Review

Waste-Based Intermediate Bioenergy Carriers: Syngas Production via Coupling Slow Pyrolysis with Gasification under a Circular Economy Model

Danai Frantzi and Anastasia Zabaniotou *

Department of Chemical Engineering, Engineering School, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; dfrantzi@cheng.auth.gr
* Correspondence: azampani@auth.gr; Tel.: +30-6945990604

Abstract: Waste-based feedstocks and bioenergy intermediate carriers are key issues of the whole bioenergy value chain. Towards a circular economy, changing upcycling infra-structure systems takes time, while energy-from-waste (EfW) technologies like waste pyrolysis and gasification could play an integral part. Thus, the aim of this study is to propose a circular economy pathway for the waste to energy (WtE) thermochemical technologies, through which solid biomass waste can be slowly pyrolyzed to biochar (main product), in various regionally distributed small plants, and the pyro-oils, by-products of those plants could be used as an intermediate energy carrier to fuel a central gasification plant for syngas production. Through the performed review, the main parameters of the whole process chain, from waste to syngas, were discussed. The study develops a conceptual model that can be implemented for overcoming barriers to the broad deployment of WtE solutions. The proposed model of WtE facilities is changing the recycling economy into a circular economy, where nothing is wasted, while a carbon-negative energy carrier can be achieved. The downstream side of the process (cleaning of syngas) and the economic feasibility of the dual such system need optimization.

Keywords: bioenergy intermediate carriers; circular economy; slow pyrolysis; biooil gasification; syngas; waste

1. Introduction

The bioenergy production technologies that focus on the utilization of organic and recyclable sources are of great importance regarding the mitigation of climate crisis and the gradual reduction of human dependence on fossil fuels. In this direction, biomass plays an incredibly promising role, not only because it is found abundantly, but also because its utilization does not result in increased CO_2 emissions, and it can significantly decrease SO_2 and NOx emissions. Biomass-derived energy made up for approximately 70% of the total energy produced by renewable sources [1]. Agricultural, forestry, fishery, livestock, and municipal waste are common types of large quantities of biomass, consisting of organic components [2].

Waste to energy (WtE) technologies could play a crucial role in the energy transition, leading to an increased share of the bioenergy consumed in the EU. However, introducing and deploying at large scale new and improved technologies entails several challenges, as regards their initial high cost, arising from bringing novel solutions to a technical environment with already reliable solutions in place. WtE processing technologies to produce bioenergy carriers include thermochemical, biological, and electrolytic methods. Due to the difficulties of biological and electrolytic methods in terms of scale-up and low rate of production, thermochemical methods prevail in producing of synthesis gas (syngas) on a larger scale. Bioenergy carriers show many advantages in terms of energy density, storability, energy content, flexible application, and related emissions, and can be

exploited in a variety of applications. Solid and gaseous biofuels, in particular, are well suited to exploiting waste and residual streams. These enhanced bioenergy carriers have the potential to considerably help the energy transition, but they require further research for commercial introduction [3].

Steam gasification is an efficient and established thermochemical method of syngas production [3]. The production of unwanted by-products is low, due to the steam that converts them to CO and H_2, through gasification, water-gas shift (WGS) and reforming reactions. It has been proven that the production of hydrogen through biomass steam gasification is up to three times higher than that of biomass air gasification. It has also been reported that using steam as a gasification agent significantly increases cost-efficiency [4]. The product of gasification (bio-syngas) is a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), nitrogen (N_2) and steam (H_2O). The produced gas is contaminated with tar, alkali metals, particulate matter, nitrogen (N_2), sulfur (S) and chlorine (Cl). The upgrading of syngas and the removal of the impurities is a necessary step after producing the gas in the gasifier to use it as fuel in an energy generation system [5].

Through pyrolysis, biomass can be converted into an easily manageable intermediate liquid energy carrier, the pyro-oil that has an increased bulk and energy density, suitable also for decreasing the transportation costs [6]. Through slow pyrolysis of agricultural, agro-industrial and food waste to produce biochar, pyro-oil is also produced, which can fuel a central gasifier for syngas production [7]. Intermediate bioenergy carriers (IBCs) are formed with biomass processing to energy denser, storable, and transportable intermediary products that can be used directly for combined heat or power (CHP) generation or further refined to bio-based products.

Compared to solid biomass and waste, pyro-oil gasification is a relatively new and promising approach to thermochemical conversion technology, classified based on the gasification agent used in the process. These types of waste can be converted by means of fuel-flexible thermo-chemical processes to produce stable, intermediate energy carriers in the form of bio-oil, the energy density of which can be increased by a factor of 10 to 15 (for the case of straw) (kJ/kg), enabling economic long-range transportation from several regionally distributed pyrolysis conversion plants to a central large scale gasification plant for biofuel production serving the circular economy models.

Scope and Objective of the Concept

The scope of this study is to highlight an alternative way of producing bioenergy carriers by using a liquid intermediate renewable energy carrier and more specifically the production of syngas from bio-oil.

It is focused on agricultural and agro-industrial waste, such as rice husk, coffee husk, wheat straw, etc., and the exploitation of the intermediate by-product (pyro-oil) to produce synthesis gas through a gasification process. The produced synthesis gas can then be upgraded to become suitable as fuel.

It proposes a circular economy waste valorization pathway, where gasification can be fueled by liquid energy carriers, such as the pyro-oils derived as by-products of the slow biomass pyrolysis plants regionally distributed and intended for biochar production. The coupling of these thermochemical processes (pyrolysis and gasification) is more relevant to a circular strategy, for the full exploitation of biomass, as Figure 1 depicts.

More specifically, the collection of pyro-oil from several decentralized slow pyrolysis plants, followed by its valorization into a gasification unit for gas fuel production is proposed in this study. Through this method, solid biomass-derived waste is pyrolyzed for biochar production (main product), while the pyro-oil being the by-product (considered as waste) is proposed to be valorized as an intermediate energy carrier through a gasification process. The cascaded valorization of agricultural waste for biochar production and the pyrolysis process's waste, that are both waste-based bioenergy carriers, in a model of coupling of various regionally distributed slow pyrolysis plants with a centralized gasification unit for syngas production, consists of a circular economy model. Biochar, produced as a

product of pyrolysis of waste biomass, shows great potential to reduce the environment impact, address the climate change issue, and establish a circular economy model.
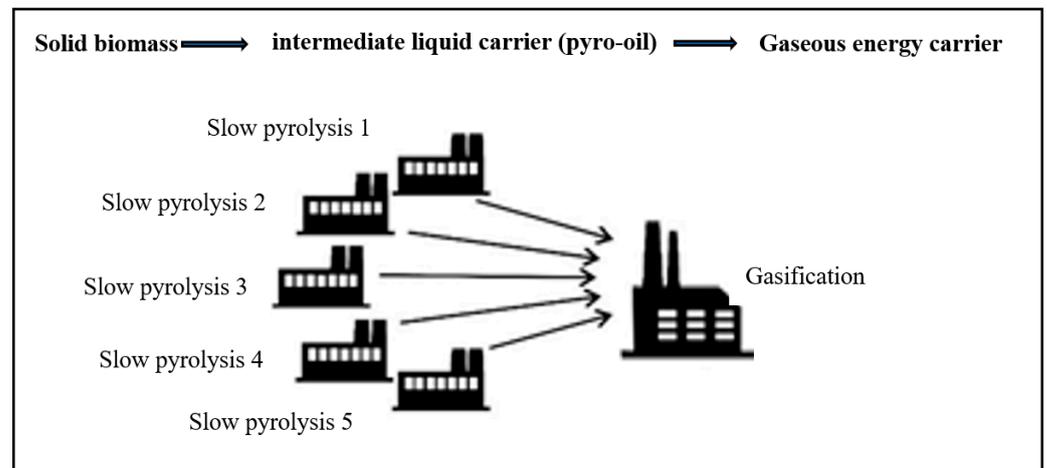
Figure 1. Conceptual circular economy model for syngas production from slow pyrolysis oils.

The scientific objectives are:

- Reviewing the pyro-oil characteristics derived from a slow pyrolysis required for being suitable fuel for the gasification.
- Gasification parameters impacting syngas quality.
- Depicting the circular economy approach's advantages.
- Screening the economic feasibility of such a project.

The dual thermochemical system has the following innovative features:

- It is a two-stage system suitable in a circular economy for bioenergy recovery from agro-industrial and agricultural waste, for the logistically optimized production of synthesis gas (syngas).
- Through the gasification of bio-oil, a better-quality synthesis gas is produced, while at the same time the transportation costs are minimized compared to solid biomass, due to the higher energy density of the pyro-oil (biooil).
- Agricultural residues, agro-industrial wastes, forestry residues, biodegradable municipal waste, can be treated regionally in decentralized plants of slow pyrolysis for biochar production and the produced pyro-oils can be further used in a central large scale gasification system, creating a symbiotic strategy for a circular economy.
- This proposed system can combine the two seemingly opposing concepts of bioenergy carrier's production via slow pyrolysis from biomass and waste in the form of bio-oil, with carbon sequestration in the form of biochar.

2. Methods and Materials

2.1. The Thermochemical System

The module of the thermochemical system is shown in Figure 2.

2.2. Research Questions

The research questions posed in this literary review are presented below and answered based on a sustainable circular economy approach:

- Through which thermochemical methods can biomass be converted into energy?
- Which bio-oil production method is the best?
- What physical and chemical properties of bio-oil are important for its subsequent processing?
- What factors affect these properties?
- Which bio-oil can be used in the gasification process to produce gas fuel?

- How does the quality of bio-oil and the conditions of gasification affect the production of gaseous fuel?
- Is the syngas production by slow pyrolysis bio-oil gasification system economically feasible?
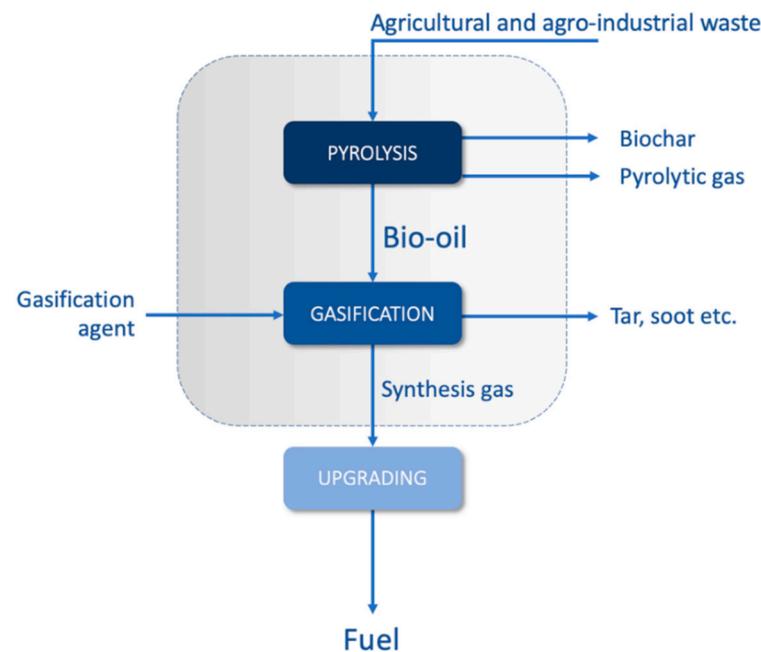
Figure 2. Thermochemical module including pyrolysis and gasification.

2.3. Bibliographic Search

A literature review was carried out, during which published articles were researched, reviewed, and analyzed. The aim of the search was to collect information and data on the gasification of bio-oil produced as a by-product derived from slow pyrolysis of agricultural and agro-industrial waste to produce syngas.

The bibliographic databases used were ScienceDirect, Google Scholar and other open access publications search databases, which offer a variety of articles and books to ensure the quality of the research. The criteria for selecting the publications in question were the title, the abstract, the keywords and finally the date of publication.

In total, two bibliographic searches were performed. For the first search, the terms used are: "slow pyrolysis" AND "agro-industrial waste", "slow pyrolysis" AND "agricultural waste", "slow pyrolysis" AND "bio-oil production". The first search yielded 8155 publications regarding the processing of agricultural and agro-industrial waste through slow pyrolysis. Seven thousand two hundred and fifty-two (7252) publications were excluded, as they were not considered directly relevant and of the remaining publications, sixty-four (64) were used as the basis for this review, containing necessary information and data for this study. Also, two books on related topics and two other online sources were used. For the first part of the search, the publication period was limited to the years 2008 to 2021 (Table 1).

In Figure 3, a statistical analysis of the publications regarding slow pyrolysis of agricultural and agro-industrial waste, per year, for the period from 2008–2021, is presented, which clearly shows the trend of the scientific research towards the exploitation of biomass and the production of bio-oil via thermochemical methods so that it can be used later, to produce heat, fuel, etc. The reduced number of publications for the year 2021 is due to the fact our literature search was conducted in the first months of the year 2021 and therefore refers to a shorter period and does not indicate any decrease in the interest of the scientific community in the direction of biomass processing using thermochemical methods.

Table 1. Screening of articles on the theme "slow pyrolysis of agricultural and agro-industrial waste".

