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Review

Recent Advances in Biochar: Synthesis Techniques, Properties, Applications, and Hydrogen Production

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Abstract: The field of material sciences has evolved vastly in the last two decades, largely due to the discovery of carbon nanomaterials such as graphene and its derivatives. Although they offer positive characteristics, the cost of production and material processing of these carbon nanomaterials has limited their application. However, scientists have started searching for cheaper and more environmentally friendly alternatives. Biochar, a carbonaceous material derived from biowaste, is the most viable alternative, as it offers characteristics on par with traditional carbon nanomaterials. This review will discuss the production of biochar from biomass, methods of production, the effects various conditions have on the production of biochar, biomass selection, current biochar applications, and the potential biochar has to produce hydrogen as an energy carrier.

Keywords: biomass; biochar; pyrolysis; biomass selection; hydrogen production

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Citation: Visser, E.D.; Seroka, N.S.; Khotseng, L. Recent Advances in Biochar: Synthesis Techniques, Properties, Applications, and Hydrogen Production. *Processes* **2024**, *12*, 1111. https://doi.org/10.3390/pr12061111

Academic Editors: Izabela Czekaj, Maria Rios and José Cleiton Sousa dos Santos

Received: 5 April 2024
Revised: 17 May 2024
Accepted: 24 May 2024
Published: 28 May 2024

1. Introduction

Due to our already large and rapidly growing population, the world produces about 1 billion metric tons of organic solid waste each year. This consists of agricultural waste (agrowaste) and municipal waste. Due to the lack of correct waste management techniques, most of this waste ends up in landfills or being burnt [1]. Traditional biomass treatment, such as landfilling, composting, and burning, contributes to environmental pollution through harmful emissions, such as greenhouse gases or contamination of the surrounding soil and water [2].

An alternative method of waste management that has gained considerable attention is the conversion of biomass into value-added by-products [3]. One of the by-products that became a major topic of research is biochar due to its versatility and wide range of applications [4]. Biochar is a carbon-rich solid product produced when organic biomass undergoes combustion in an oxygen-deprived environment. Biochar can be derived from a variety of feedstocks, such as agrowaste and solid human waste [5].

In recent years, many studies have been conducted to determine the potential of biochar since the material is inexpensive to produce and has been shown to be effective in a multitude of important applications such as soil treatment, waste management, and energy generation, which are three major areas of concern of the 17 SDGs listed by the United Nations [6,7].

Although biochar is a broad term used to describe the product of biomass that has undergone carbonisation, each biochar has its own set of characteristics determined by the biomass it was derived from, the reactor design, and operating conditions. Physical characteristics such as specific surface area, pore structure, elemental composition, functional groups of the surface, and surface morphology are very important when understanding which biochars are suitable for a specific application [8].

This review article will focus on giving a broad overview of current research on biochar, biochar preparation methods, biomass selection, applications of biochar, and potential application of biochar in green hydrogen production, and will provide an outlook of biochar's future directions.

2. Biochar Production Methods

The method by which a biochar is produced plays a pivotal role in determining its characteristics. The different types of reactor designs and reaction conditions used for the carbonisation process directly affect the chemical and physical properties that are unique to that specific biochar [9].

The most common method of producing biochar is through a process called pyrolysis, in which the biomass undergoes thermochemical decomposition. The biomass is heated to temperatures between 200–1300 °C while under low oxygen or inert atmospheric conditions [10]. The pyrolysis methods can be divided into classes that are primarily characterized by the two operating conditions, heating rate, and residence time. The classes are slow pyrolysis, fast pyrolysis, flash pyrolysis, and intermediate pyrolysis [10,11]. The operating conditions of each method can be seen in Table 1.

Table 1. Operating conditions of the six pyrolysis classes adapted from [10,11].

