




## Review

# Pyrolysis of Waste Biomass: Technical and Process Achievements, and Future Development—A Review

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**Abstract:** Pyrolysis has been applied in the human economy for many years, and it has become a significant alternative to the production of chemical compounds, including biofuels. The article focuses mostly on recent achievements in the technical and processing aspects of pyrolysis. The aim of the review is to present the latest research on the process of waste biomass pyrolysis to fuel production. The paper describes the mechanisms of the pyrolysis process, composition, and properties of the obtained fractions, namely pyrolysis gas, bio-oil, and biochar. Additionally, the technical aspects of the pyrolysis process are mentioned, with particular attention to the construction of the reactors. The process of waste biomass pyrolysis allows for obtaining many chemical compounds (second-generation biofuels). Optimization of the pyrolysis process allows obtaining the desired products that are applied in the chemical industry, energy, and transport. The application of pyrolysis gas, oil, and biochar as valuable chemical compounds are related to the intensifying effects of climate change, biofuel production, and waste management in accordance with the principles of sustainable development. In recent years, there has been large-scale research into the use of renewable energy sources through pyrolysis. This will make it possible to significantly reduce the carbon footprint and produce second-generation biofuels in a sustainable manner. Current research into the mechanisms of pyrolysis processes is promising, and will therefore provide access to clean and low-cost compounds that will have broad applications in the energy, chemical, agricultural, and transportation industries.

**Keywords:** pyrolysis; pyrolysis reactors; bio-waste; biofuels; biochar; pyrolytic gas



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## 1. Introduction

From the point of view of biomass used for energy purposes, there are three important secondary energy carriers: electricity, heat, and transport fuel (in its liquid and gas forms). The first two carriers conventionally refer to bioenergy, and the third to biofuel. The application of different technologies allows biomass to be converted to each of these carriers, and at the same time, each of the carriers can be used interchangeably. For example, transport fuel can be used to supply an electricity generator or boiler, and electricity can be used to supply vehicles. In order to distinguish the sectoral use of biofuels, it is assumed that liquid biofuels are fuels used in transport, and bioliquids, as well as solid and gaseous biofuels, are fuels used to generate heat and electricity [1,2].

The production process of first-generation biofuels has been questioned, mainly as a result of the conflict with food production and adverse environmental effects related to indirect land use change. The above reservations do not apply to the second generation of biofuels produced from lignocellulosic raw materials that do not compete with food production and have a potentially marginal degree of impact on land use changes [3].

Physicochemical transformations and conversions of fuels are processes targeted at the transformation of the chemical energy from a fuel into another type of energy (direct transformation), or the transformation of fuel from one form into another, which usually allows easier further handling (indirect transformation). An example of direct conversion

is fuel combustion. In turn, the processes of indirect fuel conversion can be divided into the following:

- Pyrolytic processes, in which the main factor of the changes taking place is the heat supplied to the processed fuel [4,5];
- Oxidative processes, where the main factor causing the fuel conversion is both free and chemically bound oxygen (e.g., in the form of  $\text{CO}_2$  or  $\text{H}_2\text{O}$ );
- Hydrogeneration processes, in which hydrogen is the main factor causing fuel conversion [6].

The process of waste biomass pyrolysis allows for obtaining many chemical compounds (second-generation biofuels) [7]. The three most common fractions involve gaseous [8], liquid (often called bio-oil) [9], and solid (biochar) [10] forms. Optimization of the pyrolysis process allows obtaining the desired products that are applied in the chemical industry, energy, and transport [11,12].

The war in Ukraine caused major perturbations in the fuel market, leading to a large price increase. Biofuels obtained in the pyrolysis process can partially fill the gaps in the fuel market. A country developing pyrolysis technology will be energy-independent to a large extent.

The aim of this review is to present the latest research on the process of waste biomass pyrolysis to fuel production. The paper describes the mechanism of the pyrolysis process, composition, and properties of the obtained fractions, i.e., pyrolysis gas, bio-oil, and biochar. Additionally, the technical aspects of the pyrolysis process are mentioned, with particular attention to the construction of the reactors.

In our literature review, we prioritized articles published in the past 2–3 years. As a result, this article contains the latest information on the global development of pyrolysis of waste biomass. In addition to the “typical overview”, a section was added on the latest research, mainly preliminary perspectives, as well as on the possibilities of further development of this technology.

## 2. Pyrolysis Processing and Technology of Biomass

The biomass pyrolysis process consists of the following steps: receipt and storage of biomass processing of the raw material (e.g., shredding, drying), the actual pyrolysis in a suitable bioreactor, separation of the solid residues (ash and carbonization), cooling and condensation of the vapor, and collection of bio-oil. Prior to condensation, the pyrolytic vapors may be catalytically reformed to achieve selectivity for the preferred product. Part of the gaseous product may be burned to obtain heat for the raw material pretreatment (e.g., drying) [13].

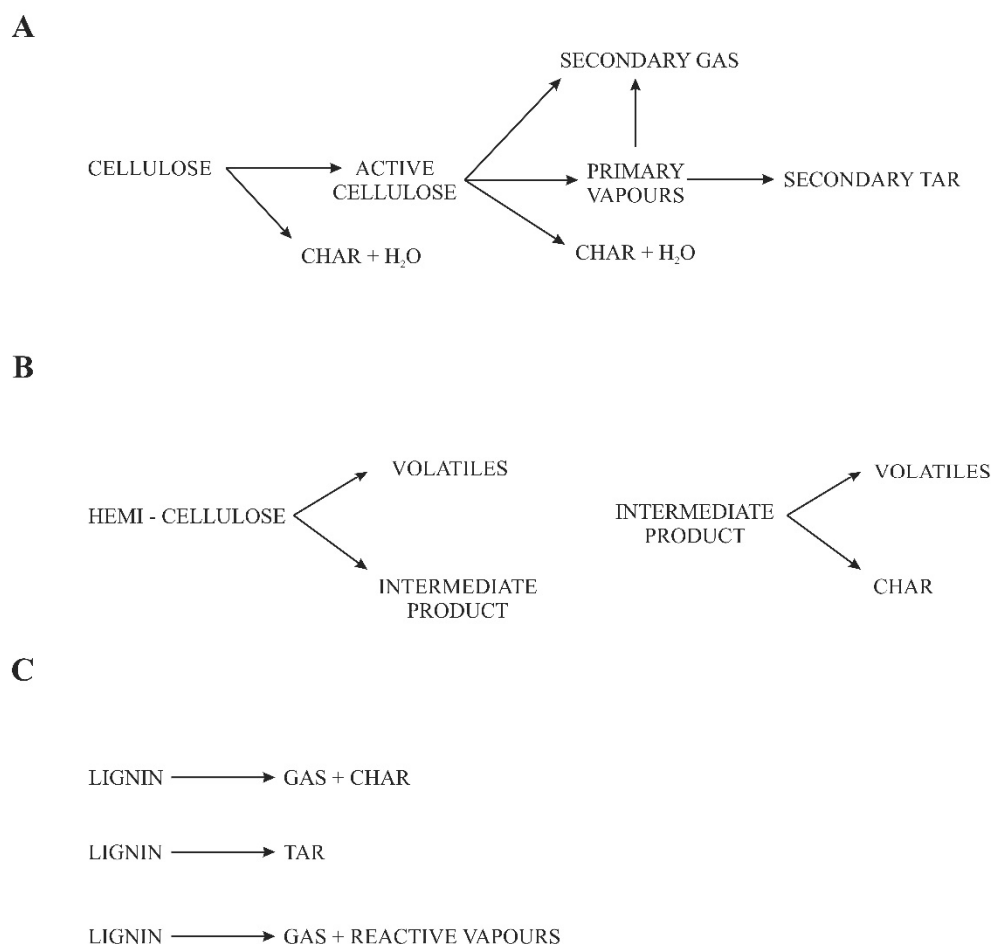
It is virtually impossible to clearly define the pyrolysis mechanism for all types of waste [14,15]. Waste is a group of materials with extending diversity in terms of types of chemical substances; therefore, the mechanism of pyrolysis of various wastes has become the subject of much research and scientific work [16,17]. The easiest way to comprehend the pyrolysis mechanism can be presented in the wood waste example. The mechanism of wood pyrolysis at low heating rates, i.e., in conditions commonly used in biochar production systems, includes the following stages:

- When the temperature of the wood rises from 105 °C to 120 °C, water is released which is not chemically bound to the organic matter of the wood (absorbed water), with a further increase in temperature from 245 °C to 265 °C;
- Water chemically bound in the cellulose structure and the release of  $\text{CO}_2$ , CO, and small amounts of condensing acetic acid and methanol vapors also begin to emit small amounts of wood tar;
- Above 265 °C to 275 °C, the process becomes exothermic, with the strong release of methanol, acetic acid, acetone, lighter hydrocarbons, wood tar, and small amounts of hydrogen, and the amount of  $\text{CO}_2$  and CO released decreases;

- At temperatures above 400 °C, the remaining organic matter is aromatized, resulting in the formation of quasi-graphite layers, and the transformation of wood into biochar (char) is practically completed [13,18].