Screening Process	Number of Publications
(1) 1st sample	8155
(2) Sample after exclusion of irrelevant publications	903
(3) Final screening	52
(4) Books	3
(5) Other (reports, studies)	4
Total	59
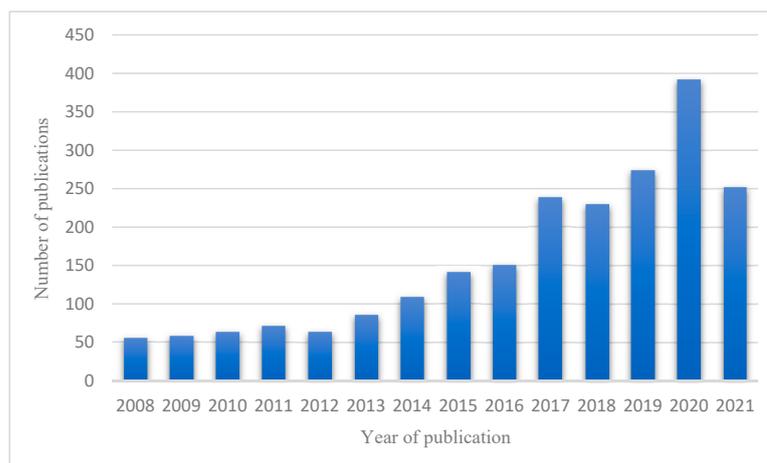
Figure 3. Statistical analysis of articles related to the topic of "slow pyrolysis of agricultural and agro-industrial waste".

Regarding the second search for the bio-oil gasification to produce synthesis gas, the terms used are: "bio-oil gasification", "bio-oil" AND "steam gasification", "bio-oil" AND "gasifiers", "bio-oil" AND "gasification parameters", "bio-oil gasification" AND "syngas production". The time limit for this search is set at 2009–2021, and after this screening, 10,870 results are obtained. The publications found are limited to 8838, when the publication type criterion is applied, i.e., articles and revised articles. Subsequently, articles that were not entirely relevant to this topic were excluded, while the rest were reviewed to select the ones that provide the most important information that will answer the questions posed in this research. The described procedure is shown in Table 2.

Table 2. Screening of articles on the theme "bio-oil gasification".

Screening Process	Number of Publications
(1) 1st sample	10,870
(2) Sample after exclusion of irrelevant publications	426
(3) Final screening	43
(4) Books	12
(5) Other (thesis, studies)	3
Total	58

Figure 4 presents a statistical analysis of the publications regarding bio-oil gasification. There is an increasing trend in research into the application of bio-oil to produce gaseous fuel. This may be because, compared to solid biomass, bio-oil gasification is a relatively new and very promising direction of thermochemical conversion technologies, and it is also a new way of producing synthetic biofuels (bio synfuels).
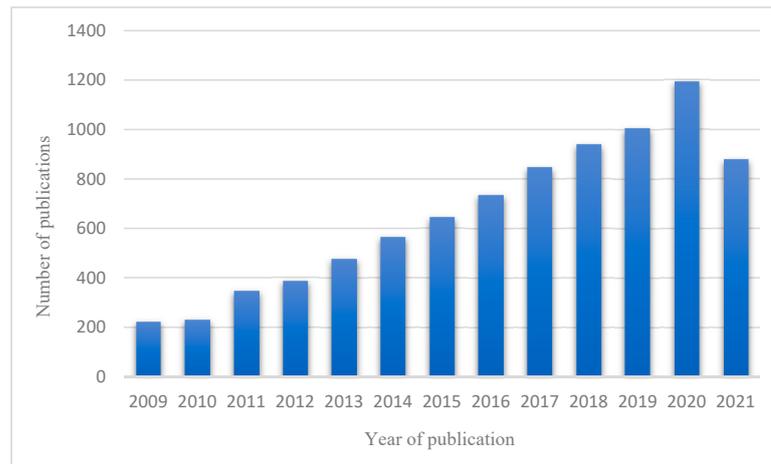
Figure 4. Statistical analysis of articles related to the topic of "bio-oil gasification".

Table 3 summarizes the results of the overall literature search for both parts of the literature review, i.e., for the biomass pyrolysis and the gasification of the produced bio-oil to produce syngas. It includes the sum of the initial number of publications from both parts of the research, the sum of the publications after the exclusion of irrelevant articles and the application of specific criteria. The final sample to be utilized is formed by the combination of the selected publications and the various internet sources that were utilized.

Table 3. Total screening process.

Screening Process	Number of Publications
(1) 1st sample	19,025
(2) Sample after exclusion of irrelevant publications	1329
(3) Final screening	95
(4). Books	15
(5) Other (thesis, studies, reports)	7
Total	117

Figure 5 presents a statistical analysis of the total publications that were studied. The conclusion may be drawn that there are several articles that offer interesting and relevant information even at the beginning of the decade and perhaps this is due to the rising need of finding sustainable, alternative, and effective practices while trying to minimize their environmental impact.
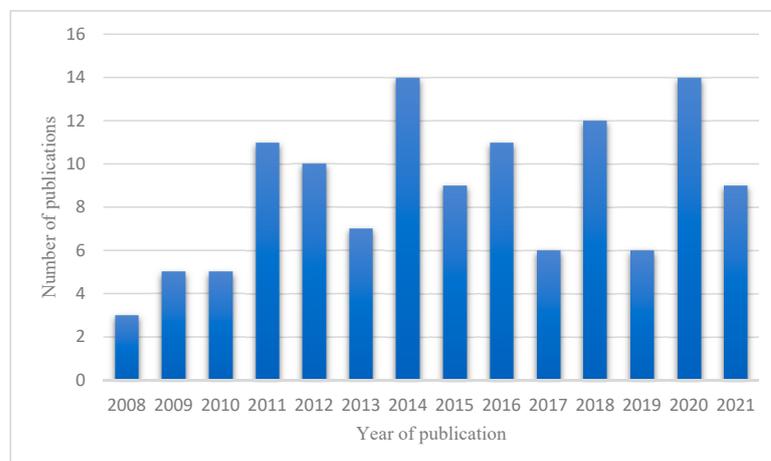
Figure 5. Distribution of total selected publications per year.

3. Discussing Pyrolysis

Pyrolysis, in general, is a thermochemical decomposition process in which biomass is heated over a range of temperatures, in the absence of oxygen. This process leads to the formation of three main products: biochar, which is used as a soil amendment, a volatile phase that can be further concentrated in a liquid phase (bio-oil) and after proper treatment it can be used as fuel and finally the non-condensable gases, such as CO, CO_2, CH_4, and H2 [8]. The process is described by Equation (1):

$$\text{Biomass} + \text{Heat (inert conditions)} \rightarrow \text{Biochar} + \text{Bio-oil} + \text{Gases} \tag{1}$$

Depending on the residence time, maximum temperature and heating rate, the pyrolysis process is divided into three categories: slow pyrolysis, fast pyrolysis and flash pyrolysis.

3.1. Slow Pyrolysis

Slow pyrolysis is mainly used to produce biochar, because it can yield about 35%wt. of good quality product at low temperatures (350–800 °C) and low heating rates [9]. Biochar is mainly used as soil amendment [10]. It can also find application as a catalyst for industrial use or as feed supplement to improve animal health and nutrient intake efficiency [10].

The residence time of the steam is usually less than 60 min [10]. The volatile organic fractions contained in the gaseous phase react with each other, producing char and liquid phase. With the increase of the residence time, the quantity of bio-oil produced decreases, due to the further decomposition, while its quality is quite low. This process has poor heat transfer, with longer retention times, which leads to increased energy requirements and consequently increased costs [11]. However, it is a quite simple process, which can be applied to small-scale units, such as at the base of a farm, to produce biochar.

Despite the relative simplicity of the slow pyrolysis process, the efficiency, and the properties of the products (biochar, bio-oil, gases) can be significantly affected by operating conditions, such as maximum temperature, residence time, pressure, and the particle size. In addition, the feedstock, i.e., the type of biomass that is subject to pyrolysis also plays an important role in the process's efficiency and the properties of the products [8].

3.2. Fast Pyrolysis

During the fast pyrolysis process, the biomass is heated, in the absence of oxygen, to a high temperature (700–1200 °C) with a high heating rate. Based on the initial mass of the feedstock, fast pyrolysis can yield 60–75% liquid biofuels with 15–25% biochar residues [9]. 10–20% of gas phase can also be produced, depending on the biomass used [9]. The process is characterized by a short residence time of vapors; however, their rapid cooling can lead to higher production of bio-oil. This process can produce liquid biofuels, which, after upgrading, can be used in turbines, boilers, engines or as feedstock for various other industrial applications. Fast pyrolysis technology produces liquid fuels with various technical advantages, such as easy storage and transportation and the use of second-generation raw materials (e.g., municipal and industrial waste).

3.3. Flash Pyrolysis

Flash pyrolysis produces solid, liquid, and gaseous products. Bio-oil production can reach up to 75% [12]. This process is carried out through rapid adaptation, in an inert environment, imposing a high heating rate and approaching temperatures around 1000 °C, while the residence time of the gas is less than 1 s [9]. The three main disadvantages of the method are the low thermal stability, the high viscosity of bio-oil due to the catalytic action of the formed char and finally the solid residues that it may contain.

3.4. Comparison of Pyrolysis Methods

Via fast pyrolysis approximately 60–75 wt.% liquid phase, 15–25 wt.% solid biochar and 10–20 wt.% non-condensable gases are produced [12]. The liquid phase, resulting

from fast pyrolysis, is called bio-oil, and plays an important role in the future of energy sources [13]. Slow pyrolysis occurs at a lower temperature, lower heating rate and relatively longer residence time of the pyrolysis gas [14]. Usually, the main product of slow pyrolysis is biochar [15]. Table 4 compares the operating conditions of the three processes and Table 5 summarizes the respective advantages and disadvantages.

Table 4. Pyrolysis types and operating conditions.

Pyrolysis Type	Temperature (°C)	Heating Rate	Pressure	Residence Time	Primary Product	Ref.
Slow pyrolysis	350–800	slow (≈10 °C/min)	atmospheric	30–60 min	biochar	[9,10,16]
Fast pyrolysis	700–1200	very fast (10–100 °C/s)	vacuum-atmospheric	10 s	bio-oil	[9–12]
Flash pyrolysis	800–1150	>1000 °C/s	atmospheric	1 s	bio-oil	[9,12]

Table 5. Advantages and disadvantages of the three different pyrolysis types regarding bio-oil production.

Pyrolysis Type	Advantages	Disadvantages	Ref.
Slow pyrolysis	+ Simple equipment. + Ability to use materials with different properties. + Standard technology.	− Possibility of requiring additional energy. − Increased biochar production.	[9,10,16,17]
Fast pyrolysis	+ More suitable technology for bio-oil production. + Simple and fast process. + Scale-up is economically feasible. + Efficient energy conversion. + Bio-oil can be upgraded to "drop-in" fuel.	− Requires attention to design and operation. − Biomass collection is its main problem of industrialization. − Limited commercial experience. − The produced bio-oil shows little stability.	[10–12,17]
Flash pyrolysis	+ Production of fuel with higher energy density. + Higher yields of bio-oil.	− Low thermal stability. − Presence of solid phase in the oil. − Corrosion and chemical instability of oil. − Increased viscosity over time − Production of pyrolytic water. − Dissolution of biochar alkali in bio-oil.	[9,12,17]

4. Properties of Bio-Oils

Bio-oil is typically a dark brown, viscous liquid with a smoky odor. It is an important product of biomass pyrolysis that, among other things, could potentially be used in engines, boilers, furnaces, and turbines to generate heat and electricity. For this reason, it is necessary to evaluate its physical and chemical properties, which determine its quality, in order to meet the fuel criteria or in general the characteristics necessary for the process in which it will be used (in this case work, as feed for the gasification process). The above can be achieved if the bio-oil has (i) low particulate matter (ii) good homogeneity and stability, and (iii) a justifiably high flash point [18].

4.1. Physical Properties

The main physical properties commonly studied during bio-oil production include density, viscosity, pour point, flash point and heating value and they are displayed in Table 6 for bio-oils produced by different feedstocks.

4.1.1. Density

Specific gravity (=density of a substance to density of a reference substance, usually water) is of little importance as an indication of combustion characteristics, but it is used to calculate weight to volume ratios, e.g., calorific value. Density is typically measured according to ASTM D 4052 at 15 °C using a digital density gauge. The density of pyrolytic liquids usually ranges from 1.2–1.3 kg/dm^3, and the accuracy of the measurements is very good (error less than ±0.1%) [19].

4.1.2. Viscosity

Viscosity is defined as the measure of resistance to the flow of a liquid. In pyrolytic liquids, the viscosity is in a wide range (35–1000 cP at 40 °C) and depends on the feedstock and the conditions of the process through which it is produced [18]. It can be measured either as kinematic viscosity using glass capillary tubes or as dynamic viscosity using a rotating viscometer. Kinetic viscosity in the second case is calculated through the relationship between the two quantities [20]:

$$\nu(cSt) = (\eta \ (mPa \ s))/(\rho \ (kg/L)) \tag{2}$$

where, ν is the kinematic viscosity, η, the dynamic viscosity and ρ the density of the liquid.

The efficient collection of volatile components in the production of bio-oil leads to the production of an oil with lower molecular weight components, lower viscosity, better solubility, and possibly better preservation during storage, where viscosity usually increases due to slow polymerization and condensation reactions [18].

Regarding the use of bio-oil as a fuel, viscosity is one of the most important properties that must be considered when designing and selecting handling, processing, and transport equipment. For example, due to the role it plays in pumping and atomization, a high viscosity makes the flow difficult, especially at lower temperatures. Compared to other fuels such as gasoline and diesel, bio-oil has a higher viscosity, however it is compared to the viscosity of unrefined petroleum when the temperature is at 35–45 °C, so to transport it through a pipeline you need the temperature of the pipeline to be maintained in this range [18].