Operating Conditions	Slow	Fast	Flash	Intermediate	Gasification	Liquefication
Temperature (°C)	100–1000	300–1250	900–1200	500–650	800–1200	200–400
Heating rate (°C/s)	0.1–1.0	10–200	>1000	1.0–10	10–300	10–300
Residence time (s)	300–500	0.5–10	<1	0.5–20	10–20	300–3600

During pyrolysis, volatile organic compounds present in the biomass undergo cleavage because of the presence of heat. The decomposition of these organic compounds produces both high- and low-weight molecular vapours, known as biosyngas, and leaves a solid called biochar. The high-molecular-weight vapours recondense to form biooils [12]. Each method of pyrolysis will produce a unique product with a specific set of physical and chemical properties, even though it is derived from the same biomass; each will have its own composition of bio-oil, biochar, and biosyngas. The effect of each pyrolysis method can be seen in Table 2 below.

Table 2. The effect of the pyrolysis technique on the product yield [10].

Process	Biochar (%)	Bio-Oil (%)	Bio-Syngas (%)
Slow Pyrolysis	35	30	35
Fast Pyrolysis	12	75	13
Flash Pyrolysis	60	20	20
Intermediate Pyrolysis	25	50	25

Slow pyrolysis is an old technique that was used in the past to produce valuable chemicals such as light-molecular-weight alcohols, carboxylic acids, and coal from wood biomass. Slow pyrolysis uses relatively low temperatures for extended periods of time and is mainly used to produce high-carbon-content biochar [13].

Fast pyrolysis is favoured for producing bio-oil. During fast pyrolysis, the biomass is exposed to high temperatures between 900 and 1200 °C for a very short residence time between 1 and 10 s. The high temperature allows for the volatile compounds present in the biomass to undergo thermal cracking, which forms syngas and then condenses to form bio-oil. The high heating rate is employed so that the compounds in the biomass sublimate without interacting with the biomass, minimising the formation of char products [11,13].

Intermediate pyrolysis is a method which lies between fast and slow pyrolysis. It is a method that produces a balance of the three products in similar amounts and can, therefore, be used to coproduce biochar, bio-oil and syngas at once. Intermediate pyrolysis is preferred for producing high-quality bio-oils, as the process produces fewer unwanted products and contaminants, such as high molecular weight tars, compared to fast pyrolysis. This method is, therefore, highly favoured for producing bio-fuels and their precursors [11,14].

Flash pyrolysis is seen as an improved method of fast pyrolysis and requires special reactor designs, which differ from fast pyrolysis. During flash pyrolysis, the volatile compounds present in the biomass undergo depolymerisation and cracking. Flash pyrolysis is favoured for the synthesis of biochar and bio-oil, as the high temperature and heating rate used for its very limited residence time limit side reactions [15].

Gasification is a thermochemical process used to produce syngas from carbon-rich biomass. Syngas mainly consists of carbon monoxide (CO) and hydrogen gas (H_2). Gasification uses a temperature range of 800–1200 °C with a relatively short residence time of 10–20 s. The product of gasification favours the formation of syngas (85%) but does form biochar (10%) and bio-oil (5%). Biochar produced by gasification as a by-product has a high surface area and is highly porous due to the volatile compounds present in the biomass that undergo decomposition into gas and are released from the material [11,16,17].

Liquefication is a hydrothermal chemical process used to produce bio-oils and biochar. Hydrothermal liquefaction uses solvents, high pressure, and moderate temperatures to convert biomass. The temperature ranges between 200 and 400 °C with pressures between 5 and 20 MPa with residence times up to 60 min. High pressure is required to keep the solvent in its liquid state. Using this method, the biomass undergoes a wide variety of chemical reactions to break down the organic compounds present in the biomass, such as fragmentation, depolymerisation, and repolymerisation [18,19].

The pyrolysis described above is the basis for how value-added products can be produced from biomass. These are known as traditional pyrolysis methods, as they use traditional heating, which uses conduction through the surface of the furnace to heat biomass [20]. With the advancement of technology, new methods of converting biomass are being researched. One method that is starting to be widely used is microwave pyrolysis. Microwave pyrolysis uses microwave energy to heat samples via noncontact heating. Microwave pyrolysis has gained interest due to its many advantages over traditional pyrolysis, such as higher temperature and heating rates, even heating of the sample as it does not rely on conduction for heating [21].

