heating value (HHV, 18.7 MJ kg⁻¹) is higher than or not significantly different from those of other crops such as sugar cane (16.8 MJ kg⁻¹), maize (18.4 MJ kg⁻¹), Miscanthus (18.7 MJ kg⁻¹), switchgrass (19.1 MJ kg⁻¹), and poplar (19.5 MJ kg⁻¹; [64]). However, the high ash production (11.3 t ha⁻¹) can be a problem for combustion in comparison to other crops (Table 3). Monti et al. [98] highlighted that the part of the plant that produces more ash is the leaves and, therefore, with proper agronomic management, this problem could be overcome. The synthesis of both biomethane and bioethanol yields reusable secondary products for the production of more bioenergy and/or bioproducts. For example, AD yields, as a secondary product, a digestate, usable as organic fertilizer [99]. In this way, the sustainability of the total energy production process is improved. Studies carried out by Corno et al. [100] on AD showed that *A. donax* was able to effectively replace maize by reducing the production costs of both biomass and electricity.

5. Cultivation Techniques

Biomass sorghum (*Sorghum bicolor* L.) has recently become a crop of extreme interest for bioenergy production because of the high yields that it can reach and the relatively simple cultivation technique that it requires. This species belongs to the family Poaceae, like grain crops and sugar cane, and is suitable for cultivation in temperate zones, with a spring–summer cycle. From the morphological point of view, between biomass and sugar sorghum there are no substantial differences. However, in terms of composition, the two varieties are quite different, and this justifies their different uses [101]. In the fiber type, the production of structural carbohydrates, and in particular cellulose, prevails; whereas in the sugar type, at least 30% of all the accumulated dry matter consists of simple sugars (sucrose, glucose, and fructose). Sorghum is native to central–eastern Africa (Sudan, Ethiopia), but it is currently widespread in Africa and the USA, although still little diffused in Europe. It has a minimum temperature for germination of 13 °C and an optimal growth temperature range of 24–25 °C. It prefers medium-textured soils and is moderately tolerant of salinity. Fiber (biomass) sorghum is a variety characterized by high efficiency in the use of water and can be grown in semi-arid and Mediterranean environments in conditions of limited water supply. Experimental tests have shown some variability in biomass yield, from 15 to over 40 t ha^{−1} of dry matter [102]. In the Mediterranean area, medium–late-cycle hybrids (emergence–flowering period of more than 90 days) are preferred as they provide maximum yield with a smaller amount of grain at the time of collection. The harvest can be carried out 10–20 days before the flowering phase—when the accumulation of dry matter and cellulose in the culm is highest [101].

Sugar sorghum (*Sorghum bicolor* L. var. *saccharatum*) belongs to the Poaceae family. The composition of the plant diverges considerably, as mentioned above, from the fiber types. The marrow in sugar types is rich in sucrose (15%–20%), but the presence of free glucose and fructose hinders the crystallization of sucrose, making it technically impossible to use sugar sorghum for the production of crystallized sugar. Sugar sorghum is usually used as fodder or for the production of molasses [101]. The pedoclimatic requirements and the main cultivation techniques are very similar to those of fiber sorghum. The high content of sugars and the high water content of the plant stems cause major problems for the storage of the collected biomass (e.g., fermentation). The fresh matter yield is around 80 t ha^{−1} [101]. Bio-ethanol, bio-ETBE, biogas, and biomethane can be obtained from this plant in yields similar to those of other common energy crops (Table 4).