4.1.3. Pour Point

The pyrolytic oil liquefies as the temperature decreases. The pour point of a fuel is an indication of the lowest temperature at which the liquid is observed to flow and represents the lowest temperature limit at which it can be pumped. For bio-oil this limit is generally low, e.g., for bio-oil derived from wood pyrolysis, it is from −20 °C to −30 °C, while bio-oil derived from peat shows very high pour points, 40–50 °C [21]. A higher pour point is an indication of the semi-solid nature of peat oils. The water content and the viscosity of the bio-oil affect the pour point.

According to the ASTM D 97 standard for finding the pour point, the sample is cooled, after warming up, at a certain rate and tested every 3 °C for changes in flow characteristics. The lowest temperature, at which oil movement is observed, is recorded as the pour point [21].

4.1.4. Flash Point

The flash point is a measure of the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. According to the ASTM D 93 method (flash point test with the Pensky-Martens closed vessel method), the sample is heated slowly, at a constant rate and with constant stirring, while a small flame is directed towards the vessel at regular intervals. The flash point is the lowest temperature at which the application of the flame leads to the ignition of steam above the sample [22].

A small flash point results in ignition of the sample and possibly subsequent explosion. Apart from its safety significance, the flash point of a fuel has no effect on its performance on an engine. In general, the auto-ignition temperature is not affected by changes in flash point and similarly by other fuel properties, such as fuel injection and combustion performance.

More specifically for pyrolytic liquids, flash points from 40–100 °C have been measured [22]. A low flash point (e.g., 40–50 °C for liquids from forest residues) is due to the high boiling point of volatile substances and the high vapor pressure. For liquids with low volatile content, the flash point is much higher. In this case, the flash point cannot be measured at a temperature of 70–100 °C, because the evaporation of water suppresses the ignition [22].

4.1.5. Heating Values

Heat of combustion is the amount of heat produced when a fuel burns completely. It can be determined by bomb calorimetric techniques, in which an adiabatic system is maintained using a temperature-controlled water bath [23]. There are two values for the heat of combustion of a fuel: the higher heating value (HHV) and the lower heating value (LHV). The difference between the two is equal to the heat of evaporation of water produced during the combustion of the fuel.

The calorific value depends on the composition of the feedstock and, more specifically, on its elemental analysis. The water content of bio-oil reduces the calorific value [24]. Bio-oil produced from dry or low moisture content feedstock has a calorific value slightly higher than that of the feed. In the literature, the calorific value of bio-oil is found mainly as higher calorific value (HHV).

4.2. Chemical Properties

Regarding the chemical properties of the bio-oil the following will be examined: moisture, acidity (pH), elemental composition (C, N, H, O) and the content of ash and heavy metals.

4.2.1. Moisture Content

Pyrolytic oils are usually dark brown, have high viscosity, their water content is typically high. It varies from 15–30% according to the type of pyrolysis method used (slow, fast, flash pyrolysis) [25] and is highly affected, as expected, by the different pyrolysis types and other process parameters. More specifically, the water content derives from the initial moisture of the feedstock, from the pyrolysis process or from the addition of water, used to condense the vapors during pyrolysis. Water is dissolved in the organic phase; however, the addition of extra water leads to separation of the phases.

Water content is particularly important because it affects other physicochemical properties. As it increases, the pH is increased, the viscosity and calorific value is reduced, both chemical and physical stability is affected, and it can also ultimately undermine subsequent upgrading processes [25].

There are three main methods for determining moisture content: oven drying or vacuum drying, titration with a suitable water reagent and distillation using a water-immiscible solvent [25]. However, for bio-oil, the water content is difficult to measure and remove, because evaporation or distillation at normal temperatures around 100 °C can cause significant and potentially harmful physical and chemical changes in the liquid.

Due to the high content of bio-oil in volatile components, with a boiling point below 100 °C, vacuum distillation, heat drying, or xylene distillation are not options. Therefore, the Karl-Fischer (K-F) titration method is the one that has been used most to determine the water content [26]. The K-F solution contains iodine, pyridine, sulfur dioxide and methanol and reacts with water. Titration can best be done with the potentiometric endpoint method and is a fast and reliable method.

4.2.2. Acidity

Bio-oils are acidic. Their pH is low, it usually ranges from 2.0–4.0 and this is due to the content of volatile acids (8–10%), mainly acetic acid and formic acid. Because of this acidity they are corrosive, especially at high temperatures, and require special types of metals for their storage equipment [27].

4.2.3. Elemental Analysis (C, H, O, N)

Pyrolytic oil is considered a highly oxygenated hydrocarbon with a high-water content and its elemental analysis resembles that of the feedstock. Thus, bio-oil contains mostly carbon, hydrogen, and oxygen, while the nitrogen and sulfur contents are quite low. Oxygen is found in relatively high concentrations in bio-oil, which is due to the feedstock and the pyrolysis mechanism reaction and determines the physical properties and chemical

reactivity [28]. For example, viscosity and density are high, while energy content is low because carbon-oxygen bonds do not release energy during combustion. In addition to the oxygen contained in the structures of organic molecules, bio-oil also contains the oxygen contained in water [28].

In Table 7, the elemental analysis of bio-oils produced by different feedstocks is displayed. The concentration of carbon ranges from to 55.8 to 75, while that of hydrogen ranges from 7.16 to 11.18, with the maximum value corresponding to bio-oil produced by apricot kernel. Peach pulp shows the maximum oxygen concentration of 31.96, while wheat husk shows the minimum concentration of 8.8 wt.%. Nitrogen concentration is relatively lower and ranges from 0.59–11.5 wt.%. Other elements found in agro-industrial and agricultural waste bio-oils are sulfur, boron, chlorine, iron, copper etc., but their concentration levels are negligible.

4.2.4. Ash Content

Due to the char removal equipment being inefficient, pyrolysis oils contain ash or char. They contain unburned carbon and some metals [29]. Depending on the fuel use, the ash content, and its composition play an important role in the occurrence of harmful effects. High ash content can lead to pump and injector wear, sediments on the combustion equipment or turbine corrosion due to the alkali metals contained in the ash [29]. Large boilers and low-speed engines have greater ash tolerance than more advanced equipment. The ash content is also undesirable, as its higher content results in a low HHV, due to the lower amount of organic matter in the bio-oil [19].

Part of the ash consists of alkali metal oxides [29]. Liquids from straw or grass pyrolysis contain large amounts of alkali metals, which during the incineration process can evaporate or form oxides, which then lead to the evaporation or oxidation of the ash. Furthermore, certain metal oxides, such as calcium and potassium, have a catalytic behavior, that can affect the conversion processes. The presence of these metal oxides in bio-oil causes the start of polymerization reactions, which make it highly unstable [19].

Generally, the ash content in bio-oils is not very high and that is why it was often overlooked in the literature reviews studied for the Tables 6 and 7 to be conducted and therefore, its values were not included in the above-mentioned tables.

4.3. Parameters That Affect the Properties of Bio-Oil

The various operating conditions of the pyrolysis process play an important role in the quantity and composition of the bio-oil. The biomass composition determines the quality of the bio-oil, due to the different chemical reactions that are favored in each case during pyrolysis, according to which compound, for example, is more abundant. During pyrolysis, biomass undergoes primary and secondary conversions/reactions, involving mass and energy transfer mechanisms. Primary reactions include the decomposition reactions of cellulose, hemicellulose, and lignin, contained in biomass and leading to the formation of primary and intermediate products [30]. The intermediates then undergo a secondary decomposition. The first category of reactions includes dehydration and char formation reactions, while the second category includes the decomposition and volatilization of intermediates [30]. The pyrolysis products resulting from these reactions are particularly sensitive to pyrolysis parameters changes and to the type of biomass used as feedstock.

The main parameters include: (i) the pyrolysis temperature, (ii) the heating rate, (iii) the particle size, (iv) the carrier gas flow and (v) the residence time. However, even if the above parameters are identical for the pyrolysis of two different raw materials, the results regarding the quantity and quality of the products may be completely different. This fact is indicative of the effect of different raw materials on pyrolysis products, which is the sixth parameter. Optimization of operating conditions can favor the production of one of the three pyrolysis products (bio-oil, gas, char).

4.3.1. Effect of Temperature

During the pyrolysis process, biomass is heated up to a peak temperature, where it remains for a defined residence time. This temperature usually ranges from 350 to 800 °C for slow pyrolysis processes [10,16]. In general, the conversion efficiency of biomass increases with increasing temperature, due to the energy delivered to the system that allows the bonds of the molecules of the feedstock to be broken. As shown in Table 6, the ideal temperature for greater bio-oil yields is in the range 450–550 °C and depends on the type of feedstock and the process parameters. Biswas et al. (2017) observed that for rice husk pyrolysis the bio-oil yield increased with increasing temperature from 300 to 400 °C (32.5 and 36.7 wt.% respectively) [31]. From a temperature of 350 °C and above there is a lower increasing rate and when the temperature reaches 450 °C there is a decrease in the amount of bio-oil produced. Similar behavior is observed in other studies. An increased temperature, therefore, favors the production of liquid phase, but at very high temperatures, the opposite phenomenon can be observed. This is due to the secondary decomposition of volatile components at these high temperatures, leading to increased gas products.

Different temperatures have been found to be more suitable for maximum bio-oil production when different raw materials are pyrolyzed, for example the ideal temperature for rice husk pyrolysis is 400 °C [32], for wheat husk 550 °C [33], while for lemon leaves 350 °C [34].

In addition to the quantity, the pyrolysis temperature also affects the quality of the bio-oil produced. Bio-oil produced at lower temperatures (400–700 °C) consists of alkanes, alkenes, fatty acids and long chain esters, aliphatic nitriles, and amides [35]. A higher temperature (>700 °C) results in the decomposition of aliphatic molecules and the formation of aromatic compounds, which lowers the H/C ratio in bio-oil and increases the content of organic nitro compounds. This bio-oil consists of smaller aliphatic molecules and lower molecular weight components, such as ketones, alcohols, phenols, and their derivatives, due to decomposition reactions [36]. The water content as well as the content in nitrates, ethers and aldehydes is not affected [37]. When the carbon and hydrogen content is increased, so is the quality of the bio-oil. On the other hand, when the oxygen content is increased, the heating value of bio-oil is decreased [35].

4.3.2. Effect of Heating Rate

The heating rate is important for the decomposition of biomass. Typically, it is approximately 10 °C for slow pyrolysis, 10 to 100 °C for fast pyrolysis and greater than 1000 °C for flash pyrolysis processes [10,16]. A higher heating rate causes rapid decomposition of biomass and promotes the formation of volatile substances [30]. The increase in the production of volatile substances is mainly due to the decomposition of tar, which increases under these conditions. The higher bio-oil production during fast pyrolysis is due to the little time available for the side reactions: tar decomposition and repolymerization. Rapid heating rates reduce the limitations of mass and heat transfer and favor the abundance of volatile components through the rapid endothermic decomposition of biomass. As a result, tar and high molecular weight volatile components are removed from biomass decomposition, leaving behind a small amount of char [30]. However, the pyrolytic behavior resulting from the application of different heating rates is directly related to the composition of the feedstock. The increase in the heating rate results in the production of a better-quality bio-oil, due to the rapid reduction of the water content. The oxygen content of the pyrolytic oil also decreases with rapid heating rates, due to the formation of oxygen-containing gases such as CO_2 and CO [30].

4.3.3. Effect of Particle Size

Biomass pyrolysis entails heat transfer problems because biomass is not a good heat conductor. The effect of the particle size of the feed is considered crucial for the quantity and quality of bio-oil produced, as well as for the reduction of problems related to heat

transfer. In general, in fast pyrolysis systems, a small particle size is preferred, which serves the uniform heating of the feed [30]. In the case of larger particles, insufficient heat transfer to inner surfaces can result to low average temperature values and ultimately lower bio-oil production. Larger particles also require higher apparent activation energy due to these heat transfer limitations.

Different particle sizes have been proposed for different pyrolysis systems. For example, particles smaller than 200 mm are more suitable for a rotating cone pyrolysis reactor, less than 2 mm for fluidized bed systems, and less than 6 mm for circulating fluidized beds [30]. However, there is a lot of conflicting information in the literature, which makes it difficult to establish a particle size as the most suitable for a particular pyrolysis system. The particle size value usually ranges from 0.2 to 1.25 mm for most of the literature found on slow pyrolysis processes. Unexpected increase in bio-oil production efficiency of larger feedstock particles may be due to the type of feedstock used. The apparent density and oxygen content of biomass are most likely related to the mechanism of heat transfer and the rate of pyrolysis reactions.

Finally, the appropriate particle size varies depending on the type of biomass and pyrolysis. Reducing the particle size brings additional costs, due to the process of grinding the raw material, so it is necessary to find a solution that minimizes the cost of grinding and operating times for a given biomass, with the intent of maximizing the bio-oil yields, because of the effect of particle size distribution.

4.3.4. Effect of Carrier Gas Flow

The environment in which the pyrolysis process takes place affects the type and composition of all products. Char is formed when pyrolytic vapors react with the solid materials, causing secondary exothermic reactions [30]. Pyrolysis conditions that support rapid mass transfer, such as vacuum pyrolysis, fast vapor removal, rapid cooling of vapors and small particle size in the feed are useful to eliminate these reactions [30]. In most of the literature that has been studied, nitrogen is used as a carrier gas, probably due to its low cost. The flow of N_2 during the process reduces the residence time of the pyrolytic vapors, and thus the possibility of their repolymerization, which maximizes the production of the liquid phase. This value usually ranges from 0.01 to 0.5 L/min for slow pyrolysis processes.