The need for more comparative studies that observe the effect that the various pyrolysis methods mentioned above have on a single feedstock is evident as the boundaries between the methods and the expected outcomes of these methods are not yet well defined. The landscape of biochar will change drastically over the next few years as the boundaries become more well-defined, and the introduction of novel pyrolysis methods that exist outside of the boundaries of the six above-mentioned pyrolysis techniques will come forward.

3. The Effect of Production Conditions on Biochar

Many studies have been conducted to find the link between production conditions such as temperature, residence time, reactor design, and the physical characteristics of biochar, such as surface area, porosity, and elemental composition [22].

Temperature is the most important factor when converting biomass into value-added products. Temperature determines not only biochar properties but also product yield. The specific surface area is an important characteristic of biochar, and research has found that the specific surface area of biochar increases with the maximum temperature up to a specific temperature limit before dropping off and decreasing as the temperature increases (Figure 1) [23].

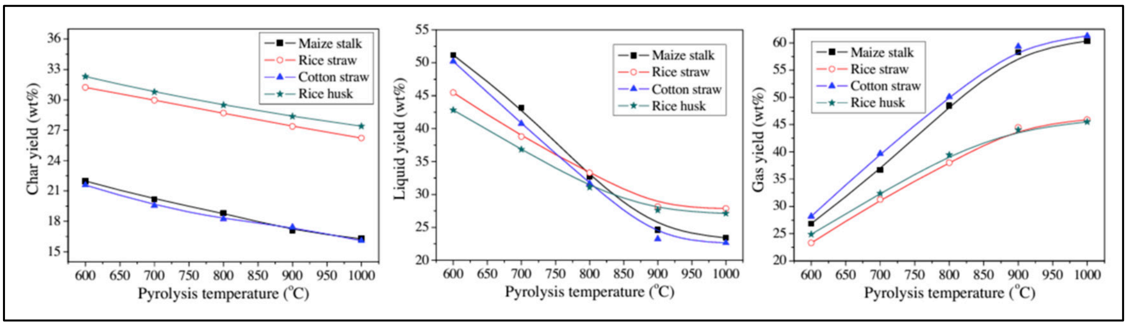


Figure 1. The effect of temperature on product yield was taken from Fu et al., 2011 [24].

Fu et al. found that an increase in the pyrolysis temperature increased the surface area and total pore volume of the biochars produced via fast pyrolysis of cornstalks, rice straw, cotton straw, and rice husks. Fu et al. produced biochars using 600, 700, 800, 900, and 1000 °C, and the BET results showed that the surface area and total pore volume increased with temperature and peaked at 900 °C for all samples before decreasing at 1000 °C [24].

Mohammed Noor et al. conducted slow pyrolysis on coconut flesh waste at different temperatures to observe the effect temperature has on biochar properties. Mohammed Noor et al. used a temperature range between 350 and 600 °C using intervals of 50 °C. They found that an increase in temperature affected the elemental composition. The most notable differences are an increase in carbon content and a decrease in hydrogen and oxygen. This was attributed to the loss of moisture, such as water [25].