The pyrolysis process mainly covers waste materials from food processing, agriculture, and forestry. The source of raw materials consists, therefore, of wood biomass (branches, chips, shavings, bark, and woody plant stems), agrarian biomass (lucerne, giant miscanthus, millet, cereal straw, fruit residues, seed shells, bagasse, food waste), water biomass (algae, animal biomass (e.g., poultry processing waste)), sewage sludge, and waste from the paper industry [19,20].

It is believed that in the process of pyrolysis of wood, it is possible to obtain the same products as the ones that would be formed during the separate thermal decomposition of its three main components: lignin, hemicelluloses, and cellulose (Figure 1) [21]. Their decomposition takes place at different temperature levels: hemicellulose, 200–260 °C; cellulose, 240–350 °C; lignin, 280–500 °C. The course of the decomposition also depends on the reaction atmosphere, pressure, and composition of the input material. As a rule, increasing the pressure and low heating rates result in an increase in the efficiency of the char (in this case, biochar) [22,23].



**Figure 1.** Decomposition mechanism of (A) cellulose, (B) hemicellulose, and (C) lignin (own elaboration from [22,23]).

The pyrolysis of lignocellulosic biomass is already fairly well understood. It is known that each of the components of lignocellulose breaks down to produce other substances—cellulose and hemicellulose form volatile products, while lignins form a solid residue. As mentioned in the introduction, other types of biomass are now increasingly being used to obtain chemicals or fuel components. Microalgae have gained prominence because

they have many advantages over lignocellulosic feedstocks: they have higher production efficiency, they do not compete with traditional agricultural products because they can be grown on wasteland or sewage land, and they are extremely rich in oil, which sometimes accounts for more than 60% of dry matter in some algal species. Lignin is a complex natural polymer in which individual units contain oxygen functional groups: carboxyl, methoxy, hydroxyl, and carbonyl. The high content of methoxy groups in lignin may hinder the formation of biochar as the pyrolysis temperature increases. This phenomenon is caused by the decomposition of methoxy groups and leads to the formation of low-molecular radicals that can stabilize the macrostructure fragments of lignin and, consequently, limit their polymerization to biochar. The main products of lignin decomposition in the range from 400 to 800 °C are phenols. During the thermal decomposition of methoxy groups, low-molecular-weight products may also be formed, e.g., methane and methanol. Additionally, oxygen groups derived from CO<sub>2</sub>, CO, or formaldehyde may remain in the side chains [24,25]. Elkhalfa et al. [26] used the Coats–Redfern model to determine the kinetic mechanism of samples using sixteen solid-state reaction processes. They found that, of all the models, those based on first-order reaction rates (F1) were the most fitting. Pyrolysis of plant waste is a highly promising option for obtaining chemicals, as indicated by the thermodynamic characteristics. Positive values of  $\Delta G^\circ$  and  $\Delta H^\circ$  and a large range of A values revealed that all samples were characterized by complex and multiphase degradation reactions.

Ansari et al. [27] reported the most important pyrolysis reactions obtained as a result of the controlled process. The mechanisms of pyrolysis reactions, such as cleavage of the glycosidic bond of cellulose (by breaking the end and middle chain), were experimentally confirmed, and included the reaction of dehydration of cellulose (or glucose)-derived sugars to levoglucosan and the indirect conversion of anhydro sugar into furans. The breakdown of hemicellulose into individual chemical compounds (formaldehyde, xylose, acetic acid, acetaldehyde, and acetone) and non-condensing gases was presented. Then, the thermal breakdown of lignin into syringes and guaiacol as well as non-condensing gases by decarbonization, decarboxylation, and demethylation reactions was discussed. It was found that the naturally occurring metals in biomass showed both catalytic and anti-catalytic activities in pyrolysis reactions [28,29]; some catalysts such as Ca<sup>2+</sup> and Mg<sup>2+</sup> favored the formation of volatile products, while others favored the production of decolorizing carbon.

Liu et al. [30] showed that the concentrations of volatiles are arranged in the sequence CO > CO<sub>2</sub> > aliphatic C-O(H) > C-O(C) in esters > aromatics > H<sub>2</sub>O > phenolic hydroxyl > aliphatic hydrocarbons > CO, reaching a peak at around 410–433 °C. The result of in situ FTIR deconvolution indicates that the dehydration of the hydrogen bond network started below 250 °C, and this dehydration weakened the bond strengths to the greatest extent in the degradation of macromolecular structures. It was also found that the formation of aromatic groups and CO were caused by intramolecular OH dehydration and condensation reactions with the removal of C-Hn (hydrocarbon groups) at 150–260 °C. It was also noted that OH and C-H groups were positively correlated. In addition, the transformation temperatures of various C-O groups suggested that the aliphatic C-O-C and C-OH groups were weaker than other C-O groups. At 500 °C, most of the oxygen-containing functional groups were eliminated.

Table 1 presents data characterizing the individual types of pyrolysis [31,32]. The composition of pyrolysis products varies depending on the chemical composition of the biomass and the conditions in which the pyrolysis process takes place. In addition, fast or flash pyrolysis is used to maximize the gas or oil production process. When rapid pyrolysis is used, the residence time at the final temperature is in the range of 0.5–5 s, and the particle size is less than 1 mm. In contrast, for flash pyrolysis, the residence time at the final temperature is less than 0.5 s, and the biochar is in the form of dust. Table 1 also shows pyrolysis conducted in vacuum (vacuum pyrolysis), steam (hydro-pyrolysis), and methane atmosphere (methane pyrolysis).

**Table 1.** Characteristics of individual types of pyrolysis (own elaboration).

Type of Pyrolysis	Duration	Heating Speed	Temperature (°C)	Products	Ref.
Slow charring	3–4 days	very slow	400	charcoal	[31]
Slow	hours/days	slow	400	charcoal, gas	[31]
Slow conventional	5–30 min	slow	600	charcoal, oils, gas	[33]
Intermediate	10 min.	intermediate	300–450	charcoal	[34]
Fast	0.5–5 s	very fast	300–1000	oils, gas	[35]
Flash liquid	<1 s	fast	650	charcoal, oils gas	[31]
Flash gas	<1 s	fast	650	oils	[31]
Ultra-flash	<0.5 s	very fast	1000	chemicals, gas	[31]
Vacuum pyrolysis	2–30 s	medium	400	chemicals, gas	[31]
Hydro-pyrolysis	<10 s	medium	500	oils	[31]
Methane pyrolysis	<10 s	medium	700	oils	[31]
				chemicals	[31]

### 3. The Biofuel Production in the Pyrolysis Processes

The rate of heating, the temperature of the process, and the chemical composition of the fuel determine the amount of products obtained in the pyrolysis process. The low temperature of the pyrolysis process (at a heating rate  $< 50\text{ }^{\circ}\text{C}/\text{min}$ ) increases the amount of the produced char [36]. Moreover, Zhao et al. [37] found that the optimal value of the heating rate equal to  $5\text{ }^{\circ}\text{C}/\text{min}$  can be indicated, at which the production of the char is the highest. Reducing the heating rate ( $10\text{--}200\text{ }^{\circ}\text{C}/\text{s}$ ) makes the liquid phase dominant over the products of the pyrolysis process.

The conventionally used pyrolysis process, where the temperature increase takes place slowly, has been used for thousands of years, and its main product was biochar. Normally, in the slow pyrolysis process, the biomass is heated to about  $500\text{ }^{\circ}\text{C}$ . The residence time of the vapors in the reactor ranges from 5 to 30 min. The long residence time of the particles in the chamber causes the secondary conversion of the originally formed products. The gas-phase components come into reaction with each other and as a result, they form a solid-carbon phase and a liquid phase [38]. The rapid pyrolysis process is a high-temperature process in which the biomass is heated at high velocity without any air access. The products obtained from this process include gaseous products, aerosols, and carbonized residue. Consequently, having obtained the process of cooling and condensation of the gas phase and aerosols, a brown liquid is developed, the calorific value of which is half that of traditionally obtained diesel fuel. Another feature of the discussed fast pyrolysis refers to careful control of the process temperature, which ranges between  $450\text{ }^{\circ}\text{C}$  and  $900\text{ }^{\circ}\text{C}$ . The third feature of the fast pyrolysis is the short residence time of the vapors appearing in the reactor (less than 2 s).

According to the above, the fast pyrolysis process presents a similar temperature range to the slow pyrolysis process but has a higher liquid yield (up to 75%), which contributes to high biofuel production. The main reason for this phenomenon is the shorter duration of the process itself. The flash pyrolysis process requires high temperatures of up to  $900\text{ }^{\circ}\text{C}$ , high heating rates of about  $1000\text{ }^{\circ}\text{C}/\text{s}$ , as well as the shortest reaction times—less than 1 s [39].

The studies on the biomass pyrolysis process also discuss the influence of the carrier gas on its efficiency. Pyrolysis takes place in an atmosphere of inert gas, including  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , or water vapor. The process of biomass pyrolysis in various gases has been investigated by Zhang et al. [40]. Their study revealed that there was a close relationship between the yield and composition of individual fractions and the carrier gas used in the process. The  $\text{CO}_2$  atmosphere resulted in a lower yield of solid residue compared to the other gases. In addition, a lower proportion of  $\text{CO}_2$  was noted than when  $\text{N}_2$  was applied



as a carrier gas. Additionally, the CO<sub>2</sub> atmosphere resulted in the highest concentration of acetic acid in liquid products.