Common cane (*Arundo donax* L.), also known as common reed, is a perennial species of the Poaceae and is typical of the Mediterranean regions. It can grow spontaneously and is cultivated in small areas, mainly for the production of supports for vines or vegetable crops [64]. It grows evergreen in different environments, but it is sensitive to low temperatures, which can also compromise the vitality of the rhizomes when they grow near the surface [101]. This species is not an aquatic plant and does not particularly like stagnant water. Regarding soil, it is widely adaptable, although it prefers deep, sandy soils that are rich in organic matter, alkaline, and rich in calcium. Clay, shallow, and impermeable soils are not appropriate for this species. Yields exceeding 40 t ha^{−1} of dry matter can be obtained from the second cropping year [101]. Propagation and implantation represent two aspects of the agronomic techniques that have not yet been optimized and which greatly influence the economics of the crop. Some studies are in progress to identify suitable solutions for the collection of rhizomes [64]. Lately, techniques that use plants obtained through in vitro micro-propagation have been increasingly gaining ground as they ensure uniformity of growth, high production standards, the possibility of mechanizing operations, and practically 100% rooting. Since domestic cane is a plant with a high photosynthetic capacity and is able to make the best use of soil fertility, soil nutrition can be easily managed—for example, using sewage sludge and/or the digestate that is normally available from the biogas producers [101]. Bio-ethanol and BMP yields are particularly high for this species when compared to other energy crops (Table 4), which consequently shows high energy yields and CO₂-saving potential (Table 5).

Table 5. Lower heating value (LHV), energy yield (difference between the energy content of the biomass produced and the auxiliary energy fed into the cropping system), yield (ratio of output and energy inputs), and CO₂ saving of principal energy crops.

Crops	LHV (MJ kg ⁻¹)	Energy Yield (GJ ha ⁻¹)	Yield	CO ₂ Saving (t CO ₂ eq. ha ⁻¹ year ⁻¹)	References
Common cane	16.7–18.3	280 first year 592 from the second year	7.4 first year 77 from the second year	37.7	[103]
Cardoon	14–17	133–344	7–31	19	[103]
Abyssinian mustard	13 straw 20 panicle	4–44	1.7–13.4	0.2–2.4	[103]
Sorghum	17.99	762 ^a	-	-	[104]
Maize	16.7	359 ^a	-	-	[104]
Miscanthus	11.92	179–378 ^a	-	-	[104]
Switchgrass	18.2	182–455 ^a	-	-	[104]

^a Estimated using dry matter (Table 3) and LHV.

Miscanthus refers to the species *Miscanthus sinensis* Anderss, one of 14–20 species within the genus *Miscanthus* (part of the Poaceae family). These plants are native to Southeast Asia and were initially introduced into Europe in the 20th century as ornamental plants. *Miscanthus* has adapted well to temperate climates and is resistant to low temperatures. Although the shoots and leaves can be damaged at temperatures close to 0 °C, the rhizomes, if well developed, can remain viable at temperatures below 0 °C for a long time [101]. Regarding soil preferences, although widely adaptable, *Miscanthus* plants prefer deep, sandy soils rich in organic matter. The biomass of *Miscanthus* benefits greatly from a supply of water and, therefore, fully develops its production potential in well-irrigated areas [101]. The interest in this species is relatively recent and, consequently, there is only a limited number of studies on the genetic variability, for both morphological and productive characters. Currently, the most used genotype in experimental sites is *Miscanthus x giganteus*, a sterile *Miscanthus* hybrid of *M. sinensis* and *M. sacchariflorus*. The different multi-year trials carried out with this genotype indicate that the average yields in the period of maximum accumulation of dry matter are equal to about 30 t ha⁻¹ year⁻¹ from the year subsequent to that of establishment. The “giganteus” variety can only be propagated by vegetative means, using rhizomes or micro-propagated seedlings. Multiplication by rhizomes can be achieved through mechanical extirpation from one-year-old plants: the stumps can be fragmented into rhizomes of acceptable size by a rotary tiller, while commercially available machines, suitably modified, can be used for the collection of rhizomes from the soil [105]. This species has an elevated bio-ethanol and bio-ETBE yield (Table 4) and a relatively low LHV (Table 5).