Although in the literature it is considered that the production of bio-oil is not affected by the flow of the carrier gas and it is therefore a secondary parameter, it is observed from various studies that increasing the flow of N_2 leads to a slight increase in the amount of bio-oil produced [30]. The limits at which there is an increase are specific, because similarly to a very high temperature, a very high flow rate of the carrier gas results in a decrease in the total amount of bio-oil produced. This is most likely because high speeds favor gas production, as volatile components are removed from the system before they can be condensed efficiently.

Besides nitrogen, steam can also be used as a carrier gas, which also works as a pyrolysis agent, because it favors the formation of liquids by the reaction of gases with char. Steam pyrolysis may be considered more suitable for bio-oil production than nitrogen pyrolysis. This is due to the formation of more gaseous products during nitrogen pyrolysis. However, the addition of steam can increase the oxygen content of the bio-oil produced, which has been reported to affect its quality as a fuel.

Other effects that the use of steam can have on the composition of the final product is the reduction of the volume of the undesired products, due to the extraction of the water-soluble components of the gases and tar. Also, at higher steam flow rates the formation of aliphatic and aromatic hydrocarbons is favored, while the formation of polar molecules is prevented. Finally, the steam promotes the creation of free radicals, due to the breaking of the bonds of heteroatoms. These free radicals then form other compounds, such as H_2S, CO, CO_2, saturated hydrocarbons, and aromatic compounds [30].

4.3.5. Effect of Residence Time

Residence time refers to the time for which the biomass remains at a certain pyrolysis temperature. In batch processes, the residence time must be such as to achieve the desired results. During longer residence times, secondary reactions of pyrolytic vapors occur, such as carbonization, gasification, and thermal decomposition, leading to the production of lower quality bio-oil [38]. In addition to the above, residence time is a parameter for the design of the pyrolysis reactor [39]. Typically, residence time ranges from 30 to 60 min for slow pyrolysis, while for fast and flash pyrolysis processes it is approximately 10 and 1 s, respectively [10,16].

4.3.6. Effect of Biomass Composition

Another parameter that affects the pyrolysis process is the composition of the biomass used. As mentioned above, biomass consists of lignin, hemicellulose, cellulose and a small fraction of inorganic matter, the percentage of which depends on the different types of biomasses. Even biomass of the same type may have a different composition if grown for example in another soil, under different conditions or if it is of a different age [40]. The quality and quantity of the pyrolysis products are greatly affected by these changes in the composition of the raw material.

Biomass with higher cellulose and hemicellulose content usually results in a higher bio-oil yield than biomass with higher lignin content. The decomposition of lignin is difficult due to its stable structure, and leads to the production of a larger amount of char. However, the use of higher temperatures and heating rates can lead to the decomposition of this material, favoring the production of a liquid phase [39].

Ash also affects the amount of the pyrolysis products. A high ash content results in reduced bio-oil production and increased char and gases production. Sodium and potassium have a significant effect on the reduction of the liquid phase and sulfides and ammonia salts can also affect the production of bio-oil and promote the formation of char [39]. Other factors that affect the products are the large amounts of volatile components and differences in the structure of the main components of biomass.

The composition of bio-oil is necessary to determine the most appropriate application for the product. A bio-oil rich in phenolic compounds can be used to replace mineral phenols in phenolic resins to produce chemicals. After being upgraded, a bio-oil containing a considerable amount of long chain carboxylic acids, ketones, and hydrocarbons becomes more appropriate as a fuel [39]. Finally, the moisture content of biomass is another critical factor. The amount of water contained in bio-oil varies, depending on the feedstock, the process of production and its collection. The total water content derives from the moisture of the pyrolyzed biomass and the dehydration reactions that take place during pyrolysis. A typical specification of the feed material is 10% maximum moisture, to minimize the bio-oil content in water [39]. The result of a high-water content is the reduction of the heating value, the improvement of the stability and the reduction of the viscosity of the bio-oil.

4.4. Combined Implications of Pyrolysis Parameters

The result of pyrolysis, i.e., the quantities of the products and their chemical and physical properties is the result of a combination of all the above parameters. Not many researchers have studied the combined effect of the process parameters. Usually, the effect of the parameters is analyzed separately, while keeping the other variables constant.

Tables 6 and 7 show the effect of the parameters mentioned, applied on biomass derived from agricultural and agro-industrial waste of Mediterranean origin. Bio-oils produced by slow pyrolysis of this biomass were examined and their chemical and physical properties were studied. Although the most suitable method, as mentioned above, to produce bio-oil is fast pyrolysis, due to the advantages it shows in terms of quality and quantity of bio-oil produced, in this work slow pyrolysis is considered.

Table 6. Slow pyrolysis operating conditions of different feedstocks and characteristics of produced bio-oil.

Feedstock	Pyrolysis Operating Conditions						Bio-Oil Characteristics						
	Temperature (°C)	Heating Rate (°C/min)	Carrier Gas Flow (L/min)	Particle Size (mm)	Residence Time (s)	Bio-Oil Yield (wt.%)	Pour Point (°C)	Flash Point (°C)	Higher Heating Value (MJ/kg)	Kinematic Viscosity (mm²/s)	Density (g/mL)	pH	Ref.
Agro-industrial waste													
Rice husk	300 400 500 300 400 500 300 400 500	5 5 5 10 10 10 20 20 20	-	≈0.231	3600 5400 7200 7200 3600 5400 5400 7200 3600	28.70 ± 4.50 32.14 ± 0.06 36.82 ± 0.5 15.82 ± 5.0 39.84 ± 1.26 38.20 ± 0.71 6.03 ± 2.35 34.94 ± 0.15 39.80 ± 2.4	-	-	-	-	-	≈3	[32]
Corn cob	300 350 400 450	20	0.05	0.5–2	-	42.8 45.0 45.6 47.3	-	-	-	-	-	-	[31]
Processed sesame seeds	350	25	0.00151	-	-	18.6	−5	182	25.5	39.6 at 40 °C	1.029	-	[41]
Sunflower husk	400	10	0.1	-	-	34	-	-	-	-	-	-	[42]
Wheat husk	550	15	0.02	-	3600	31.8	-	-	6.02	-	1.06	6	[33]
Apricot kernel after oils extraction	450	20	0.05–0.2	0.25	3600	43.66	−6	96	39.12	37.9 at 40 °C	1.0012 at 20 °C	3.2	[43]
Apricot kernel	400	10	0.05–0.2	0.425–0.600	-	≈21	-	-	27.19	-	-	-	[44]
Pomegranate peel	750	25	0.1	1.5–5	3600	35	-	-	20.4	-	-	-	[45]
Pomegranate seed	400 800	5	≈0.01	≈3.2	3600	8.88 21.54	-	-	34.76 33.96	-	-	-	[46]
Apricot pulp	550	5	0.1	0.85–1.25	-	23.3	-	-	26.82	-	-	-	[47]
Peach pulp	550	5	0.1	0.85–1.25	-	23.2	-	-	25.76	-	-	-	[47]
Potato peel	550	5	0.2	0.81	-	27.11	-	-	32	-	-	-	[48]
Tomato peel	600	20	-	-	-	40	-	94	33.04	11.82 at 40 °C	0.973	-	[49]
Flaxseed residues	350 500 650	5	0.06	-	1800	43.3 52.7 55.0	-	-	-	-	-	-	[50]
Sunflower residues	400	0.67	0.05	1	-	21	-	-	-	-	-	-	[51]
Date kernel	500	20	0.01	0.05–0.1	≈1800	66.5	-	-	29.06	1.4179 at 25 °C	1.029	2–4	[52]
Cherry kernel	500	5	0.025	-	-	≈20	-	-	32.46	-	-	-	[53]
Grape seed	500	10	0.2	-	-	≈20	-	-	-	-	-	-	[54]
Winery wastes	600	≈50	-	-	-	47.7	-	-	-	-	-	-	[55]
Olive residues	500	20	1	-	1800	45	-	-	-	-	-	-	[56]
Coffee residues	450	10	-	-	3600	27.77	-	-	-	-	-	-	[57]
Agricultural waste													
Mushroom substrate	470	20	≈0.27	-	-	14.4	-	-	24.82	-	-	-	[58]
Lemon leaves	350 450 550	10	0.1	0.125–0.250	-	39.3 32.8 27.7	-	-	-	-	-	-	[34]
Grape residues	600	5	0.15	<2	1800	41.4	-	-	-	-	-	-	[59]

Table 6. *Cont.*

| Feedstock | Pyrolysis Operating Conditions | | | | | | Bio-Oil Characteristics | | | | | | |
	Temperature (°C)	Heating Rate (°C/min)	Carrier Gas Flow (L/min)	Particle Size (mm)	Residence Time (s)	Bio-Oil Yield (wt.%)	Pour Point (°C)	Flash Point (°C)	Higher Heating Value (MJ/kg)	Kinematic Viscosity (mm²/s)	Density (g/mL)	pH	Ref.
Grape bagasse	550	10	-	0.425–0.600	>1800	≈23	-	61	32.95	23 at 40 °C	0.992 at 20 °C	-	[60]
Wheat straw	300 350 400 450	20	0.05	0.5–2	-	32.5 36.0 36.7 29.2	-	-	-	-	-	-	[31]
Date residues mix	500	20	0.01	0.05–0.1	≈1800	30.1	-	-	24.35	1.367 at 25 °C	1.011	2–4	[52]
Cotton stalk	400	13	0.5	1–3	3600	23.63	-	-	-	-	-	-	[61]
Energy crops													
Cotton thistle	550	40	-	0.6–0.85	>1800	≈17	-	-	32.6	-	-	-	[62]
Canola	500	10	0.0012	0.425–1.25	-	32.7	-	-	34.75	-	-	-	[63]
Flaxseed	550	5	0.1	0.425–2.8	≈1800	46.4	-	-	34.58	-	-	-	[64]
Castor seed	550	20	0.1	-	<3000	64.4	<5	31	≈35	83.19 at 40 °C	0.966	3.7	[65]

Table 7. Chemical composition of bio-oil.

| Feedstock | T (°C) | wt.% Dry Ash Free (daf) | | | | | | | | | | | HHV (MJ/kg) | Ref. |
		C	H	O	N	S	B	Cl	Fe	Cu	Zn	Al		
Agro-industrial waste														
Processed sesame seeds	350	55.8	8.34	28.91	7.0	0.17	-	-	-	-	-	-	25.5	[41]
Wheat husk	550	60.9	9.7	8.8	11.5	-	-	-	-	-	-	-	6.02	[33]
Apricot kernel after oils extraction	450	74.19	11.18	13.60	1.03	-	-	-	-	-	-	-	39.12	[43]
Apricot kernel	400	64.45	8.24	26.5	0.81	-	-	-	-	-	-	-	27.19	[44]
Pomegranate seed	400 800	64.26 67.99	8.21 8.07	25.43 21.17	2.06 2.66	0.04 0.11	-	-	-	-	-	-	34.76 33.96	[46]
Apricot pulp	550	61.5	7.8	28.96	1.76	-	-	-	-	-	-	-	26.82	[47]
Peach pulp	550	59.58	7.88	31.96	0.58	-	-	-	-	-	-	-	25.76	[47]
Potato peel	550	58.82	8.54	31.41	1.22	-	-	-	-	-	-	-	32.00	[48]
Tomato peel	600	75	9.28	11.2	4.4	0.12	-	-	-	-	-	-	33.04	[49]
Cherry kernel	500	67.18	8.48	21.86	2.45	0.03	-	-	-	-	-	-	32.46	[53]
Agricultural waste														
Mushroom substrate	470	65.29	7.16	21.72	5.83	-	-	-	-	-	-	-	24.82	[58]
Grape bagasse	550	71.72	8.69	16.90	2.69	-	-	-	-	-	-	-	32.95	[60]
Energy crops														
Cotton thistle	550	68.9	8.9	20.3	1.7	-	-	-	-	-	-	-	32.6	[62]
Canola	500	-	-	-	10.87	1.08	-	0.157	0.0036	0.0004	0.0007	0.0077	34.75	[63]
Flaxseed	550	74.2	10.5	13.8	1.5	-	-	-	-	-	-	-	34.58	[64]
Castor seed	550	69.33	-	2.25	-	-	28.25	-	-	-	-	-	≈35	[65]

5. Gasification

Energy production through biomass gasification counts over 100 years of existence. The first report of the use of gasification concerns the lighting of London in 1812 [66]. A gasification method designed by Bischoff in 1839 and modified by Siemens in 1857 was used for a century [67]. One of the main problems of this method, however, was the production of tar. To avoid this phenomenon, substances were added to the reaction that favored the cracking of tar.

Gasification is a thermochemical process, through which a relatively clean gaseous fuel is produced, following pyrolytic reactions and reforming reactions. The produced gas, called synthesis gas or syngas, can be an important energy source, suitable for direct combustion, application to engines and turbines, or to produce synthetic natural gas (SNG) and diesel (e.g., Fischer-Tropsch diesel). Gasification of organic materials to produce gaseous fuels is an established technology [68].

5.1. What Kind of Bio-Oil Is Suitable for Gasification?

Bio-oil is quite different from solid biomass, but its properties depend on the biomass from which it originates, but also on the conditions under which its production takes place, such as temperature, particle size and pyrolysis rate (fast, flash, or slow pyrolysis).