Based on thermogravimetric analysis, there were no significant differences in the course of pyrolysis of spent brewer's grain at a heating rate of 5 °C/min under nitrogen, argon, and CO<sub>2</sub>. For each of the gases, the maximum conversion of samples was found at 284 °C. Analyzing the composition of the oil, it was found that the predominant group of organic compounds was acids (up to 68% of content) under argon atmosphere at 600 °C. The tests carried out showed a correlation between the content of the acids obtained and the carrier gas as follows: Ar > N<sub>2</sub> > CO<sub>2</sub>. It was noted that a smaller amount of acids was obtained at 600 °C and 700 °C for CO<sub>2</sub> as a carrier than was the case for N<sub>2</sub> and Ar. Moreover, the highest content of hexadecenoic acid was found, which was probably due to fat degradation. CO<sub>2</sub> promoted a decrease in the concentration of this compound in the oil at 600 °C and 700 °C. At 600 °C and 700 °C, argon provided more N-containing compounds. Charcoal obtained under CO<sub>2</sub> has the highest carbon content in indirect pyrolysis. The pro-environmental aspect is also important—CO<sub>2</sub> is used, which can indirectly lead to a reduction in the amount of CO<sub>2</sub> in the environment [23].

Then, Bieniek et al. [41] researched the effect of biomass particle size on the yield of pyrolysis products. It was found that the small particles promoted cracking of the intermediates in the pyrolysis reaction, resulting in greater production of H<sub>2</sub> and CO and less CO<sub>2</sub>. The spherical shape of the biomass particles resulted in a lower gas yield compared to the process in which flat or cylindrical particles were pyrolyzed.

In addition, Xu and Gholizadeh [42] obtained softwood char for the tests characterized by fine graining. The average grain size was only 0.50 mm, and the number of fractions below 1 mm accounted for over 84% by weight. The average grain size for the coke breeze was 1.45 mm, with almost 60% of fractions below 1 mm. The carbon content was at the level of 75% in the char and 81% in the coke breeze. The char practically did not contain any harmful sodium, chlorine, zinc, or copper. The sulfur content was also at a low level, 0.33%, compared to 0.9% in a coke breeze.

Niesler et al. [43] proposed an integrated process for the gasification and pyrolysis of biomass. H<sub>2</sub> content increased by 6.22% due to the synergistic action of S pairs and S free radicals. It should be noted that the free radicals modified the entire reaction system, facilitating condensation with dehydrogenation, which allowed the formation of new functional groups. In addition, the synergistic effect caused the conversion of N from nitriles to amines, which then condensed to N-PAH. If the moisture content of the wet sludge was in the range of 30–70%, more H<sub>2</sub> could be obtained, and thus also a higher calorific value of the pyrolysis gas.

Bio-oil is produced during pyrolysis (of biomass) and is a mixture of volatile substances [44]. The production of second-generation biofuel from bio-oil by hydrotreating has been widely studied in many research centers. The results are so promising that the technology is already being implemented and used in industry. The most important problem that arises is the formation of coke (mainly at high temperatures). Coke is formed because biomass contains complex organic compounds, as well as due to the presence of organic compounds in bio-oil with their reactive oxygen-containing functions. The main component of heavy organics in bio-oil formed from biomass is pyrolytic lignin (PL). The article discusses progress on the study of the physicochemical properties of PL and the possibility of separating PL from bio-oil. The conversion of PL to other value-added products (i.e., chemicals such as phenols, aromatics, hydrogen, antioxidants, biofuels, resins, binders, and carbonaceous materials) is proposed. An economic and technical analysis of various PL conversion routes was also conducted.

### 3.1. Pyrolytic Gas

Nevertheless, the gas mixture obtained in the pyrolysis process mainly contains CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> and small amounts of gases such as NH<sub>3</sub>, C<sub>3</sub>H<sub>8</sub>, sulfur oxides, nitrogen oxides, and alcohols with a low carbon number. The typical energy value of

pyrolytic gases is 10 to 20 MJ/m<sup>3</sup>. Before the practical use of pyrolysis gas, the elimination of undesirable components such as tar, dust, aerosols, water vapor, NH<sub>3</sub>, HCN, and H<sub>2</sub>S is required [11].

Pyrolytic gas has many potential applications, such as direct application to the production of heat or electricity (e.g., gas combustion in spark-ignition and diesel engines). In addition, the gases obtained are often used for auto-feeding pyrolysis reactors operating in a continuous system for preheating the inert gas in the chamber, or they can play the role of carrier gas in pyrolysis fluidized bed reactors [13].

Additionally, methane, and above all, biomethane, constitute an important and future energy carrier. Zhang et al. [45] proposed a new approach to the direct synthesis of methane-rich gases from reed pyrolysis performed under atmospheric pressure. Ni catalysts embedded in cane biocarbon were used. It was found that nickel catalysts supported by biochar performed better than cane catalysts supported by biochar from seawater. It was noticed that this was influenced by homogeneous Ni dispersion, large specific surfaces, and appropriate Ni–biochar interactions.

### 3.2. Pyrolytic Oil

For further explanation, pyrolytic oil is also referred to as bio-oil, pyrolysis liquid or tar, liquid wood, or wood oil [46]. The oil itself, as a condensation product of volatile substances, is a dark brown organic liquid, which in its composition contains significant amounts of water (usually 15–35% by weight) and numerous organic compounds such as alcohols, acids, ketones, aldehydes, ethers, phenols, esters, sugars, furans, alkenes, nitrogen compounds, as well as a small solid particles. Thus, before its application in engines, it is necessary to refine the pyrolysis oil. Currently, the production of liquid transport fuels from bio-oils is possible thanks to the developed technology of catalytic cracking and high-pressure hydro-processing. The potential application of pyrolysis oil is its use for the production of valuable chemical compounds, including food flavors or phenols for the production of resins, fertilizer, and pharmaceutical additives [47–49].

Several dozen organic compounds have been identified in pyrolysis oil; the most important of them are presented in Table 2 [31].

**Table 2.** List of chemical compounds occurring in the highest amounts in bio-oil from rapid pyrolysis (own elaboration from [31]).

Component	Content in Bio-Oil (%)
Hydroxyacetic aldehyde	0.9–13.0
Acetic acid	0.5–12.0
Formic acid	0.3–9.1
Acetaldehyde	0.1–8.5
Hydroxyacetone	0.7–7.4
Isoeugenol	0.1–7.2
Furfuryl	0.1–5.2
Alcohol 2,6-dimethoxyphenol	0.7–4.8
Etanedial	0.9–4.6
Phenol	0.1–3.8
Formic aldehyde	0.1–3.3.
Acetone	2.8
Eugenol	0.1–2.3
Ethylene glycol	0.7–2.0
1,4-dihydroxybenzene	0.1–1.9
Cellobiose	0.6–3.2
1,6-anhydroglycofuran	3.1
Fructose	0.7–2.9
Levogluconan	0.4–1.4
Glucose	0.4–1.3

Bio-oil, after separating the carbon residue, can be used to drive diesel engines without additives facilitating self-ignition. Bio-oil can also play an intermediary role in obtaining valuable chemical compounds through their selective extraction. The carbohydrate fraction can be used to extract hydroxyacetaldehyde, hydroxyacetone, or levoglucosan, and the phenolic fraction can be used in the synthesis of phenolic resins.

It was found that the pyrolysis of peanut shells carried out with a termite hill as a catalyst resulted in bio-oil with a different chemical composition. Analyses showed the presence of C4-C31 hydrocarbons. The main hydrocarbons detected included tetrahydro [2,2']bifuranyl-5-one, 1,2-benzenol, 1-(4-hydroxy-3-methoxyphenyl)-propanone, 1-(4-hydroxy-3-methoxyphenyl)-ethanone, and cyclopropyl carbinol. The termite thalamus was shown to play a critical role as a catalyst in the pyrolysis process in improving the quality of bio-oil.

Nisar et al. [50] have undertaken the refining of bio-oil to the fractions of gasoline, diesel fuel, and heavy hydrocarbons in the process of fast pyrolysis thermal pyrolysis (TFP) and catalytic pyrolysis (CAT). The obtained results depicted that the use of waste gases from the pyrolysis process for the production of synthetic natural gas with an external hydrogen source can provide up to 48.2% (TFP) and 61.2% (CAT) reduction in the use of biomass resources. This is a significant improvement in the carbon efficiency of hydrogen-enhanced designs that created the savings. Although the CAT process had a lower biofuel efficiency than the TFP process, it presented a higher hydrogen upgrade potential and achieves a higher biofuel efficiency than TFP when fully enriched with hydrogen from the outside.