Switchgrass (*Panicum virgatum* L.) belongs to the family Poaceae. It is an herbaceous plant, C4, rhizomatous, perennial, and native to North America, where it has spread from the 55° N latitude down to Mexico as an important species in the prairies and pastures. It is used for many different purposes, including the production of energy [71]. Varieties from America can adapt to the climatic conditions of the Mediterranean area. Switchgrass is an undemanding crop, adapted to resist water stress and long periods of intense cold. Regarding the characteristics of the soil, its growth is generally favored in moist and loamy soils. The main processing of the soil and subsequent preparatory work do not differ from those normally applied for other renewal crops sown in late spring, such as maize and sorghum [101]. Switchgrass requires an optimal seedbed preparation in order to achieve good seedling emergence. In the first year of cultivation, dry matter production levels of 6 to 12 t ha⁻¹ are expected, while in the following years, from 14 to 24 t ha⁻¹ of dry matter can be obtained [101]. A relatively high LHV has been reported for this species (Table 5).

Sunflower (*Helianthus annuus* L.) belongs to the family Asteraceae (Compositae) and is the most important among the 100 species of the genus *Helianthus*. Sunflower is a crop with a spring–summer cycle that shows good adaptability and does not have an excessive demand for soil macronutrients. Being originally from environments with a temperate climate, it prefers relatively high temperatures [101]. Sunflower plants do not grow well in loose substrates, as they tend to be sterile and unable to retain water, and prefer medium-textured, deep, or organic soils. This species is moderately tolerant of salinity. Although its root system has a tapering structure, sunflower does not possess a strong penetrative capacity in the soil and, therefore, it needs adequate preparatory interventions, especially in the most challenging soils. Sunflower, due to the rapidity of its development, normally has a suffocating effect on weeds. It must, however, be protected in the initial phases of the growing cycle [106]. Biodiesel, pure vegetable oil and biogas/biomethane can be obtained from this species (Table 4).

Rapeseed (*Brassica napus* L.) belongs to the group of oleaginous plants, and in particular, to the family Brassicaceae (Cruciferae) and the genus *Brassica*. Spontaneous in Europe and in the Northwest of Africa, it is believed to have been domesticated after the nutritional value of the seeds of this weed, often infesting fields of cereals, was discovered. In the Mediterranean climate, the biological cycle of rapeseed is autumn–spring [106]. Rapeseed is a microthermic plant and, therefore, does not need high temperatures to develop. This crop does not resist drought periods well, especially during the stages of rising and flowering. Rapeseed prefers temperate climates, humid and not too sunny. The crop is not particularly demanding: it prefers deep, fresh, fertile, and light soils, but it adapts to clay, calcareous, and peat ones, provided they are well drained. It shows moderate tolerance of salinity and low soil pH. For instance, in the dry regions of central and northern Italy, rapeseed can alternate with wheat. Particular attention must be paid to the preparation of the seedbed as the seeds are small. At the end of the growing cycle, the crop helps to enrich the soil with organic matter and nutritive elements derived from the abundant mass of its residues. As this species performs a good part of its cycle in cold and rainy months, it actively explores the soil, intercepting and taking up nitrate, thus helping to limit the risk of leaching [101]. The average yields in central Europe (France–Germany) vary from 3 to 4 t ha^{−1} [106]. The energy yield depends very much on the cultivation techniques and conditions and can vary between 4 and 44 GJ ha^{−1} (Table 5). In terms of CO₂ emissions, the savings are much lower for liquid biofuels than for solid ones; for rapeseed, they are estimated to be 0.2–2.4 t ha^{−1} year^{−1} in CO₂ equivalents [107].

Sugar beet (*Beta vulgaris* L.) is cultivated for the production of sugar. It has been exploited with this aim since 1700, allowing sugar, once produced only from sugar cane, to become a product for general use. The sugar produced is sucrose, a disaccharide composed of glucose and fructose. The cultivation of sugar beet particularly benefits from deep and permeable soils that are well drained. The plant has good tolerance of saline soils. The preparation of the soil for sugar beet cultivation is done following normal agricultural practices, according to the type of soil: the tap-root must be able to penetrate deep in the soil and find no (hard) layers that limit its development, while waterlogging should be avoided [108]. The yield of tap-roots varies between 45 and 50 t ha^{−1} [101]. Bio-ethanol, bio-ETBE and biogas can be obtained from this species in elevated yields (Table 4).