Bio-oils produced by fast pyrolysis are suitable for gasification because they do not show phase separation and have a lower viscosity [69]. In general, bio-oil, which results from fast biomass pyrolysis, is usually a single-phase solution with an adequate heating value and a relatively low viscosity [70]. In contrast, bio-oil produced by slow pyrolysis is prone to phase separation and is often consisted of a viscous organic phase and an aqueous phase. Thus, such bio-oils are not preferred for processes with oxygen as a gasification agent but find application in steam gasification [71]. In the latter, fast-pyrolysis bio-oils can also be used, but compared to slow pyrolysis oils, the phase separation is more difficult. This separation can be achieved either by adding water or by fractional distillation [72].

An important criterion for selecting a bio-oil for gasification is the yield by each pyrolysis process. Fast pyrolysis allows the production of a larger amount of bio-oil and shows better prospects for larger scale production compared to slow pyrolysis. Thus, fast pyrolysis is proven to be a more suitable method for bio-oil production even for a bio-oil steam gasification process [69]. The organic phase of slow-pyrolysis bio-oils is usually too thick to be atomized and may lead to catalyst deactivation due to blockage of its pores during catalytic steam gasification [69]. Finally, all bio-oils intended for gasification must be filtered to remove char particles.

5.2. Bio-Oil Feed to the Gasifier

Before gasification, it is necessary to separate the bio-oil into many small drops with the help of an atomizer. The diameter of a typical bio-oil droplet usually ranges from 10 to 80 µm and its formation is directly related to its physical properties, such as viscosity, surface tension and temperature [69]. Although it was accidentally discovered that the combustion characteristics of bio-oil bear several similarities to those of light fuels, differences in viscosity, pH, stability, ignition, heating value and emission levels have been observed [73].

Viscosity is particularly important for bio-oil atomization and should typically be in the range of 5–30 cP (mPa s) [70]. The bio-oil usually needs to be preheated before being fed to the atomizers to reduce its viscosity and surface pressure, making it easier to atomize than heavy liquid fuels.

However, it is preferred that the atomizers used in the bio-oil gasification processes be water-cooled or air-cooled to avoid any coking in the atomizer nozzles [69]. Some water is already contained in the bio-oil and has a significant effect on its spraying and gasification. The typical water content of bio-oil is in the range of 15–30 wt.% [70]. The presence of water reduces the viscosity of bio-oil and serves in its atomizing. However, if the bio-oil content in water exceeds 30 wt.%, phase separations can occur, which inevitably leads to

poor atomization. In addition, each kilogram of water in bio-oil consumes at least 2.26 MJ of additional energy during gasification, for its evaporation, an amount of energy that is usually not recovered [69]. For this reason, a bio-oil with a humidity of 20–25 wt.% is generally preferred. Finally, bio-oil droplets tend to agglomerate under cold conditions due to surface tension and tend to break into smaller droplets when the temperature is high. Therefore, for improved atomization, high temperatures are preferred [73].

5.3. Stages of Gasification

During gasification, bio-oil droplets undergo several stages, including drying, evaporation of water and light volatiles, pyrolysis, thermal decomposition of volatile components, and oxidation/reduction, the reactions of which are shown respectively below [6,69]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \text{ and } H_2 + 0.5O_2 \rightarrow H_2O. \tag{3}$$

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + \left(n + \frac{m}{2} - k\right)H_2 \text{ και } CO + H_2O \leftrightarrow CO_2 + H_2 \tag{4}$$
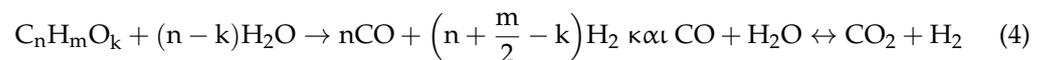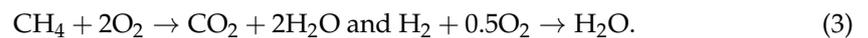
This is followed by tar decomposition, gasification of the solid carbon residue, reforming and the water-gas shift reaction. During these reactions, the effects of deformation and small explosions occur almost simultaneously. This behavior helps to eliminate the constraints of mass transfer and to enhance the gasification reactions. With a very high heating rate and a small size of bio-oil droplets, all the steps described above can occur simultaneously [69]. Therefore, it is worth mentioning that there is no clear boundary between these phases, and they can often overlap.

In the drying phase, the water contained in the bio-oil begins to form bubbles and it is then removed irreversibly from it, making it more viscous at temperatures above 100 °C [68]. Light volatiles begin to evaporate as the temperature rises. When the temperature exceeds 200 °C, the bio-oil droplets undergo swelling, shrinkage, distortion, and small explosions, resulting in mass reduction [68]. This stage lasts until temperature reaches 350–450 °C. In the pyrolysis phase, the thermal decomposition of the unstable components contained in the droplets takes place. Since the bio-oil droplets are very small, the pyrolysis process is fast and does not involve major reactions with a gasifying agent. Two undesirable products of the pyrolysis phase are soot and ash [68].

Soot is a mass of carbon particles often referred to in the literature as char or coke. Soot formation leads to reduced cold gas efficiency (CGE) and carbon conversion efficiency (CCE) values. Chhiti et al. proposed a model for describing the formation of soot during bio-oil gasification [74]:

$$C_2H_2 \rightarrow 2C(coke) + H_2. \tag{5}$$

Soot can occur because of some form of pyrolysis due to the lack of oxygen. In fact, bio-oil droplets undergo a pyrolysis step during the gasification process. Soot can also form during the combustion of various types of fuels, even in the presence of sufficient oxygen. The above-mentioned study also shows that the amount of soot produced increases in a temperature range of 1000–1200 °C but decreases immediately after due to steam gasification. Increasing oxygen during the above processes can significantly reduce soot production [69].

Tar is a sticky liquid, which creates significant difficulties in the industrial use of the produced gas. However, the amount of tar contained in the gas produced by bio-oil gasification is relatively small [69]. The phase after pyrolysis involves chemical reactions, including oxidation and reduction reactions between the organic components of bio-oil, oxygen, biochar, steam, and other gases. The main reactions that take place in a gasifier, as well as enthalpy and Gibb's energy are shown in Table 8.

Table 8. Main gasification reactions [69,75].

Reaction	Mechanism	$\Delta H^{\circ}_{r(298)}$ (kJ/mol)	$\Delta G^{\circ}_{r(298)}$ (kJ/mol)
	Carbon reactions		
R1 (Boudouard)	$C + CO_2 \leftrightarrow 2CO$	205.3	140.1
R2 (heterogeneous WGS)	$C + H_2O \leftrightarrow CO + H_2$	130.4	89.8
R3 (methanisation)	$C + 2H_2 \leftrightarrow CH_4$	123.7	168.6
R4 (partial oxidation)	$C + 0.5O_2 \leftrightarrow CO$	−111	
	Oxidation reactions		
R5	$C + O_2 \leftrightarrow CO_2$	−394	
R6	$CO + 0.5O_2 \leftrightarrow CO_2$		
R7	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$		
R8	$H_2 + 0.5O_2 \leftrightarrow H_2O$		
	Shift reaction		
R9 (WGS)	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41.47	−28.5
	Methanization		
R10	$2CO + 2H_2 \leftrightarrow CH_4 + CO_2$		
	Steam reforming reactions		
R11 (methane reforming)	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	172.6	118.4
R12	$C_nH_mO_k + (n - k)H_2O \leftrightarrow nCO + (n + m/2 - k)H_2$		

More specifically, according to the Boudouard equilibrium (R1), solid phase carbon can react with carbon dioxide, resulting in the formation of carbon monoxide. It is an endothermic process that occurs at temperatures higher than 768 °C, it is favored by reduced pressure and is inhibited in the presence of CO [76]. During the water-gas shift heterogeneous reaction (R2) solid carbon and steam react. It is an endothermic reaction, and it is also favored by high temperatures and low pressures. Methanization (R3) is generally a very slow process, and it is favored by higher pressures. The reactions of carbon dioxide and oxygen (R4 and R5) are exothermic and if they are carried out at a sufficient rate, they provide the necessary energy to carry out the pyrolysis reaction. An increase in temperature can lead to a shift in the chemical equilibrium of the homogeneous water-gas shift reaction (R9) between CO, steam, hydrogen, and CO_2. This reaction can have a direct effect on the composition of the gaseous mixture produced, affecting the CO/H_2 ratio. Methane and all hydrocarbons contained in the gaseous phase will be reformed according to reaction (R11), either by steam or by CO_2, increasing the concentration of CO and H_2. The endothermic reactions, that take place during gasification, require energy, which is provided by the combustion of some part of the feedstock [76]. This can be avoided by an external energy input, such as solar energy.

From the above reactions, it is obvious, that pressure and temperature conditions and residence time are crucial for determining the properties of the produced gas. It has been found that the heating value of the produced gas changes slightly from gasification at atmospheric pressure to gasification at higher pressure, under the same temperature conditions [77]. The quality of the gas depends on the CO and H_2 content as well as on the CO/H_2 ratio.

For energy production, the characteristics of syngas that are examined are the heating value, the composition, and the possible impurities. Regarding the heating value, it is affected by the hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and water content of the gas. The composition of syngas depends on the properties of the feedstock as well as the process conditions. For a given gasification system, the conditions of the process play a decisive role in all its characteristics. The latter include carbon conversion, syngas composition, tar, and soot formation [68]. In a steam gasification or air gasification process the necessary steps are: (i) cracking, (ii) partial oxidation, (iii) decomposition of tar, (iv) gasification of solid carbon residues, (v) reforming and (vi) water-gas shift reaction to produce syngas, water, carbon dioxide and undesired products such as tar, methane, and carbon.

A schematic representation of the gasification process is shown in Figure 6.
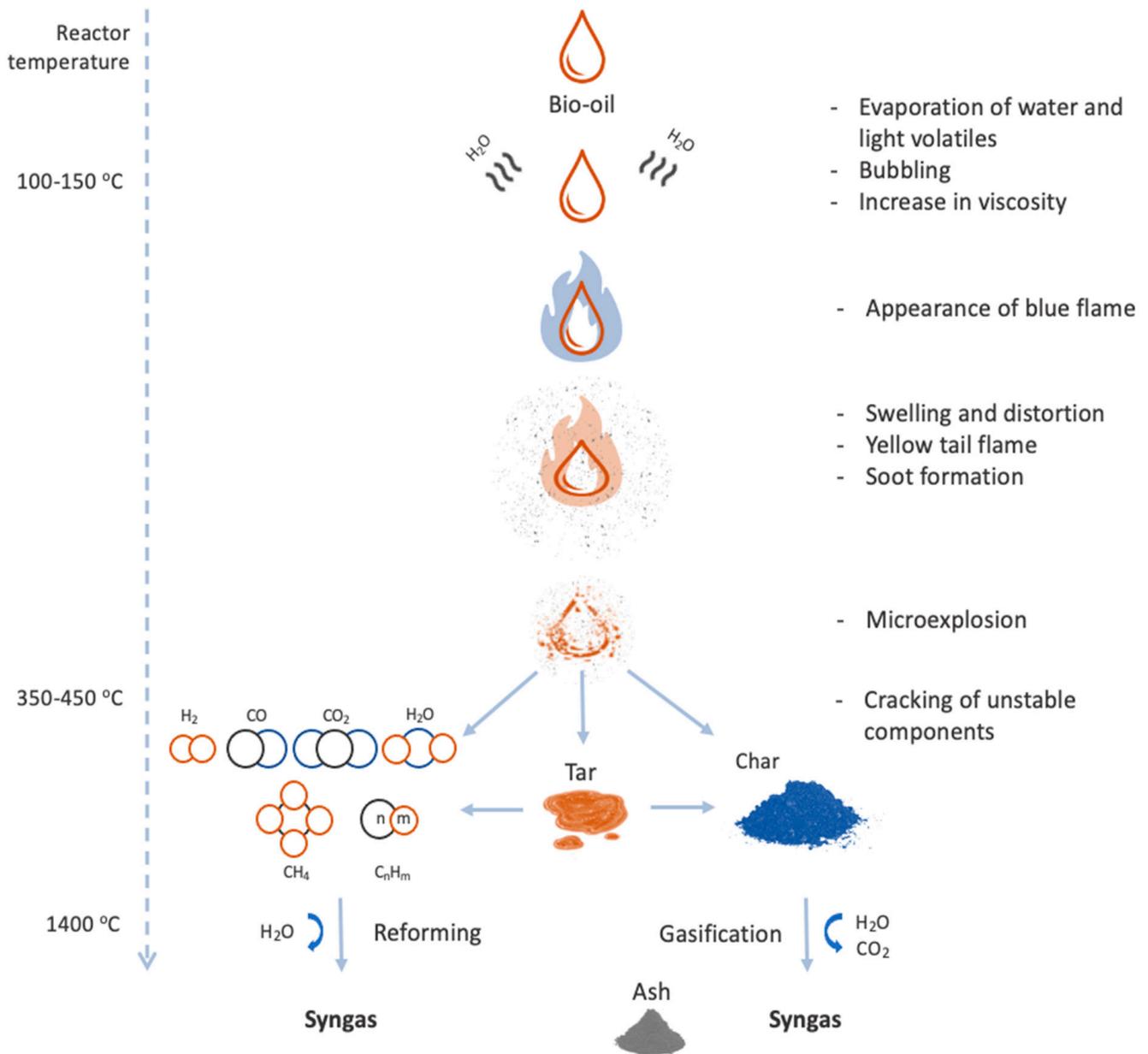
Figure 6. Schematic representation of gasification.