Shen et al. [51] performed the catalytic pyrolysis of rice husk (RH) with various potassium compounds (i.e.,  $K_2CO_3$ , KOH, and  $K_2C_2O_4$ ) for the production of porous carbons and biofuels. The process of decomposition of biomass took place at a lower temperature, which was influenced by potassium compounds, in the following order: KOH >  $K_2CO_3$  >  $K_2C_2O_4$ . Due to the rapid pyrolysis of RH with potassium compounds, the number of organic compounds was significantly reduced. More hydrocarbons (e.g., long-chain alkanes, benzene) were generated by in situ catalytic upgrading (e.g., deoxidation) of bio-oil. The pyrolysis of biomass with potassium compounds was also able to accelerate the production of unsaturated aliphatic hydrocarbons. In particular, the pyrolysis of RH with  $K_2C_2O_4$  could result in bio-oil with a high content of hydrocarbons and a low content of oxidized compounds (e.g., acids and phenols).

Then, Fan et al. [52] studied non-thermal synergistic plasma catalysis to improve the efficiency of biomass pyrolysis towards obtaining second-generation biofuels. They investigated the effect of ternary catalysis on the stability of the catalyst and on the yield of bio-oil improvement. Although some reduction in bio-oil yield was found, the analyses showed that the obtained chemical compounds had better physico-chemical parameters.

Kumar et al. [53] performed the extraction of biofuel from *Martynia annua* seeds in the process of slow pyrolysis and tested this biofuel for use in a diesel engine as a fuel. The physicochemical properties of the obtained biofuel were also tested. The suitability of mixing biofuel with diesel fuel was determined. The pyrolysis process was carried out in a fixed-bed batch reactor with an electric heater after the sample had been subjected to the pre-treatment process. The process of pyrolysis was carried out at a temperature of 650 °C with a reaction time of 3 h and a particle size of 250 µm. The obtained biofuel was tested in a diesel engine environment in various proportions with diesel fuel. It was found that the biofuel obtained by pyrolysis of *Martynia annua* seeds can replace diesel fuel up to 40% in an unmodified diesel engine without major changes in emissions and efficiency.

It requires stressing that the heat necessary for the pyrolysis process can be transferred to the converted fuel directly (so-called allothermal pyrolysis) or indirectly (autothermal pyrolysis). The temperature and rate of heating also affect the composition of the pyrolysis products. Armer et al. [54] observed an increase in the proportion of carbon and a decrease in the amount of oxygen and hydrogen in the char with an increase in the temperature of the process. In addition, it has been found that an increase in temperature results in a higher acid content in the liquid pyrolysis products.



However, much research concerns the use of catalysts in the pyrolysis process to improve the quality of the produced liquid phase, mainly by removing  $O_2$ , so that it could potentially be an alternative to liquid fossil fuels [55]. For this purpose, the following metal oxides are applied:  $Al_2O_3$ ,  $SiO_2$ ,  $ZnO$ ,  $K_2O$ ,  $MgO$ ,  $CaO$ ,  $La_2O_3$ ,  $CaO$ , and  $MgO$ .

Zhang and Sun [56] have examined the process of ketonization of vapors obtained in the process of biomass pyrolysis using  $CeO_2$  as a catalyst. The analysis of TG-GC/MS and TG-MS detected that bagasse was suitable for ketonization owing to the high content of cellulose and hemicellulose. Additionally, it was found that a temperature of 380 °C was favorable for the ketonization of bagasse with a maximum ketone yield of over 34%. Thus, it was advantageous for the production of ketones to introduce an appropriate amount of metal elements into the treated seawater.

Table 3 summarizes the properties of bio-oil obtained by different upgrading methods. The highest yield (86.87%) of biofuel was found for pyrolysis of palm shells at 700 °C, with a process duration of 20 min, and in the presence of an Amberlyst15 catalyst.

**Table 3.** Properties of bio-oil obtained by different upgrading methods.

Feedstock	Reaction Condition	Catalyst	Oil Yield (%)	References
Peanut shells	3–30 °C/min, 30–800 °C	termite hill	max. 57	[50]
Martynia annua seed	650 °C, 3 h	-	30.77% of BTE	[53]
Corn leaf waste	300–450 °C, constant flow rate of nitrogen	-	57–73% of diesel fraction	[54]
Poplar wood	350 °C, 90 min	Pd/C	23.6	[57]
Beech wood	450 °C, 4 h, 35 MPa $H_2$	Ru/C	60	[58]
Pine wood	350 °C, 4 h, 14 MPa $H_2$	NiMo/ $SiO_2$ - $Al_2O_3$	42.4	[59]
Wheat straw	340 °C, 1.6 h, 8 MPa $H_2$	NiW/AC	18.2	[60]
Wheat straw	340 °C, 1.6 h, 8 MPa $H_2$	Ni/ $TiO_2$	76.8	[61]
Corn stover	300 °C, 4 h, 12.5 MPa $H_2$	Ru/C	54.4	[62]
Rice husks	465 °C, 30 min	$SO_4^{2-}$ /ZrO <sub>2</sub>	56	[63]
Palm shell	700 °C, 20 min	Amberlyst15	86.87	[64]
Swine manure	400 °C, 30 min, 0.69 MPa $N_2$	Modified zeolite	45	[65]
Sewage sludge	330–1200 °C	Graphite	7.16–49.79	[66]
Bagasse	300 W	Activated carbon (35%, 55%, 75%),	13.95–18.95	[67]
Sugarcane bagasse	493–532 °C	NiO, CuO, CaO, MgO	18.4–35	[68]
Oil palm shell	180–720 W	Activated carbon (18.8–91.2%), CaO, MgO, CuO,	16.43–36.75	[69]
Food waste	300–600 W	$Fe_2O_3$ , $MnO_2$ , $CuCl_2$	10–36	[70]
Agricultural waste	400–600 °C	SiC	14.56–31.86	[71]

### 3.3. Biochar

Biochar has practical applications in agriculture all over the world and has been used for many centuries. In recent years, interest in biochar has been growing, as it can be used in many industrial and environmental applications [71]. Biochar is characterized by favorable physicochemical properties such as significantly developed porosity, high porosity, and

high content of stable organic carbon and mineral substances. Biochar can be successfully used:

- In the composting process as a structural material or ammonia abatement additive;
- In bioenergy as a renewable fuel;
- For carbon sequestration in soil;
- For the production of organic fertilizers;
- To remove pollutants from aqueous solutions, industrial and municipal wastewater, and process gases;
- For the remediation of soils contaminated with organic and inorganic compounds;
- To reduce ground and surface water pollution by retaining nutrients in the soil;
- For improving the properties of agricultural soils [72].

Biochar is widely used in environmental protection. The production of biochar from various types of (preferably waste) biomass by pyrolysis also makes it possible to obtain gaseous and liquid fuels for energy production. Moreover, the use of biochar in environmental protection has many benefits, including improving soil properties, such as increasing the amount of soil carbon or soil water capacity, the possibility of replacing fossil fuels with renewable fuels, reducing the use of inorganic and organic fertilizers and plant protection products, and thus lowering the risk of surface and groundwater pollution [73].

Biochar obtained as a result of low-temperature pyrolysis of biomass waste is widely used in various applications. Depending on its physicochemical properties, it can be used as a substrate for the production of activated carbon, in the power industry as a solid biofuel, or as a pollutant sorbent. The obtained biochar [74] is characterized by a lower O/C ratio and a significant increase in the carbon content (up to about 70% C).

One study used waste: date palm seeds [75]. The pyrolysis process was carried out at different heating rates of 2.5, 5, 7.5, and 10 °C using a fixed-bed apparatus. Research showed that biochar contained 33.1% cellulose, 24.3% hemicellulose, and 22.6% lignin. The conversion rate profiles indicated that the complex degradation of date seeds during pyrolysis took place in the active pyrolysis zone [75].

Duan et al. [76] optimized the pyrolysis temperature of peanut shells. The obtained biochar was modified with HCl in order to obtain a better pore structure and surface properties of the biochar. The study presented that peanut shells could be widely used as raw materials and catalysts for the production of chemicals, obviously with a high added value.

Table 4 summarizes the characteristics of biochar (activated carbon) from raw biomass with various preparation methods [77].

**Table 4.** The characteristics of activated carbon from pyrolysis with various preparation methods.

Raw Biomass	Agent	Temperature (°C)	Time (min)	Surface (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)	Ref.
Barley straw	Steam	700	60	552	0.2304	[78]
Barley straw	Steam	800	60	534	0.2186	[79]
Barley straw	CO <sub>2</sub>	700	60	211	0.0830	[80]
Orange peels	K <sub>2</sub> CO <sub>3</sub>	700	60	477	0.21	[81]
Orange peels	K <sub>2</sub> CO <sub>3</sub>	950	60	1352	0.22	[81]
Orange peels	ZnCl <sub>2</sub>	700	60	822	0.09	[81]
Soybean oil cake	K <sub>2</sub> CO <sub>3</sub>	600	60	643	0.272	[82]
Soybean oil cake	KOH	600	60	600	0.213	[82]
Soybean oil cake	KOH	800	60	619	0.143	[82]
Tomato	ZnCl <sub>2</sub>	400	60	648	0.086	[83]
Tomato	ZnCl <sub>2</sub>	600	60	1093	0.129	[83]
Tomato	ZnCl <sub>2</sub>	800	60	492	0.058	[83]
Chestnut shell	H <sub>3</sub> PO <sub>4</sub>	750	20	1138	0.424	[84]
Chestnut shell	H <sub>3</sub> PO <sub>4</sub>	850	20	1413	0.562	[84]

In the technology of removing chromium ions from aqueous solutions, biochar adsorbents were becoming more and more frequent research objects. The mechanisms of removing Cr(VI) and Cr(III) ions using biochar are slightly different. In the case of Cr(III) ions, these mechanisms are (i) complexation of Cr(III) ions by oxygen functional groups, (ii) ion exchange, and (iii) electrostatic interactions between positively charged Cr(III) ions and the negatively charged biochar surface. In the case of Cr(VI) ions, these mechanisms are as follows: (i) electrostatic interactions and (ii) reduction of Cr(VI) to Cr(III) ions through oxygen groups (hydroxyl and carboxyl), which are then complexed on the surface of the biochar [29].