Maize (*Zea mays* L.) is a species native to the tropical and subtropical climate zones of the American continent. Introduced into Spain in 1493, maize spread quickly in other European countries, first for ornamental purposes, and a century later as a food resource. From Europe, mainly by the Portuguese, maize was spread in Africa and Asia, while it was taken to North America by the British. Maize is a plant with a summer cycle and is sown in spring; it is sensitive to cold, especially during the early stages of development [101]. Regarding soil requirements, deep soils with pH between 6 and 6.5 are excellent for maize cultivation, which has high water requirements. Maize plants are large and have a root system that reaches to a depth of 1.5–2 m. Traditional soil preparation is based on plowing to 25 cm for loose soils and to 30–35 cm in heavy soils. Water availability is often one of the limiting factors, and about 300–400 m³ ha^{−1} of water has to be supplied for irrigation. The dry matter yield varies from

22 to 26 t ha⁻¹. The grain is harvested with a moisture content of 21%–28%, usually 10–15 days after maturation [108]. Different bio-ethanol and biogas yields can be obtained when different parts of the plants are used for biofuel production (Table 4).

Cardoon (*Cynara cardunculus* L.), also known as the artichoke thistle, is a traditional horticultural multi-year crop characterized by high rusticity, being widespread throughout southern Europe. The cultivation is simple, as the cardoon can be propagated by seeds and normally does not need irrigation. In terms of productivity, the results obtained from experiments demonstrate that for low-input cultivation regimes, the biomass yields vary between 14 and 20 t ha⁻¹ of dry matter [109]. With regard to oil production, taking into account the average results obtained from various studies carried out in Sicily and in Spain, a seed yield ranging from 0.4 to 2.8 t ha⁻¹ is expected, with an oleic content that varies between 18% and 27%. The achenes (the achene represents the typical fruit of the Asteraceae, the botanical family to which the genus *Cynara* belongs), where the seeds are contained, represent, in total, 30% of the dry matter of the flower heads and about 8%–10% of the total biomass [110–113]. It should be noted that in the cultivation of cardoon, both for biomass and for seed, yields decrease with time and tend to decrease more or less significantly from the third year onwards [107]. From an energetic point of view, the biomass of the cardoon has an LHV equal to 14–17 MJ kg⁻¹ (Table 5), with a considerable ash content (10%–16%) that increases the risk of slagging and fouling, even if the overall silica content is less of a problem and the melting temperature exceeds 1200 °C [114]. The average energy yield fluctuates around 133–344 GJ ha⁻¹, influenced by different crop factors. As far as carbon emissions are concerned (Table 5), cardoon can save about 19 t ha⁻¹ per year of CO₂ eq [107].

Abyssinian mustard (*Brassica carinata* A. Braun) has an annual crop cycle and is mainly destined to the production of oil for biodiesel as it is not intended to be used as a food or fodder crop. It has been studied since the 1990s, together with other species of the Brassicaceae, for its content of seed oil rich in long-chain fatty acids, which is of interest to the lipochemical industry. These studies have shown the excellent adaptability of this crop to southern European environments, in relation to the early flowering, the non-dehiscence of the siliqua (the typical fruit of the botanical Brassicaceae family), the resistance to lodging and the main biotic adversities, and the adaptability to the typical rainfed agriculture conditions [103]. In rotations, *B. carinata* can follow both cereals and legumes, while the cultivation of successive crops of *B. carinata* is not recommended due to the possible establishment of plant pathogens. In relation to yields, the available data show an average production of about 1.4 t ha⁻¹, with minimum and maximum values of 0.5 and 3.5 t ha⁻¹, respectively [103,115,116]. The average seed moisture content at harvest is 5%, with an oil content of 43% and a total yield of about 1.44 t ha⁻¹. From an energetic point of view, this species has an HHV of about 40 MJ kg⁻¹, with low viscosity values, which makes it particularly suitable for the needs of the main engine manufacturers and better in comparison to the most common raw vegetable oils [117]. However, this species shows moderate energy yield and CO₂ saving values (Table 5).