5.4. Steam Gasification of Bio-Oil

Steam gasification of bio-oil is a complex process that results in the production of a hydrogen-rich gas, in which the use of catalysts is frequent. This process mainly includes reforming, cracking and liquid-gas shift reactions. Initially, bio-oil reacts with water to produce CO and H_2 according to the following reforming reaction [69]:

$$C_nH_mO_k + (n - k)H_2O \rightarrow nCO + \left(n + \frac{m}{2} - k\right)H_2 \qquad (6)$$
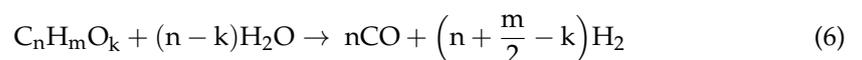
Carbon monoxide is then converted to carbon dioxide and hydrogen via the water-gas shift reaction [69]:

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 \qquad (7)$$

The above two reactions can be written as one [69]:

$$C_nH_mO_k + (2n - k)H_2O \rightarrow nCO_2 + \left(2n + \frac{m}{2} - k\right)H_2 \qquad (8)$$
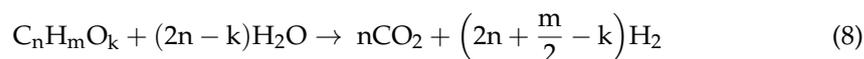
Since this process takes place at high temperatures, the reactions of thermal decomposition and catalytic decomposition also take place, which lead to the production of molecular fragments, gas and char [69]:

$$C_nH_mO_k \rightarrow C_xH_yO_z + (H_2, CO, CO_2, CH_4, \ldots) + char \qquad (9)$$

In addition, the disproportionation reaction of carbon monoxide may occur [69]:

$$2CO \rightarrow CO_2 + C \qquad (10)$$

In addition to hydrogen, the gas produced also contains CO_2 and CO and a small amount of CH_4 and C_2H_4. There are two main ways to produce methane. One is the thermal decomposition of oxygenated organic compounds in bio-oil and the second is the methanization reactions of carbon dioxide and carbon monoxide. Ethene can be obtained from the decomposition of alcohols contained in bio-oil.

More specifically, bio-oil contains many different ingredients, such as acids, alcohols, ketones, phenols, and their derivatives. The small molecules of bio-oil usually consist of carbon, hydrogen, and oxygen, joined together to form bonds like C-C, C-H, C-O, C=O and O-H [69]. The most representative molecules contained in bio-oil are acetic acid, ethanol, and phenol [69]. The reaction paths of acetic acid, a major component of the aqueous phase of bio-oil, that emerged during the catalytic vaporization of steam are particularly complex and the likelihood of the formation of various intermediates and other products varies depending on the catalyst used and the conditions under which the reactions are taking place [69]. Reducing methane levels is necessary to increase the selectivity to produce hydrogen-rich gas. This is because methane is a hydrogen-rich compound and does not promote the formation of molecular hydrogen. Thus, a highly active catalyst must be selected for the catalytic reforming of acetic acid vapor [78].

The ethanol steam reforming mechanism involves two main pathways. The first involves the dehydrogenation of ethanol, which results in the production of acetaldehyde and hydrogen. Acetaldehyde is then broken down to produce CH_4 and CO. Methane reforming ultimately produces hydrogen and carbon monoxide [69]. The second route involves the dehydration of ethanol. This reaction, then, produces ethylene, which either decomposes and produces hydrogen and biochar or reforms and produces hydrogen and carbon monoxide. In the latter case the carbon monoxide is converted to dioxide and water via the water-gas shift reaction. Based on the thermodynamics, it can be concluded that higher temperatures, lower pressures, and a higher water/carbon ratio could increase hydrogen production [69]. Finally, phenol reforming is favored using supported metal catalysts with many oxygen vacancies [24].

5.5. Factors That Affect Syngas Quality

The yield and composition of the produced gas varies depending on the properties of the input streams, the type of reactor used, the operating conditions as well as the output conditions of the syngas. The input streams include the feedstock (type and components) and the gasification agent (type and flow). The output conditions of the produced gas include its cooling and the removal of particles and tar. Finally, the operating conditions refer to the temperature, pressure, and residence time, which can be changed to control the gasification reactions [79].

From the research conducted in the present work, there has been found an increased interest in gasification under different operating conditions, such as the use of different types of gasifiers, different gasification agents (e.g., air, oxygen, steam, CO_2, or mixtures)

and finally possible use of catalysts and the effect they have on the production of final products and their composition.

5.5.1. Effect of the Gasifier Type

Gasifiers can generally be divided into various types such as fixed bed (upstream and downstream), fluidized bed (bubble or recirculation) or entrained bed. Gasifiers are categorized into different types based on the type of contact the reactants have, the direction of flow of the feedstock and the gasification agent, and the way in which the heat is provided to the reactor [79].

Fixed Bed Gasifiers

In general, this type of gasifiers is characterized by simplicity of design and operation, as well as a high level of combustion and heat exchange, which results in gases escaping at low temperatures and this ensures a higher efficiency of the gasification process. Due to the heat exchange, the fuel (bio-oil) dries at the top of the gasifier, which makes it possible to use fuels with high moisture content (up to 60 %) [80,81]. In addition, the produced gas is somehow filtered/purified, since the particulate matter, that is carried away by it, is retained by the bed material [80]. This helps to reduce the particulate matter of the gas. Moreover, the humidity of the air involved in gasification plays an important role in temperature control.

One of the disadvantages of this type of gasifier is the relatively large amounts of tar and other pyrolysis products that form, because the pyrolysis gas does not pass through the base of the reactor and therefore does not burn. This is especially important for the subsequent use of the fuel gas. If it is used in direct heating processes, no treatment is required, but if the gas is intended for use in engines, then cleaning is necessary [81]. However, the tar content of the gas produced by the downstream gasifier is lower than that of the upstream gasifier [80]. Due to the wide range of temperature profile of the gasifier, fixed bed gasifiers are mainly used for small or medium scale processes (5–100 MWth) [82]. In addition, the gas is prone to contamination by ash or other particulate matter and therefore requires a separation device to clean it [82]. Despite these disadvantages, this type of gasifiers is particularly popular due to their low tar content [80]. Tar is easy to condense inside an engine and it causes operational problems and frequent shutdowns for cleaning. Thus, a gas with a low tar content for use in gas engines and turbines is preferred.

Fluidized Bed Gasifiers

The first fluidized bed gasifier ever made is the Bubbling Fluidized Bed Gasifier (BFB) and it is a small or medium scale system (<25 MWth) [83], where the gasification agent enters at a relatively fast rate (0.5–1.0 m/s) [84]. The analysis and modeling of this type of gasifier requires detailed knowledge of the hydrodynamics of the bed [83].

The gasification agent can also be introduced into a second zone above the bed, to convert the volatiles and the char particles into gaseous fuel. Finally, a gas fuel with a relatively low tar content is produced. The ash is later removed from the syngas in gas-solid separation units [84].

Circulating fluidized bed gasifiers (CFBs) are in many ways like bubbling fluidized bed furnaces [81,85]. CFBs use one fluidized bed unit to perform the pyrolysis reaction, and then supply the inorganic heat carrier with the produced char to a second fluidized bed unit. This second unit is used to burn the char contained in the inorganic heat carrier to produce the heat required for the first unit, to which the inorganic carrier is returned [80].

These types of gasifiers are especially beneficial when the inorganic heat carrier has catalytic properties, which cause the char to adhere to the surface of the catalyst. Burning the char from the surface is the only possible way to remove it, to enable the immediate recirculation of the clean catalyst in the first bed [80].

Entrained Flow Gasifier

This type of gasifier is commonly used in integrated gasification combined cycle (IGCC) applications [86]. Gasification reactions take place under extreme conditions of pressure and temperature (approximately 1400 °C and 2–5 MPa) and very short residence times (a few seconds) [87]. The increase in temperature is much higher than the melting point of the ash, resulting in the complete destruction of tar and oil. Such high temperatures usually lead to high levels of carbon conversion.

Zheng et al. conducted a series of gasification experiments to produce a gaseous fuel from bio-oil, derived from fast pyrolysis of rice husk, to exploit the latter to make it suitable as a transport fuel [88]. The bio-oil was gasified using air and steam as gasification agents and two factors were studied at a time: the vapor/bio-oil ratio and the temperature of the gasifier, to determine their effect on the quality of the syngas produced. The type of gasifier used was that of the entrained flow. This type of gasifier is also the most suitable for gasification using oxygen as a gasification agent of bio-oil [88,89]. The main advantages of the entrained flow gasifier are its simple design and the low tar and methane content of the produced gas, while the main disadvantages are the lower outlet gasifying rate, the poor heat transfer conditions, and the higher outlet temperatures [81,90]. The characteristics of the different types of gasifiers are summarized and compared in the schematic Figure 7 and comprehensive Table 9.
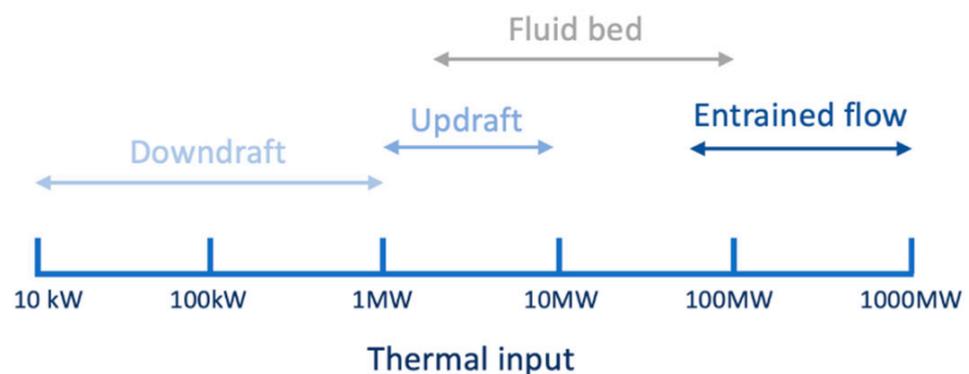
Figure 7. Range of power generation applicability for biomass gasifier types.

Table 9. Comparison between different types of commercial gasifiers [69,91].

Characteristic	Fixed Bed	Fluidized Bed	Entrained Flow
Feed size	<51 mm	<6 mm	<0.15 mm
Tolerance for fines	limited	good	great
Tolerance for coarse	very good	good	poor
Gas exit temperature	450–650 °C	800–1000 °C	>1260 °C
Feedstock tolerance	suitable for biomass	suitable for biomass (especially MSW)	unsuitable for biomass
Oxidant requirments	low	moderate	high
Reaction zone temperature	1090 °C	800–1000 °C	1990 °C
Steam requirment	high	moderate	low
Nature of ash produced	dry	dry	slagging
CGE	80%	89%	80%
Capacity	small	medium	large
Bio-oil application	steam gasification	steam gasification	non-catalytic oxidation
Problems	tar production and utilization of fines	carbon conversion	gas cooling
Range for power applicability of each biomass gasifier type	10 kW–10 MW	1–100 MW	70–1000 MW
Ref.	[9,79–82]	[9,80,83–85]	[9,81,86–90]

5.6. Effect of Gasification Agent on Syngas Composition

Tables 10 and 11 summarize several studies of bio-oil gasification resulting from fast pyrolysis. Through these tables, the effect of various gasification agents on the composition of the produced gas becomes clear. However, there are some gasification systems that work in the absence of gasification agents. These can also be considered steam gasification, given that bio-oil contains 15–30% water. Thus, all bio-oil gasification processes occur in the presence of steam [69].

When air is used as a gasification agent, the gas produced contains some nitrogen. This makes it unsuitable for Fischer-Tropsch synthesis [92], but it can be used for heat or energy generation. In the case of decentralized bio-oil production and its transfer to an industrial plant for gasification, it is possible to produce gas fuel on a large scale, which would serve for example the fuel requirements of a large gas-fired power plant [69].

In addition to the gasification agent, the composition of the gas produced is related to the feedstock, from which the bio-oil was produced, and to the gasifiers, catalysts and operating conditions (e.g., temperature, ER, etc.). As shown in Table 11, the concentrations of H_2 and CO have quite a difference. This is due to how easily they are affected by various gasification conditions, and by different gasification agents. The concentration of CH_4 is affected by the hydrothermal gasification of the aqueous phase of the bio-oil. This process occurs at temperatures higher than 374 °C and pressures higher than 22.1 MPa and shows some similarities to the formation of natural gas [69]. The H_2/CO and CO/CO_2 values show a relatively small deviation. The first depends on steam reforming processes and is particularly important for CO hydrogenation reactions, which include the Fischer-Tropsch synthesis. The second value is an indication of the ratio of carbon converted to CO, a main component of syngas. The value of this ratio is usually reduced as the steam-carbon ratio reduces [93]. To produce syngas, slightly higher H_2/CO values and lower CO/CO_2 values are usually preferred [69]. In addition, a significant amount of CO_2 is produced during gasification. Since zero carbon dioxide emissions are not possible, its subsequent use or capture is recommended [94].

5.7. Effect of Equivalence Ratio (ER)

ER (equivalent ratio) is an important parameter for the design of the gasifier and the process during the gasification of bio-oil and it is defined as the ratio of the supplied oxidizing agent (oxygen or air) to the amount of oxidizing agent required for the complete combustion of the fuel. Thus, in the case of combustion the oxidizing agent is in excess so ER > 1, ensuring the complete oxidation of the fuel, in pyrolysis, which takes place in the absence of oxygen the ER value equals 0, for the thermal decomposition of the fuel, while in gasification a lower amount of oxidizing agent is used and so it is 1 > ER > 0. ER is also a key factor for the design of a gasifier, and it is considered that slightly larger ER values can generate greater amounts of heat from the partial combustion of bio-oil during its steam gasification reactions [95].