Table 5 presents a summary of the sorption capacities of biochars from various raw materials used for the sorption of Cr(III) ions from aqueous solutions [82–85].

**Table 5.** The sorption capacity of biochars obtained from various raw materials and the pyrolysis temperature of their production.

Raw Material	Pyrolysis Temperature (°C)	Initial Concentration Cr(III)	Sorption Capacity	References
The husk of rice	300	185 (µg/dm <sup>3</sup> )	15.1 (µg/dm <sup>3</sup> )	[39]
Soybean stalks	400	260 (mg/dm <sup>3</sup> )	14.6 (mg/dm <sup>3</sup> )	[50]
Slurry	600	300 (mg/dm <sup>3</sup> )	40.0 (mg/dm <sup>3</sup> )	[17]
Wood of conifers	700	650 (mg/dm <sup>3</sup> )	32.0 (mg/dm <sup>3</sup> )	[75]

It cannot be denied that the constantly growing world demand for electricity, caused by population growth, industrial development, and urbanization, forces us to search for efficient alternative energy sources [86]. Mierzawa-Hersztek et al. [87] carried out the pyrolysis of miscanthus straw and sawdust. It was found that pyrolysis reduced the content of volatile compounds, and the calorific value of the obtained biochar was 26.6 MJ/kg and 23.4 MJ/kg for miscanthus straw and sawdust, respectively.

Owing to its physicochemical properties, biochar can be applied in composting as a structural material and as an additive limiting the emission of ammonia. Composting materials with a narrow C/N ratio results in increased ammonia emissions during the composting process and, consequently, reduced nitrogen content in the resulting compost. Biochar as a structural material in the composting process is able to increase the total porosity, air porosity, and water capacity [88]. Moreover, the addition of biochar accelerated the biodegradation processes and reduced the emission of ammonia by 64%. Then, it was found that biochar can be used as a structure-forming material for composting nitrogen-rich waste.

The analysis of biochar obtained in the pilot plant depicts its energetic suitability in the case of sewage sludge and straw, and as a soil improver or material for forest land reclamation with regard to chaff and straw. Biochar obtained from sewage sludge with a calorific value of about 17 MJ/kg presented appropriate parameters for a good quality fuel for co-incineration in the cement industry and energy, better quality than dried sludge [73].

So far, research has been carried out on the use of biochar from various substrates (e.g., straw, manure, anaerobically stabilized biomass, bamboo, sugar cane, hickory tree, etc.) to remove, e.g., pharmaceutical residues such as endocrine disruptors or bacteriostatic antibiotics (e.g., sulfamethoxazole) from sewage; copper, nickel, mercury, cadmium, lead, and chromium from aqueous solutions or municipal sewage; and pesticides such as carbaryl, atrazine, simazine, and acetochlor [89].

Soil contamination with organic and inorganic substances has become increasingly common in many regions of the world, posing a threat to human health and living organisms [90]. For this reason, new, effective, and cheap solutions for in situ remediations are sought, which would enable the natural removal of toxic and harmful substances from soil, while revitalizing the soil ecosystem and also stimulating plant growth. Such a solution could be the addition of biochar to contaminated soils. Research shows that organic

pollutants in soils undergo sorption processes on biocarbon twice as fast as on naturally occurring organic matter [91].

Biochar introduced into the soil allows for long-term storage of the carbon element. It has also been estimated that the addition of biochar to the soil at a dose of 13.5 Mg/ha (which is 3% of the upper layer 30 cm deep) ensures carbon storage for at least two centuries [92]. Moreover, the carbon stored in the soil remains chemically stable for millennia. If 10% of the world's biomass resources were converted to biochar with a process efficiency of approx. 50% and obtaining 30% of energy from volatile substances, carbon sequestration in the amount of 4.8 GtC/year would be possible, which is approx. 20% of the current annual growth in the amount of atmospheric carbon (i.e., 4.1 GtC/year) [92,93].

#### 4. Pyrolytic Reactors—The Technical Aspects and Influence on the Process

Along with the existing interest in pyrolysis technology, many reactor designs have been studied to optimize pyrolysis efficiency and enable high production quality of bio-oil. However, each type of reactor possesses some specific characteristics; some types of them have limitations and others have advantages in obtaining biofuels [92].

The fixed-bed pyrolysis reactor includes a gas cooling system and a cleaning system. Fixed-bed reactor technology is simple, reliable, and proven for fuels that are uniform in size and low in impurities. In this type of reactor, the solid moves down a vertical tube and contacts the gas stream in countercurrent. Fixed-bed reactors generally operate with high coal efficiency, long solid residence time, low gas velocity, and low ash transfer [93].

Li et al. [94] studied the pyrolysis of waste date palm seeds to produce biochar in a fixed-bed apparatus at different heating rates of 2.5, 5, 7.5, and 10 °C/min. The analysis of date seed powder showed that carbon, oxygen, and hydrogen were present mainly in the lignocellulosic structure, which consisted of 33.1% cellulose, 24.3% hemicellulose, and 22.6% lignin.

Fluidized bed reactors seem to be popular for fast pyrolysis as they provide fast heat transfer, good pyrolysis reaction, residence time control, large liquid–solid contact area per unit bed volume, good thermal transport within the system, and high relative velocity between the phases of liquid and solid [95,96].

Moreover, the bubble bed reactors (Figure 2) are characterized by rapid heat transfer combined with uniform bed temperatures; these appear to be the essential attributes of the fast pyrolysis process. Once the appropriate size of the fluidized bed is selected, the gas flow can be designed such that the residence time of the gas/vapor in the void upstream of the bed can be set to the desired value, typically in the range of 0.5–2.0 s. Experiments proved that an operating temperature of 500–550 °C in the bed and a residence time of about 0.5 s would usually lead to the highest liquid yield [92,96,97].

The simple design and long-term use in the bubble bed reactor pyrolysis process make it considered a reliable and virtually trouble-free reactor. Fast pyrolysis of (waste) biomass can be successfully carried out in this reactor. The efficiency of the reactor depends on the amount of heat input. The bubble bed reactor must use small particles of biomass (less than 2–3 mm) to achieve a high degree of heating [92,96,97]. The main problem of fixed-bed reactors is tar removal; however, recent advances in the catalytic and thermal conversion of tar have provided real opportunities for tar removal [98,99].

Moving circulating fluidized bed reactors had similar features to bubble bed reactors, with the exception of a shorter residence time for the char and vapors (Figure 3). This results in higher gas velocity and higher char content of bio-oil compared to bubble fluidized bed reactors. One advantage is that this type of reactor is suitable for large throughputs, even though the hydrodynamics are more complex [100]. There are basically two types of circulation for fluidized bed reactors: single circulation and double circulations [96,99,101].

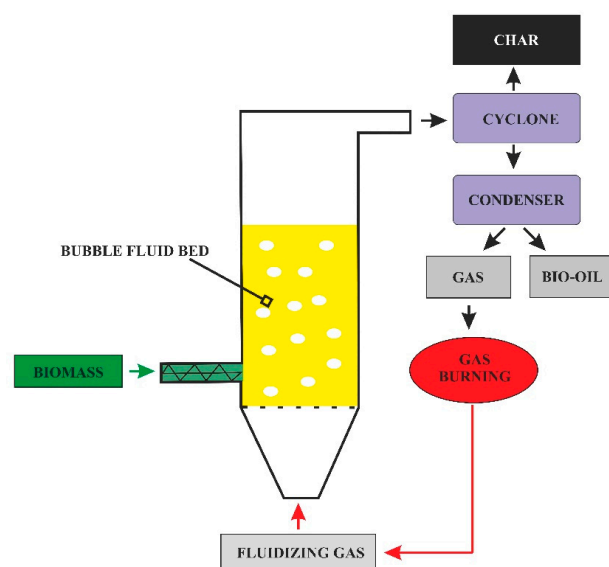


Figure 2. Bubble fluidized bed reactor.