It can be therefore summarized that biomass sorghum has characteristics that allow its use in direct combustion and in energy cogeneration. The different parts of the plant can be used differently depending on their chemical composition and their percentage presence in the total biomass. Common cane, despite the variability in biomass production, produces much more biomass than other energy crops, leading to a much higher fuel/energy production per unit area (592 GJ ha⁻¹ from the second year; Table 5). The data collected here suggest the use of this crop as a substitute for traditional energy crops, which would also reduce the costs of biomass production. Indeed, large-scale approaches confirm previous findings that the use of common cane was able to reduce both the costs of producing biogas and the total area needed to produce the energy crop, thus making biogas production more sustainable. This plant species can produce about 160 m³ of biogas per tonne, but considering the high biomass production, one hectare of common cane produces a similar amount of biogas to 1.5 hectares of maize, but with a lower use of resources. The calorific value is comparable to that of other crops used for this purpose, but also in this case, the high productivity per hectare makes it very competitive, allowing

energy performances above 200,000 kWh ha⁻¹ (twice as much as other herbaceous crops and trees). This plant species could replace maize as a bioenergy crop, reducing the production costs of both biomass and electricity, due to either the higher biomass productivity or the reduction in the cost of the biomass. However, the colonizing capacity of common cane, due to its subterranean organs, could compromise the conditions of habitability of the soil (for the subsequent crop) at the end of the cropping cycle, which is why many agricultural producers are reluctant to cultivate it. For this reason, at the end of the cycle, it is necessary to implement a reclamation program consisting of a series of alternating cultivation operations, involving deep processes and chemical weeding before soil preparation for the next crop [103]. Cardoon, like common cane, is an endemic multi-year herbaceous species characterized by high productivity, and it is particularly adaptable to Mediterranean environments. Moreover, due to its low water and nutritional requirements, it is possible to hypothesize its cultivation in low energy-input systems. In fact, apart from the operations of planting, the interventions in the cultivation cycle are limited to the fertilization and collection of biomass. The use of cardoon as a bioenergy crop allows for more scenarios consisting of the exclusive production of biomass or the double production of biomass together with seeds for oil extraction [110,111,118]. The low quantity of moisture present in the harvested biomass enhances its commercial quality for combustion. Despite the higher oil content of rapeseed (*B. napus*) [115], the cultivation characteristics of *B. carinata* give it greater production stability compared to rapeseed. Moreover, in the case of *B. carinata*, an advanced phase of experimentation is underway to confirm its adaptability to the hot, arid environment of Mediterranean arable land and to cultivation regimes with reduced use of technical means, as well as its suitability for inclusion in rotation programs with other food and fodder plants.

6. Conclusions and Perspectives

In order to address the increasing demand for energy production and at the same time deal with environmental protection issues, the European Union has set the goal of increasing the share of renewable energy to 20%, among other objectives of the “Europe 2020 Strategy”. The studies carried out to date show that some plant species have particular physical and chemical characteristics for their use as biomass crops for bioenergy production, with clear advantages both in terms of energy production and at the economic level. Moreover, it is clear that the different techniques used to obtain bioenergy require different characteristics in plant biomass. For example, in direct combustion, the biomass at harvest should have low water (<10%–12%) and ash content and a high amount of lignin. In the production of ethanol or in gasification systems, the lignocellulosic components (such as cellulose and hemicellulose) are important. The most suitable materials for the production of biogas through the process of AD are those with a high content of organic matter; for example, the biomasses obtained from energy crops such as maize.

The use of plant biomass for the production of (bio)energy can therefore be considered a suitable and environmentally friendly option to achieve the desired renewable energy share. The appearance of new and alternative plant species, like the ones described in this review, may help to pave the way to the implementation of the different energy production alternatives that are currently being established and/or developed, particularly in southern European countries. The lower fertilization needs and higher adaptability to different soil types, including degraded and contaminated ones, of some of these species compared to conventional crops used for bioenergy production, together with their elevated energy yield potential, make the cultivation of these plants both economically and environmentally profitable. In addition, the competition for land use and agricultural resources with food crops would be significantly diminished, a relevant step towards the necessary sustainability of agroecosystems in southern Europe.

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