The quality of the gas obtained from this process depends significantly on this parameter. The levels of CO, H_2 and CH_4 in the produced gas usually decrease with increasing ER, because an increase in ER means that oxygen is abundant and is able to oxidize larger amounts of CO, H_2 and CH_4 to produce CO_2 and H_2O [69]. More specifically, a very high ER value will lead to the formation of products of perfect combustion, e.g., the undesired products [96].

Table 10. Effect of bio-oil gasification parameters on the produced gas.

	Gasification Parameters							Gas Characteristics					
Feedstock for Bio-Oil	T (°C)	Gasifying Agent	Steam/ Bio-Oil	Gasifier Type	ER (kg/kg)	Bio-Oil Flow Rate (kg/h)	Air Flow Rate (kg/h)	Gas Yield (m³/kg bio-oil)	CGE (100%)	CCE (100%)	LHV (MJ/Nm³)	Oxidation Degree	Tar (mg/Nm³)	Ref.
						Agro-industrial waste								
Rice husk	1000	air-steam	0 1 2 2.5 3 4 5	entrained flow	0.4	9.0	21.32	1.30 ± 0.002 1.75 ± 0.01 1.81 ± 0.01 1.90 ± 0.01 1.86 ± 0.02 1.65 ± 0.02 1.47 ± 0.02	0.54 ± 0.007 0.72 ± 0.012 0.79 ± 0.014 0.90 ± 0.012 0.84 ± 0.009 0.51 ± 0.007 0.40 ± 0.006	0.62 ± 0.02 0.75 ± 0.02 0.82 ± 0.05 0.93 ± 0.05 0.89 ± 0.06 0.87 ± 0.02 0.81 ± 0.02	6.50 ± 0.10 7.20 ± 0.11 7.63 ± 0.13 8.26 ± 0.12 7.88 ± 0.01 5.34 ± 0.04 4.78 ± 0.08	0.17 ± 0.002 0.20 ± 0.002 0.25 ± 0.005 0.31 ± 0.001 0.43 ± 0.005 0.46 ± 0.003 0.54 ± 0.003	280 ± 8.89 180 ± 3.61 100 ± 1.73 52 ± 1.0 58 ± 1.00 67 ± 2.65 90 ± 4.00	[88]
	700 750 800 850 900 950 1000	air-steam	2.5	entrained flow	0.4	9.0	21.32	1.10 ± 0.01 1.22 ± 0.01 1.32 ± 0.01 1.43 ± 0.01 1.60 ± 0.02 1.71 ± 0.02 1.90 ± 0.03	0.37 ± 0.005 0.44 ± 0.008 0.52 ± 0.007 0.58 ± 0.007 0.66 ± 0.008 0.78 ± 0.012 0.90 ± 0.014	0.69 ± 0.01 0.74 ± 0.01 0.80 ± 0.03 0.84 ± 0.03 0.87 ± 0.05 0.87 ± 0.02 0.93 ± 0.04	5.85 ± 0.09 6.23 ± 0.09 6.83 ± 0.12 7.02 ± 0.10 7.21 ± 0.10 7.9 ± 0.05 8.26 ± 0.14	0.19 ± 0.002 0.22 ± 0.003 0.26 ± 0.005 0.31 ± 0.001 0.32 ± 0.004 0.31 ± 0.003 0.31 ± 0.003	270 ± 8.88 230 ± 4.36 200 ± 3.46 150 ± 2.65 93 ± 3.00 65 ± 2.65 52 ± 2.00	
Rice husk	1000	air air-oxygen oxygen	-	entrained flow	0.3	-	-	-	0.747 0.732 0.749	-	8.00 11.10 13.80	-	1300 820 490	[95]
						Agricultural waste								
Corn stalk	500–800	steam	-	dual fixed beds	-	0.0144	-	-	-	-	0.87	-	-	[97]
Wheat straw	1272	oxygen	-	entrained flow	-	-	-	-	-	-	0.89	-	-	[98]
						Other								
Hard wood	1000–1400	steam	-	entrained flow	-	0.018	-	-	-	-	-	10.6	-	[99]
Birch wood	800	steam	-	entrained flow	-	-	-	≈0.72	-	0.59	-	-	-	[99]
Coal/bio-oil slurry	1300	steam	-	entrained flow	-	-	-	-	-	0.924	10.7	-	-	[96]
Poplar wood	725	oxygen	-	entrained flow	0.27	-	-	-	-	0.80	12.48	-	-	[100]
Pine wood	1321	oxygen	-	entrained flow	-	-	-	-	-	0.96	-	-	-	[98]

Table 11. Effect of bio-oil gasification parameters on the composition of the produced syngas.

Bio-Oil	Gasification Agent	T	H_2 (vol%)	CO (vol%)	CH_4 (vol%)	CO_2 (vol%)	N_2 (vol%)	S/C (mol/mol)	H_2/CO	CO/CO_2	LHV (MJ/Nm^3)	Ref.
					Agro-industrial waste							
Rice husk	air-steam	1000	30.6	15.3	0.6	20.6	32.2	4.36	2.00	0.74	8.26	[88]
Rice husk	air air-steam oxygen	1000	25.0 30.1 37.3	22.3 28.1 32.5	3.4 5.2 6.7	5.6 12.5 18.3	41.6 20.3 -	0.4	1.12 1.07 1.15	3.96 2.25 1.78	8.00 11.10 13.80	[95]
					Agricultural waste							
Corn stalk	steam	500–800	72.5	0.75	0.06	27.3	-	10.6	-	-	-	[97]
Wheat straw	oxygen	1272	30.3	46.4	1.98	23.1	-	-	-	-	-	[98]
					Other							
Hard wood	steam	1200	55.3	16.0	4.7	22.4	-	7.39	3.45	0.71	10.60	[99]
Coal/bio-oil slurry	steam	1300	55.44	18.97	3.1	22.49	-	5	2.92	0.84	10.7	[96]
Poplar wood	oxygen	725	48.3	42.6	5.3	3.8	-	0.023	1.13	11.2	12.48	[100]
Pine wood	oxygen	1321	30.1	45.6	2.0	22.5	-	-	-	-	-	[98]

For the oxygen bio-oil gasification the ER value should be between 0.2 and 0.3 [69]. When air is used as a gasification agent, then an increase in ER inevitably means an increase in nitrogen in the system, and since this is an undesirable product for any application of the gas produced, the optimal ER value should be kept as low as possible. As expected, an increased ER value will result in reduced LHV, regardless of the gasification agent. It has also been found that the LHV is lower when air is used, which is also confirmed by Table 10. As the ER value increases, the tar concentration decreases. Thus, when an application requires a small tar concentration, then the highest possible ER value is preferred. As for the CCE value, it increases as the ER increases, but decreases when the value of the latter continues to increase [69]. In general, the effect of this parameter is similar in bio-oil and solid biomass gasification processes [101].

5.8. Effect of Steam/Carbon Ratio (SC)

The steam/carbon (SC) ratio is defined as the total moles of water, including the water contained in bio-oil, to moles of carbon in the feed [69]. It is one of the most important parameters for the gasification of bio-oil, alongside with the ER value. The superheated steam, which contributes to the production of hydrogen, is used either alone in bio-oil steam gasification, or in combination with air/oxygen. In air-steam gasification, an increased value of the SC ratio leads to a decrease in the concentration of CO and CH_4 and an increase in CO_2. This is mainly due to the increase in the produced CO_2 through the water-gas shift reaction, at the expense of CO, and the conversion of CH_4 through steam reforming reactions [96]. Typically, methane and carbon dioxide are inert compounds when CO hydrogenation reactions take place, and a reduced CO_2 concentration is considered favorable [69].

Hydrogen levels usually show a gradual increase followed by a gradual decrease as the SC increases, while the nitrogen concentration has the exact opposite behavior [69]. Regarding the tar levels, they show a significant decrease followed by a slight increase as the SC value increases [69]. Tar reforming can take place resulting in the formation of hydrogen and carbon monoxide. Excessive use of steam, however, can intensify thermal decomposition reactions that lead to tar production.

In general, a higher SC favors steam reforming and water-gas reactions, resulting in the production of gases of smaller molecules, such as CO, H_2, CO. However, as already mentioned, more steam can intensify the thermal decomposition reactions or reduce the gasification temperature and it can contribute to the inhibition of the above reactions. Thus, the yield, the lower heating value and the CCE and CGE values of the gaseous product will reach their maximum values in bio-oil air-steam gasification processes [69].

In bio-oil steam gasification, a higher SC value favors its conversion to hydrogen, prolongs the life of the catalyst and reduces carbon deposition [102]. Thus, with increasing SC, the concentrations of hydrogen and carbon dioxide increase and the concentrations of carbon monoxide and methane decrease. Increasing the SC, however, will also increase the operating costs of the process. Typical values for this parameter range from 4–6 [69]. Valle et al. (2018) used two values for the steam-carbon ratio, S/C = 1.5 and 6 respectively, for bio-oil steam gasification at 700 °C. Using the higher SC value, they managed to produce a gaseous product rich in hydrogen (66 vol% H_2), while avoiding a higher energy cost, that the choice of a higher SC value would have [103].

5.9. Effect of Temperature

The gasification temperature is a determining factor for the quality of the syngas produced and the tar concentration. The temperature in a gasification process is generally controlled by the rate at which the fuel is introduced into the system and by the ER value [104].

With increasing temperature, in a temperature range of 720–860 °C, the concentration of CO and H_2 in syngas increases, while the mole fraction of CO_2 decreases [104]. As it is known the water-gas shift and the Boudouard reactions lead to the formation of CO and

H_2, that are favored at higher temperature. Regarding gasification at higher temperature (1200–1300 °C), the results are different from the above. The CH_4 content decreases, heavier hydrocarbons or tar are formed and the production of CO and H_2 increases [79].

In the case of air gasification taking place in a fluidized bed reactor at a temperature range of 700–1000 °C, with increasing temperature, CO, H_2, and CH_4 are increasing, while the concentration of CO_2 decreases. At higher temperature, biochar and tar yields decreases, while the lower heating value (LHV) increases, and the gas yield approaches a maximum value at temperature of 1000 °C [105].

At lower temperatures (400–600 °C) the opposite phenomenon was observed by Wongsiriamnuay et al., whose experiments showed that an increase in temperature caused a decrease in the gas content in CO and H_2, while CO_2 increased [106]. A decrease was also observed in CH_4 content, due to its reforming reaction with steam, which was used as a gasification agent in the experiment. However, these results change when different gasification agents are chosen, which verifies the importance of this factor and at the same time points out the overall effect of the conditions under which a gasification process takes place on the produced gas.

In the same study, the lower heating value decreases, due to the decrease of the gas content in hydrogen and carbon monoxide at higher temperatures. Carbon conversion efficiency (CCE) increases as the CO_2 content increases, while the gas yield does not appear to be affected [79].

From the studies examined, the following results can be extracted regarding the effect of temperature on the produced gas. Higher temperatures contribute to lower concentrations of biochar and higher concentrations of H_2 gas and generally an increase in the gas yield, due to the release of more volatiles. The increase in hydrogen production is due to the thermal decomposition reactions of tar, which at the same time reduce its concentration. According to the Le Chatelier principle, an increase in temperature favors the formation of products of endothermic reactions and reactants of exothermic reactions. Thus, endothermic hydrocarbon reforming is favored by increasing temperature (reactions 1, 2 and 11 of Table 8). Hydrogen concentration increases due to reactions (1) and (2), while methane concentration decreases due to the steam-methane reforming reaction. At the same time, the exothermic reaction of the partial combustion of biochar (R4) affects the composition of the gas produced. High temperatures are not favorable to CO production, so its concentration decreases with increasing temperature. The increase of CCE is due to the conversion of carbon and steam through the Boudouard endothermic reaction (R1) and the water-gas shift reaction (R2). In general, high temperature favors hydrogen production and the gas yield, but this is not always the case for the heating value, which decreases at very high temperatures.

5.10. Effect of Catalysts

Catalysts commonly used in catalytic steam gasification include mainly transition metal catalysts such as nickel (Ni), cobalt (Co) and copper (Cu), noble metal catalysts such as rhodium (Rh), platinum (Pt), ruthenium (Ru) and palladium (Pd) [69]. Although noble metals are usually more expensive than transition metals, they have better catalytic activity and resistance to carbon deposition. Nickel and cobalt catalysts have better activity than copper catalysts, while the activity of noble metal catalysts follows the order: Rh > Pd > Pt > Ru for steam reforming of ethanol in bio-oil [69]. Nickel catalysts are most commonly used in the steam reforming of the acetic acid contained in bio-oil. However, some noble metal catalysts, such as rhodium and ruthenium, have better activity than nickel.

Catalytic steam reforming takes place at relatively high temperatures, leading to high energy consumption. However, electrochemical catalytic reforming of bio-oil for hydrogen production can be carried out at a moderate temperature (400–500 °C) and in this case the hydrogen production efficiency can exceed 90% [69].

6. Syngas Characteristics for the Downstream Part of the Combined Process

6.1. Gas Lower Heating Value (LHV)

The heating value of the gas produced is related to its composition. As shown in Table 10 the lower heating value (LHV) of the gases produced ranges from 4.8 to 13.8 MJ/Nm^3. The highest heating value corresponds to the oxygen bio-oil gasification. In this case the concentration of CH_4 is the highest in the table, namely 6.7 vol%, which explains the increased LHV. All gases produced from these experiments are suitable for power generation at a power plant that uses gas turbines, since the latter requires a minimum calorific value of 4.18 MJ/Nm^3 [69].