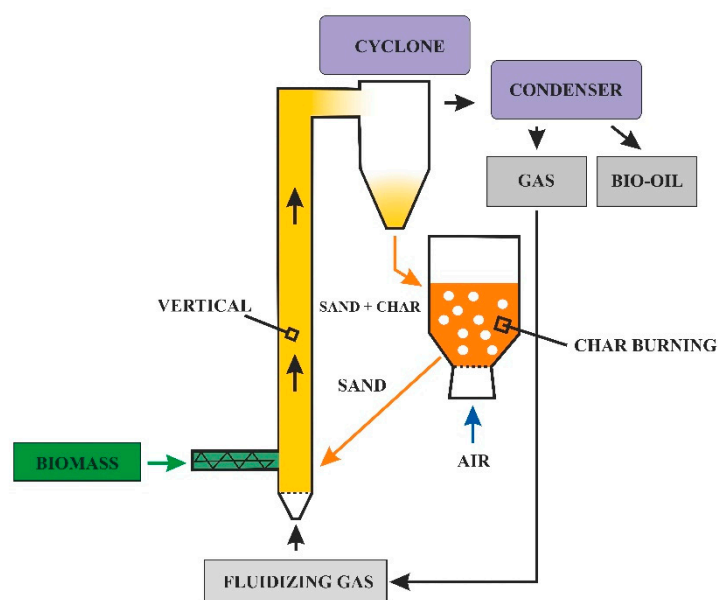


Figure 3. Moving circulating fluidized bed reactor.

A reactor with a screw conveyor is used to move the raw material in a cylindrical, heated, and oxygen-free tube (Figure 4). The further step of the process involves the passage of the raw material through the pipe, heating it up to the desired temperature during pyrolysis in the range of 400–800 °C. Due to the high thermal conductivity of heat carriers, the energy necessary for rapid pyrolysis was transferred to the biomass. The generated vapors are quickly directed to the condensation in order to minimize the reaction time, and the produced char was separated from the heat carrier independently of the thermal decomposition reaction [100–103].

Pyrolysis in an ablation reactor is significantly different from other fast pyrolysis methods. In other methods, the rate of reaction is limited by the rate of heating of the (waste) biomass particles, necessitating the use of small biomass particles. The mechanism of action in the ablative pyrolysis reactor (Figure 5) was compared to “melting butter in a pan”—the melting rate could be greatly accelerated by pressing and sliding it against the heated surface of the pan. In ablative pyrolysis, the heat is transferred from the hot wall of the reactor to the “molten” biomass, which is in contact with it under pressure. As



the biomass is moved, the molten layer evaporates. The wall temperature in the ablation reactor is less than 600 °C. The bio-oil yield in the ablation reactor is 70–75% [100,104].

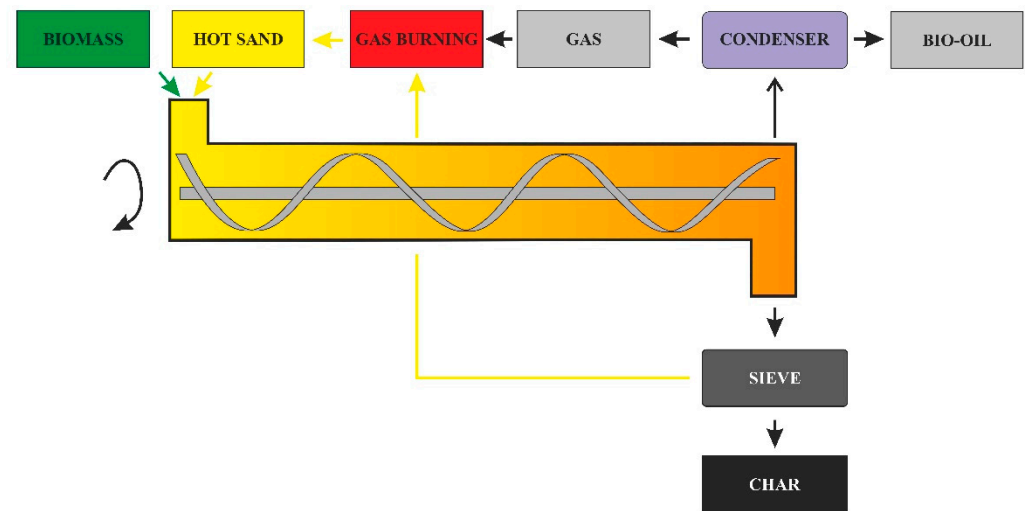


Figure 4. A reactor with a screw conveyor.

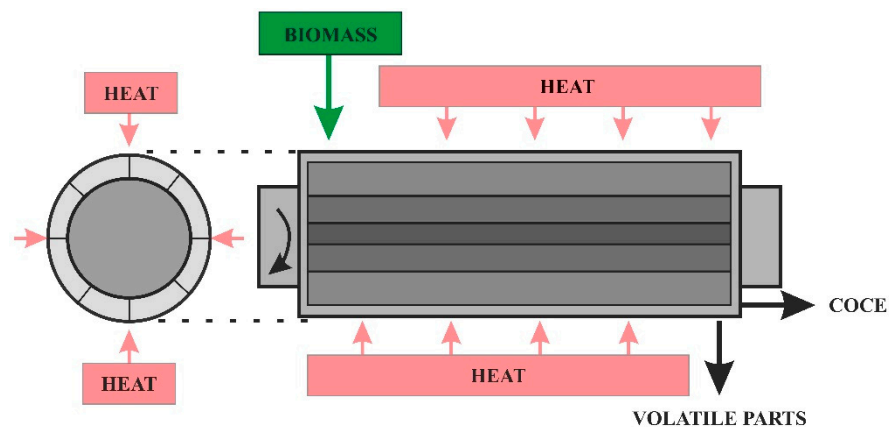


Figure 5. Ablative pyrolysis reactor.

The advantages of an ablative pyrolysis reactor include the following:

- Inert gas is not required;
- Large particle sizes can be used;
- Sufficient heat transfer;
- Controllable residence time [100–105].

#### Reactor Heating Method

Pyrolysis is an endothermic process and requires a significant amount of heat to raise the temperature of the biomass. There are two important requirements for heat transfer in a pyrolysis reactor:

- The heat is transferred to the reactor by the heat carrier;
- From the carrier, the heat is transferred to the biomass to be pyrolyzed [47].

In fast pyrolysis, biomass particles can be heated in two main ways. The first is gas–solid heat transfer, such as in a flow reactor where heat is obtained by the biomass particles from the hot pyrolysis gas mainly by convection. The second is solid–solid heat transfer, which takes place by conduction. In addition to convection and conduction, heat transfer by radiation is also performed in all types of reactors [47].

The heat to the pyrolysis reactor could be supplied by the following [47]:

- Heat exchange surfaces placed in appropriate places in the reactor;
- Heating with fluidizing gas;
- Removal and reheating of the bed (sand) in a separate reactor;
- Adding some air, which can create hot spots and grow cracks, leading to tar formation.

## 5. Prospects and Developments in the Pyrolysis Technology

It must be stressed that economic development leads to an improvement in the quality and comfort of people's lives; however, its negative effect is the constant degradation of the natural environment, the cause of which is the emission of man-made pollutants into the atmosphere, surface- and groundwater, and soil. There is increasing awareness in society of the need to protect the environment, and this requires extensive efforts to reduce adverse impacts of human activity on the natural environment [106].

It is the industry and energy sectors that constitute an extremely important domain of each developed economy and, to a large extent, determine its development. At the same time, they use and influence environmental resources. Awareness of this state of affairs has for several decades resulted in the industry and energy sectors taking a number of organized, pro-ecological activities aimed at irreversible and clear improvement in the functioning of enterprises, resulting in a measurable reduction in the negative impact on the environment. Novel environmentally friendly technologies are being implemented, including the conversion of waste from biomass in the pyrolysis process [107,108].

For a long time, traditional incineration or landfilling of organic waste has weakened the resources of soil and water. Food is wasted often. In order to achieve positive ecological effects, it is worth paying more attention to the pretreatment of organic waste and using pyrolysis to obtain second-generation biofuels [107,108].

The use of waste biomass resources is gaining more and more interest around the world due to the depletion of fossil fuels and concern for the protection of the environment. Pyrolysis is a process that plays a significant role in the conversion of biomass to chemicals and biofuels. The development of industry and energy requires new chemicals that can be delivered by pyrolysis [107,108].

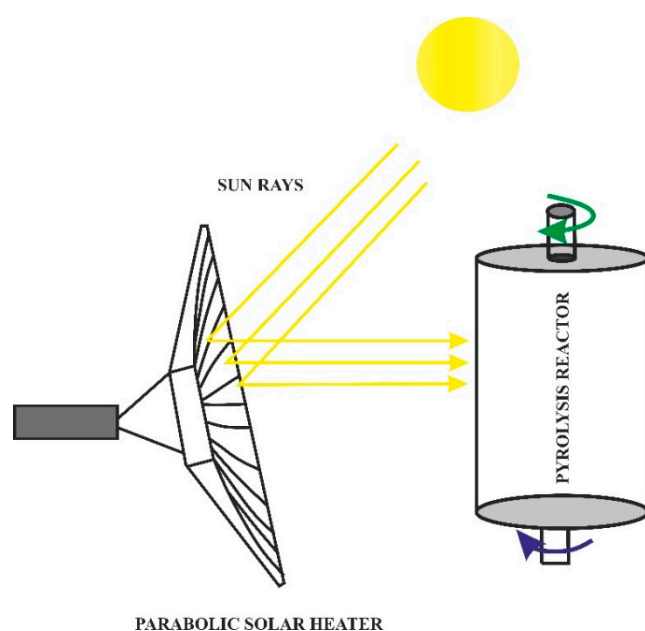
The pyrolysis of biomass has become a promising renewable, sustainable source of fuels, petrochemical substitutes, and valuable chemicals, hence the growing interest of the world of science and industry in the further development of this biotechnology. Moreover, it can be noted that the number of possible substrates that can be pyrolyzed is constantly increasing and includes different types of waste biomass such as wood waste, energy crops, agricultural waste, food waste, municipal waste, sewage sludge, sewage, etc. Agricultural waste consisting of fruit peels, rice husks, or corn cobs is an easily available and cheap material used to generate energy and biochar. One of the most valuable agricultural wastes is orange peel, which consists mainly of cellulose, hemicellulose, and pectins. A significant stream of this waste often ended up in landfills, but now, it is economically used for the production of chemical compounds and biofuels of the second generation. The pyrolysis process allows for "waste-to-energy". A specific compound or a mixture of chemical compounds is obtained with ever-greater efficiency and ever-greater purity, which allows for a broad spectrum of pyrolysis product management [104,105].

Scientific and technical research is underway that will allow obtaining more biofuels with less energy intensity. The pyrolysis process is more and more often "fueled" by renewable energy, which has a significant, positive environmental impact. Research is being conducted on microwave pyrolysis, solar pyrolysis, plasma pyrolysis, hydrogen production by biomass pyrolysis, co-pyrolysis of biomass with synthetic polymers and wastewater, pyrolysis of exotic biomass (cotton husks and coffee grounds), selective preparation of fine chemicals, and the comparison of terrestrial biomass and algae biomass pyrolysis [104,105].

The choice of substrates depends, among other factors, on physicochemical properties (e.g., organic matter and water content, particle size), potential use (e.g., energy production, agricultural use, and pollution removal), logistic aspects, and the pyrolysis process and its parameters [104,105].

Thus, in the future, new materials for the construction of pyrolysis reactors will be introduced, which will allow the process to be optimized. This pre-process will run faster, with greater efficiency, lower energy consumption, and, finally, cheaper pyrolysis substance production [104,105].

Solar pyrolysis depends on concentrated solar energy as the heat source required for biomass pyrolysis (Figure 6). The energy transformation takes place by storing solar energy in chemical form in the produced pyrolysis products (biocoal, bio-oil and biogas) [106]. High yields of pyrolysis gas were achieved by solar pyrolysis for forestry and agricultural waste, including peach kernels, pine sawdust, grape stalks, and grape pomace. Factors affecting gas efficiency were investigated, including temperature (800–2000 °C), biomass type, and heating rate (10–150 °C/s). The gas yield increased with the increase in hemicellulose and cellulose content in the biomass. Higher heating rates favored gas formation. Higher temperatures also increased gas yield. Pine sawdust produced 63.5 wt. gas by solar pyrolysis at a heating rate of 50 °C/s and a temperature of 2000 °C [105–112].



**Figure 6.** Principle of solar pyrolysis.

Table 6 presents a summary of solar-simulated biomass pyrolysis.

**Table 6.** Summary of solar-simulated biomass pyrolysis.

Biomass	Reactor	Concentrator	Light Source	References
Wood	Quartz tube	Direct concentration	5 kWarc Xenon bulb	[108]
Waste biomass	Indirect (conduction)	Elliptical reflector	1.6 kW Xenon arc lamp	[109]
Mixed biomass components	Integrated sphere	Converging lenses	A xenon lamp	[110]
Pine sawdust	Cylindrical quartz reactor	Deep-dish parabolic concentrator	5 kW Xenon arc lamps	[111]
Chicken litter	Copper, indirect (conduction)	Elliptical reflector	0.6 kW Xenon arc lamp	[112]

Thus, pyrolysis products are suitable alternatives to fossil fuels, particularly in the adsorbents industry. Combining hydrogen production with solar pyrolysis would be the most environmentally friendly process in the near future. As green hydrogen is an

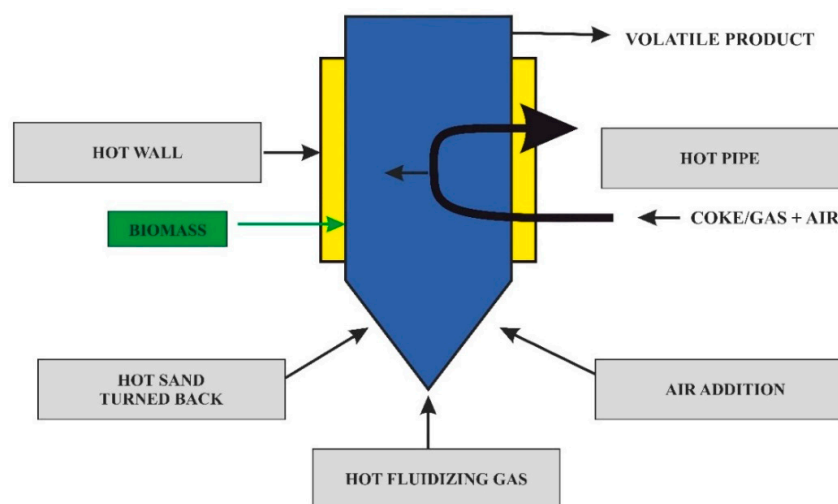
intensively developed fuel, the full-scale hydrogen production during the pyrolysis process can help to reduce climate change caused by CO<sub>2</sub> emissions [113].

In vehicles, biohydrogen can be applied as fuel in two ways: first, to generate electricity in fuel cells (when it combines with oxygen, only energy and clean water are created), and second, to power internal combustion engines as fuel.

In the near future, the pyrolysis process can be combined with the production of energy from renewable sources (RES). Surplus energy from RES can cover the energy needs of the pyrolysis process. The development of RES and pyrolysis will increase energy and fuel security [114].

There are numerous advantages of RES, which make the ongoing energy transformation not only a necessity but also a real benefit for the economy, society, and the environment. While all non-renewable energy sources, i.e., coal, gas, or oil, will terminate one day and their further extraction will not be possible anymore, RES constitute a constant and reliable source that appears not to run out. Thus, we can rely on a safe and predictable energy supply, without any significant risk. The energy transformation will continue as more and more countries are choosing to switch substantially or completely to obtaining energy only from RES [114].

The main difference between the process of conventional pyrolysis and microwave pyrolysis is the method of heating the raw material [114] (Figure 7). In classical heating, the heat is transferred from the surface of the material to its center by convection, radiation, and conduction. It is a relatively slow process and requires sufficient grinding of the raw material. Microwave heating, on the other hand, is the process of converting electromagnetic energy into thermal energy. Microwave energy induces molecular motion through the rotation of the dipoles and the migration of joins. Microwave heating is non-contact, fast, and covers the entire volume, so heat is generated in the entire volume of the material. In addition to this, microwave heating is selective, which means that not all materials will behave the same in a microwave field. The most susceptible to microwaves, and thus to heating, are dielectric materials, e.g., water and methanol. These types of materials are referred to as microwave radiation absorbers. Materials that do not exhibit dielectric properties will reflect or transmit microwave radiation without being heated. Thus, raw materials that completely or partially absorb microwave radiation can be subjected to microwave pyrolysis, thanks to which it is possible to heat them [114].



**Figure 7.** Diagram of the microwave-assisted biomass pyrolysis process.

Possible methods of heating a pyrolysis reactor are shown in Figure 7.

Recently, there have been high hopes for algae (microalgae, algae) (sometimes referred to as third-generation biofuel) [115]. Algae are a group of thalli organisms, most often self-nourishing, living in an aquatic environment or in humid places. In the context of

alternative fuels, algae are miniature biological “factories” that, through photosynthesis, convert CO<sub>2</sub> and sunlight into biomass rich in minerals.

The rapid production of algal biomass and its high lipid content and simple “cultivation” make algae a promising third-generation energy crop [116].

Algae biochar generally has higher content of extractable inorganic nutrients (Mg, K, Ca, and P) than lignocellulosic biochar. This composition is beneficial for soils and is associated with higher crop productivity [117]. Algae biochar can be used as an adsorbent to remove inorganic and organic pollutants from wastewater. It is assumed that there are four main mechanisms of inorganic ion removal: surface complexation with functional groups, precipitation, ion exchange, and electrostatic interactions [118].

Worldwide, the demand for electric vehicles and energy storage is growing and will continue to grow. Capacitors can be an alternative to lithium-ion batteries. Their advantages include a high charging speed, high efficiency, and low operating costs. The electrochemical properties of biocarbon electrodes from algae are determined by the type of algae and the conditions used during its bioconversion. As a rule, the surface of algae biochar is usually relatively small, which makes it suitable for use in supercapacitors [118,119]. Table 7 shows examples of recent developments in supercapacitors derived from algal biochar.