6.2. Wobbe Index

The gases produced could also be used to meet the energy needs of urban areas. However, to replace one gaseous fuel (e.g., natural gas) with another (syngas), it is necessary to examine the Wobbe index [107]. The Wobbe index is an indicator of interchangeability, defined as the higher calorific value of a fuel gas divided by the square root of its relative density, under the same conditions [108]. The higher the calorific value of a certain quantity of a fuel gas, the higher the Wobbe index. It is also used to compare the energy released during the combustion of gaseous fuels of different compositions in a certain application. If the indexes of two different fuels are identical, then for a given pressure, the energy released will also be the same [69]. Usually, the Wobbe index of syngas is lower than that of natural gas [108].

6.3. Tar and Particulates in Syngas

During the gasification process of bio-oil, a certain amount of tar is produced. As mentioned above, tar is a thick brown/black liquid and is a complex mixture of condensable organic substances, such as aromatic hydrocarbons, phenol derivatives and oxygen compounds, which usually have a molecular weight greater than benzene [109]. Tar is undesirable because it can lead to corrosion, plugging and fouling of pipelines and equipment and poisoning of the catalysts for syngas applications [69]. Typical tar levels in gases resulting from bio-oil gasification using entrained flow or fluidized bed gasifiers are between 50 and 2600 mg/Nm^3 [69]. In general, these levels are lower than those of biomass gasification gases, due to the extremely high temperatures used in bio-oil gasification, for example in an entrained flow gasifier [69]. In these gasifiers, bio-oil is atomized and separated into a large number of droplets, which can instantly be pyrolyzed or evaporated to form steam during the pyrolysis step. The steam reacts with the gasifying agent and the gas is produced. Thus, these gasification processes are much faster when bio-oil is used rather than solid biomass [69]. Also, the water contained in the bio-oil can react with tar through reforming reactions, which result in the production of hydrogen and carbon monoxide. However, it is reported in many studies, such as that of Feng et al. (2016) that tar-free gas production is possible even from solid biomass through a two-stage gasification process (pyrolysis and reforming) [96].

Regarding steam gasification in fixed bed reactors, there is not much information about the quantities of tar produced. This may be due to the use of the water contained in the bio-oil during this process, while tar is known to be derived from lignin derivatives contained in the organic phase of the bio-oil [69]. Another reason is the use of pressure pumps to feed the bio-oil to the reactor and thus the whole surface of the catalyst is covered. Steam reacts with the bio-oil, which is a continuous flow phase, producing hydrogen. Tar forms on the surface of the catalyst. Carbon deposition or catalyst deactivation often occurs due to the formation of biochar during these processes [78].

In general, the gas produced from bio-oil gasification does not contain particulate matter. Bio-oil has a low ash content and is relatively clean. The ash contained in the original biomass is concentrated in biochar, which is separated from the bio-oil using solid-liquid separation equipment, such as cyclones and filters during the pyrolysis process. In addition, carbon or soot deposits are not frequently observed during bio-oil gasification in entrained

or fluidized bed gasifiers because bio-oil droplets are gasified easily [95]. Similarly, particulate matter is not carried away by the hydrogen-rich gas during steam gasification in fixed bed gasifiers [110]. Therefore, there are no restrictions on the application of this gas due to particle concentration.

As for tar, the produced gas can be used in direct combustion systems and there is no need for cleaning, because such systems usually do not have restrictions regarding the concentration of tar. However, the gas should not be cooled to temperatures below the dew point of tar during transportation [69]. The produced gas is also suitable for use in a Stirling engine, which has a high tar tolerance, for energy production. However, the gas cannot be fed directly into internal combustion engines or gas turbines. Finally, the restrictions regarding the tar concentration of fuel cells are even stricter. Therefore, it is often necessary to clean the gas before inserting it into an energy or heat generator.

6.4. Soot and Coke

Soot formation is a problem in gasification processes, regardless of the gasification agent. For oxygen gasification, soot is the result of pyrolysis due to incomplete combustion and its particles can cause serious environmental problems and they are associated with health hazards [69]. Also, the formation of soot leads to a decrease in the CCE value and leads to blockage and contamination of the equipment. Reducing or controlling soot formation is of great importance when it comes to bio-oil gasification. Zheng et al. did not find any significant amount of soot in their studies [88,95], while Chhiti et al. confirmed through their study that high temperature and the addition of oxygen or steam could reduce soot production [74].

The bio-oil steam gasification is usually accompanied by the formation of coke. Coke is high in carbon and can lead to catalyst deactivation, which is why it is undesirable during catalytic gasification. Molecules such as glucose, m-xylene, acetone and some phenols are responsible for coke formation when found in high concentrations in bio-oil [78] Increasing the temperature and the steam to air ratio can lead to the reduction of coke. However, in this case the operating costs increase as the steam reforming of bio-oil is an endothermic process [69].

6.5. Comparison of Bio-Oil and Heavy Fuel Oils Gasification

Vaezi et al. studied the gasification of heavy fuel oil for syngas production. Through their model, they predicted that using a low ER of 0.32, makes it possible to obtain a syngas with a LHV of about 15 MJ/m^3, when oxygen is used as a gasifying agent [111]. Comparing these results to the results of the studies shown in Table 10 regarding bio-oil gasification, and more specifically the gasification of bio-oil produced by pyrolyzing rice husk, for the same ER value and gasification agent, the LHV of the produced syngas is slightly lower. The H$_2$/CO ratio appears to be higher for the syngas produced by bio-oil gasification, which makes it even more appealing for the production of pure hydrogen for fuel cells applications. Finally, both are suitable for applications like gas turbines for power generation.

7. Looking at the Economic Viability of Bio-Oil Gasification

The production of advanced biofuels from the utilization of bio-oil can be economically advantageous. This is due to the simplicity that characterizes the production of bio-oil through pyrolysis. Bio-oil itself, as a liquid fuel, has several advantages, including more efficient and economical handling and storage, improved fuel properties and higher energy density compared to solid fuels [112].

The cost of producing bio-oil can range from $0.41 to $1.21 per gallon [113] and can be transported very economically using liquid tank trucks, when it comes to small-scale production, while for a larger scale production (>1700 m^3/day), it can be transported through pipelines (transport distance > 100 km) [69]. In addition, bio-oil can be upgraded and utilized in various processes and potential applications (e.g., energy and heat genera-

tion, transport fuels, chemicals, and materials), which has led to increased interest in the commercialization of the pyrolysis technology [112].

Another reason why the production of liquid fuel from solid biomass is particularly advantageous is the decoupling of bio-oil production (location, time, scale) from its use [69]. A BTL2 unit (biomass to liquid in two steps = local bio-oil production and central bio-oil gasification unit and synthesis for Fischer-Tropsch liquids) can have a quite large capacity, even when operating costs are at a minimum value [69].

Anex et al. compared the capital and operating costs of six scenarios of biomass conversion technology into liquid fuels, using pyrolysis, gasification, and biochemical methods [114]. Each unit studied had a capacity of 2000 tons/day and corn cob was used as feedstock. Their study showed significant differences in the total investment required for the three conversion methods, ranging from $200 to $610 million, with pyrolysis being the method with the lowest capital cost. Operating costs also varied considerably, with product prices ranging from $2.00 to $5.50 per gallon, with the lowest price corresponding again to the pyrolysis method.

Li et al. studied the economic feasibility of bio-oil production, bio-oil gasification, and conversion of syngas into Fischer-Tropsch liquid utilizing a unit of a 2000 tons/day capacity [115]. Based on an internal rate of return (IRR) of 10%, the minimum selling price of the fuel was calculated at $5.59 per GGE (gasoline gallon equivalent). Thus, it is understood that this energy production system still has some risk in the present technical and economic situation and a unit of larger capacity might be needed to make such a project economically feasible.

Bio-oil steam gasification or bio-oil reforming is mainly focused on hydrogen production. Sarkar and Kumar developed a techno-economic model to determine the operating costs of hydrogen production through fast pyrolysis followed by bio-oil steam gasification for three different feedstocks for a unit of 2000 dry tn/day capacity [116]. Total production costs (capital, operating, maintenance, administrative, bio-oil production, bio-oil transportation) were found to be $2.40 per kg H_2, $3.00 per kg H_2 and $4.55 per kg H_2, respectively. The relatively higher production costs may reflect on the smaller capacity of the unit.

Zhang et al. carried out a comparative techno-economic analysis of bio-oil reforming and bio-oil non-catalytic partial oxidation for hydrogen production [117]. The data input included a 2000 tn/day of feed, a capacity of 160 and 147 tn/day and an internal rate of return 18.6% and 8.4%, respectively. The sensitivity analysis showed a great impact of the hydrogen price and yield on the internal rate of return. Thus, given that the gas mixture is richer in hydrogen when it is produced via the bio-oil reforming method, the latter was proven to be more profitable. According to Zheng et al. when it comes to hydrogen production, it can be assumed that a higher internal rate of return could be achieved when bio-oil is produced locally, while bio-oil reforming is performed centrally in a central site [69].

8. Discussion

Although slow pyrolysis is mainly applied to produce biochar, as it is the main product in quantity and the process conditions (slow heating rate) favor its properties, the formation of some by-products, i.e., bio-oil and a mixture of gases is inevitable. Valorizing this bio-oil via gasification promotes a circular economy approach, as it minimizes process wastes and energy losses.

The literature search revealed several sources that utilize solid biomass derived from agricultural and agro-industrial waste of Mediterranean origin, because the method of slow pyrolysis is very common and already well established, and although bio-oil is a by-product, almost all the articles found, apart from the char properties, also studied those of the bio-oil produced. Other raw materials that are largely utilized are various types of wood, algae, various sludges, and animal manure.

The literature search on bio-oil gasification did not reveal much on the use of bio-oil resulting from slow pyrolysis of biomass. Instead, all sources found, examined bio-oil

gasification resulting from fast pyrolysis of various raw materials. Thus, in the present study, various solid raw materials were included, to compare as many different composition materials and operating conditions as possible.

Regarding the bio-oils produced by slow pyrolysis compared to those produced by fast pyrolysis, although as mentioned before the latter is more suitable for steam gasification processes, it is considered that the properties that make them suitable for specific methods is particularly prone to changes of the process parameters. This means that it may be possible to form two bio-oils, one from slow and one from fast pyrolysis, which, after proper adjustment of the operating conditions, show the same properties.

Advantages of Coupling Pyrolysis and Gasification for Syngas Production

Examining the coupling of the two processes of pyrolysis and gasification of biomass derived from agricultural and agro-industrial waste, several benefits as well as drawbacks were arisen. In Table 12 the possible advantages and disadvantages of the overall process are listed.

Table 12. Advantages and disadvantages of pyrolysis and gasification coupling.

Advantages	Disadvantages
+ It contributes to the rise of the use of renewable energy sources and the restriction of the use of fossil fuels.	
+ Can be used to fight against climate change.	
+ Recovery of a higher percentage of products through pyrolysis as opposed to simple combustion.	
+ Bio-oil is more suitable for gasification on a larger scale than solid biomass.	
+ High conversion efficiency	− High initial investment cost.
+ The production of high energy density bio-oil on a large scale can reduce its transport costs to central gasification units in contrast to the high costs for solid biomass transport.	− Not economically feasible for smaller scale production − Complex process − Necessary cleaning/upgrading of produced gas before use or complete gasification of char.
+ Bio-oil can be produced where biomass is available and then transported for processing.	− Possible carbon deposition and catalyst deactivation during catalytic steam reforming of bio-oil.
+ Possible economic growth and job creation in rural areas	− Possible carbon deposition and catalyst deactivation during catalytic steam gasification of bio-oil.
+ Gas production with a minimum amount of tar, the presence of which damages the equipment.	− During conventional gasification a significant part of the feedstock is combusted to provide the necessary heat for the endothermic gasification reaction.
+ The reaction temperature can be optimized independently for the pyrolysis and reforming stage.	
+ Deactivation of the catalyst by contamination can be avoided.	
+ Syngas produced from bio-oil is cleaner than that produced from direct biomass gasification.	
+ Ability to recover green chemicals from bio-oil before gasification.	
+ Gas product with relatively low methane content.	

9. Conclusions

This study proposes a circular economy conceptual approach to produce syngas via bio-oil gasification. Biooil derives as the byproduct of pyrolysis-to-biochar process fueled with agricultural and agro-industrial waste of Mediterranean origin.

Factors that affect the quality of bio-oil, such as pyrolysis temperature and the properties of the raw material are found to be of the utmost importance. The conditions under which the gasification reactions take place (e.g., temperature, gasification agent, etc.) have a catalytic role in the syngas yield and quality.

Bio-oil (pyro-oil) is an interesting alternative energy carrier because of the advantages it offers over the solid biomass and waste. Solid biomass and waste energy production is lacking uniformity, have low energy densities and large amounts of ash. They are also local-

availability dependent. Pyro-oil is a better intermediate energy carrier than solid biomass for feeding a gasifier due to its lower transportation cost to the site of the gasification plant.

The literature search has shown that studies on bio-oil gasification are very limited; the proposed pathway is innovative under the concept of circular economy. The proposed model of WtE facilities is changing the recycling economy into a circular economy where nothing is wasted, while a carbon negative energy carrier can be achieved.

Regarding the economic feasibility of such a model, there are advantages and disadvantages. Although the transportation cost of bio-oil gasification can be lower compared to that of the solid biomass, a bio-oil gasification system requires a higher capital investment and can only be profitable at large scale. In addition, although the concept of coupling of agricultural and agro-industrial waste slow pyrolysis with pyro oil gasification for syngas production could be a very promising circular economy model for zero waste and carbon negative energy production, there is a need for R&D to be conducted for feasibility and viability of such a project.

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