**Table 7.** The recent developments in supercapacitors derived from algal biochar.

Algae	Specific Surface Area (m <sup>2</sup> /g)	Energy Density (Wh/kg)	Cycle Stability	Cycle Stability Percent (%)	References
<i>Chlorella</i>	1337.9	20	10,000	92	[120]
<i>Cladophora glomerata</i>	354	42.4	5000	99.2	[121]
<i>Cladophora glometa</i>	957	41.5	10,000	93.1	[122]
<i>Enteromorpha prolifera</i>	2000	7	10,000	96	[123]
<i>Kelp</i>	4425	8	20,000	92	[124]
<i>Nannochloropsis salina</i>	1784	26.1	5000	83	[125]
<i>Ulva fasciata</i>	376.82	46.1	5000	97.5	[126]
<i>Undaria pinnatifida</i>	3270	42	10,000	94	[127,128]

The study of the microwave pyrolysis process, in which the raw material was freshwater algae *Chlorella* sp., was conducted by Li et al. [97] (Table 8). Algae were grown in special bioreactors. A paste with 85% water content was obtained, which was dried to obtain an algae paste. The obtained paste poorly absorbs microwave radiation; therefore, it was mixed with char. The biomass prepared in this way was subjected to pyrolysis at various powers of microwave heating: 500 W, 750 W, 1000 W and 1250 W, which corresponded to process temperatures of 460 °C, 570 °C, 600 °C, and 625 °C, respectively. Volatile reaction components were cooled in five condensers with cooling water, and non-condensable gases were collected in special gas bags. The total pyrolysis time was 20 min.

**Table 8.** The efficiency of individual fractions depending on the power of microwave heating.

Fraction Yield (%)	Heating Power (W)			
	500	750	1000	1250
Oil fraction	26	28.5	25	17
Water fraction	21	20	20	22
Carbonizate	28	24	25	25
Gaseous fraction	24	26.5	29	35

Sun et al. [129] showed that so far, most studies have been conducted using direct or hybrid microwave heating. In indirect heating, the particles of (waste) biomass are heated mainly by contact with absorbents and heated surfaces. Compared to direct or hybrid heating, indirect heating can provide a high heating rate. Further studies should investigate



heat transfer between microwave-absorbing particles and biomass particles and microwave absorption to understand the temperature profiles of different heating methods and their effects on reactor performance [130].

Wang et al. [131] developed a method for microwave-assisted pyrolysis of woody biomass using a needle-shaped metal. The characteristics of the pyrolysis process were examined using pine sawdust as a feedstock. The properties of pyrolysis products with and without microwave–metal interactions were determined. The mechanism of microwave–metal interaction in the intensification of the pyrolysis process was investigated. The increased density of the electromagnetic distribution after the introduction of the iron wire into the microwave and even the microwave discharge resulted in the intensification of the pyrolysis process.

Haeldermans et al. [132] investigated the microwave copyrolysis of plastics and biomass. Microwave copyrolysis of plastics and biomass was found to increase the yield of bio-oil(s) and shorten the reaction time. In addition, an improvement in the formation of high-calorie components (diesel and gasoline components) and a reduction in the oxygen content of the bio-oil were found. As a result of the increase in the content of aliphatic hydrocarbons and the decrease in the oxygen content, the chemical energy of the bio-oil increased from 1.76 to 6.40 MJ/kg. It was found that the energy consumption of pyrolysis of cow manure with 50% addition of low-density polyethylene was three times lower than in the case of pyrolysis of cow manure alone.

The economy of pyrolysis consists of production cost, capital cost, and revenues. As shown in the table, compared to traditional heating pyrolysis, microwave pyrolysis needs higher financial outlays. The main reason is the limited penetration depth of the microwaves, which requires more parallel reactors to achieve equal efficiency to traditional heating pyrolysis [133]. The unabsorbed reflected power can be hazardous to electricity, especially at the end of pyrolysis. Moreover, to guarantee microwave heating efficiency, a multimode cavity requires careful size design. Therefore, the cost of a traditional reactor is USD 80,574 [134], while the cost of a microwave heating reactor is USD 200,000 [135].

Table 9 shows a comparison of costs of traditional heating pyrolysis and microwave pyrolysis [135].

**Table 9.** Comparison of costs of traditional heating pyrolysis and microwave pyrolysis [135].

Costs	Traditional Heating Pyrolysis	Microwave Pyrolysis
Capital costs	+++	+++ Electrical panels, magnetron, reactor design
Production costs	++ High throughput	++ Low pyrolysis temperature and time
Revenue	+	++ High-quality products

+ low, ++ moderate, +++ high.

The widespread use of biochar in environmental protection brings many benefits, including the improvement of soil properties, e.g., by increasing the carbon content of the soil or the water capacity of the soil, the possibility of replacing fossil fuels with renewable fuels, and limiting the use of organic and inorganic fertilizers and plant protection products, and thus the risk of groundwater and surface water pollution. Biochar can be used as an additive to waste with high water and/or nitrogen content and as a soil-structuring material [134,135].

The addition of biochar to compost mixtures can reduce ammonia emissions, reduce total nitrogen losses during composting, and increase water absorption and nutrient retention. Moreover, biochar can act as a carrier for microorganisms and constitute a component of biofilters in composting plants. Thus, depending on the chemical composition and physicochemical properties, biochar added to compost mixtures primarily increases their

initial air porosity, binds excess water, and provides nutrients and microelements. Therefore, with the above, it is possible to ensure the correct course of the composting process during the composting process. The obtained composts, in which one of the components is biochar, may have additional functional properties, such as improved sorption properties, increased retention of nutrients, increased water capacity, etc. [135,136].

## 6. Energy Requirement of Pyrolysis Process

Gradually, efforts are being made to ensure that the energy and heat necessary in the pyrolysis process come from renewable sources. It has been reported that, depending on the size of the plant, pyrolysis plants would use 179 to 278 kWh of electricity for each portion of biomass processed [99,137–140]. Electricity will also be used in biomass processing and pre-treatment plants. Most electricity is used by mills and dryers, and less by conveyors. These loads are relatively independent of the size of the installation and have been estimated at 40 kWh [99,137–140]. This would give a total electricity consumption of around 240 kWh.

Table 10 presents energy consumed by the pyrolysis unit to process one ton of date palm wastes (as an example).

**Table 10.** Energy consumption in the pyrolysis process [99,137–140].

Steps in Pyrolysis Process		Energy Consumed (MJ/kg)	Energy Consumed (kWh/ton)
A. Electrical Energy			
(i)	Electricity consumption by fluidized bed pyrolysis unit	-	200
	Electricity consumed for biomass handling and		40
(ii)	pre-processing (chopping and grinding)	-	
Total electric energy consumed per ton			240
B. Thermal energy			
(i)	Drying (removal of residual moisture from 8% to 0%), about 80 kg/ton	0.3	6.66
(ii)	Heat required to raise the biomass to 500 °C and	1.5	383.3
	Heat required to raise fluidizing gas up to 500 °C from 50 °C quenching		
(iii)	temperature (2.75 kg of fluidizing gas per kg of biomass)	0.60	458.33
(iv)	Radiation, convection, and conduction losses (3% of heat input to pyrolysis reactor)		
	Total thermal energy required per ton of date palm waste, kWh	-	25.45
			872.74

Other economic aspects of pyrolysis include income opportunities for farmers/foresters supplying biomass. The construction of facilities will increase farmers' income and provide solutions for agricultural waste management. This makes it possible to link small-scale production systems to larger ones, creating closed-loop models in which waste from one process can be used as an input to another, having beneficial social, economic, and environmental effects and promoting regenerative economic sustainability. The following economic benefits are cited: cost savings in waste disposal and reduced greenhouse gas emissions. Using a range of methods and procedures, this application of regenerative economic sustainability reduces waste while increasing the value of the resources used.

A multi-unit model would often be useful in breaking down strategies to increase efficiency, modernize operations, and sensibly allocate environmental burdens to achieve environmental benefits [99,137–140].

## 7. Conclusions

The process of waste biomass pyrolysis allows for obtaining many chemical compounds (second-generation biofuels). The three most common fractions involve gaseous, liquid, and solid (biochar) forms. Optimization of the pyrolysis process allows obtaining the desired products that can be applied in the chemical industry, in energy, and in transport (integrated biorefinery).

Along with the existing interest in pyrolysis technology, many reactor designs have been studied to optimize pyrolysis efficiency and enable high production quality of bio-oil. However, each type of reactor possesses some specific characteristics—some types of them have limitations and others have advantages in obtaining biofuels.

Pyrolysis products have become a viable alternative to fossil fuels. The waste pyrolysis process brings many benefits that may affect the natural environment, including reducing the consumption of fossil raw materials and reducing the volume of waste in landfills. The optimization of the pyrolysis process by applying various types of waste, newly designed reactors, and the integration of the process with RES confers higher biofuel yields and lower energy consumption. The continuing research on the mechanisms of the pyrolysis processes will provide access to cheap and clean chemicals that can be widely used in the chemical, energy, transport, and agricultural industries to give rise to a biocircular economy.

In the coming years, pyrolysis technology is expected to develop further, achieving higher yields, the desired chemical composition of products, as well as lower energy and economic costs. Optimization of the pyrolysis process will make it a strongly competitive method for obtaining biofuels and chemical compounds.

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