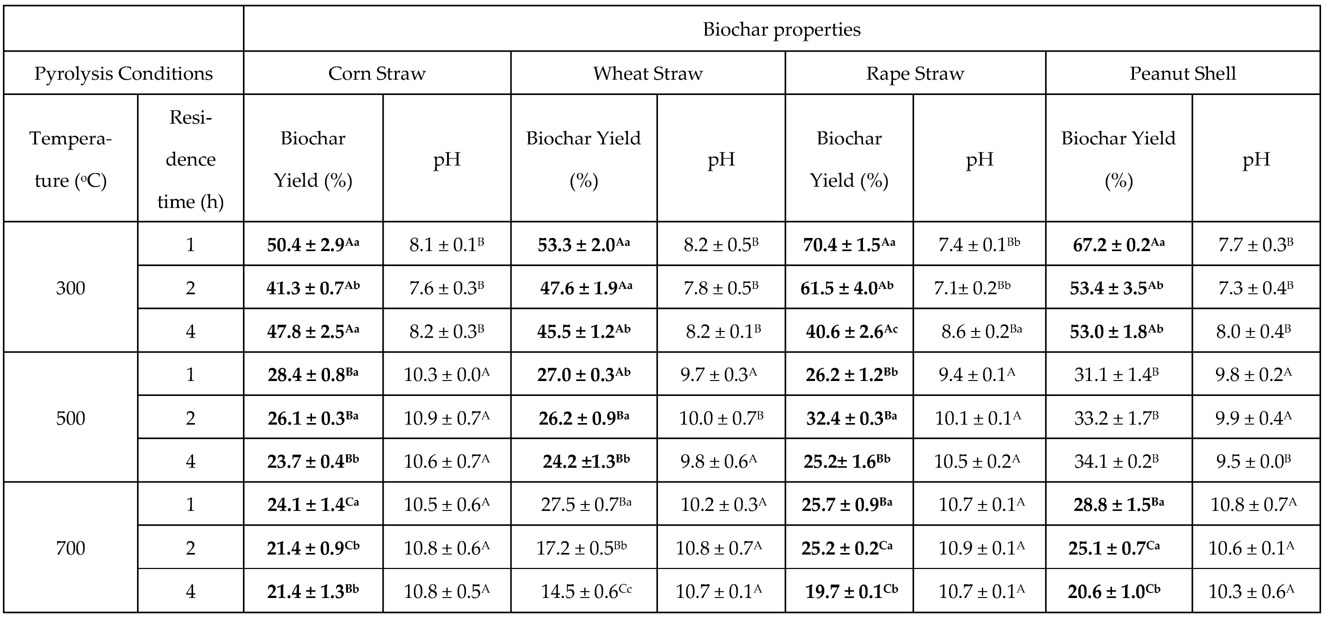
Residence time affects factors such as biochar yield and physicochemical properties. Zhao et al. conducted tests on rapeseed stems to see the effect of varied residence time. The test was carried out at 500 °C and residence times between 10, 20, 40, 60, 80, and 100 min with a heating rate of 20 °C/min. Zhao et al. found that prolonged residence times slightly decreased the biochar yield, and that optimum yield can be achieved using lower residence times. The drop in yield can be explained as a longer residence time, which allows and exposes the biomass to the heating point of the seat for a longer period, allowing more biomass to volatize to other products such as biogas and bio-oil [26].

Wang et al. (2020) conducted experimentation to determine the effects of varying temperatures between 300 and 700 °C and residence times of 1, 2, and 4 h on the biochar yield and the pH of biochars derived from corn stalks, rape straw, wheat stalks, and peanut shells (Figure 2) [27].

The experimentation showed that longer residence times and higher pyrolysis temperatures lead to a decreased yield in biochar due to more heat being put into the sample, causing the decomposition of many of the volatile compounds found in the feedstocks. The pH level increased towards the basic region as more of the acidic functional groups were burnt off [27].

Wang et al. carried out experiments on bamboo wood, elmwood, rice straw, wheat straw, cornstalks, rice husks and coconut shells using residence times of 4, 8, and 16 h and setting temperatures of 500 and 700 °C in a muffle furnace. The results showed that as the residence time increased, so did the BET surface area [28].

Different pyrolysis methods require different heating rates, and they vary from as low as 0.1 °C/s for slow pyrolysis to >1000 °C/s for flash pyrolysis. These heating rates affect the products formed during pyrolysis and their yield percentages [10]. Low heating rates are associated with better conditions for biochar production, as low heating rates allow greater heat conduction, while high heating rates are associated with better conditions for bio-oil production, as high heating rates cause rapid decomposition of volatile compounds in biochar, which are released as vapours and then condense to form bio-oil [7,21,29].



		Biochar properties							
Pyrolysis Conditions		Corn Straw		Wheat Straw		Rape Straw		Peanut Shell	
Temperature (°C)	Residence time (h)	Biochar Yield (%)	pH	Biochar Yield (%)	pH	Biochar Yield (%)	pH	Biochar Yield (%)	pH
300	1	**50.4 ± 2.9^{Aa}**	8.1 ± 0.1^{B}	**53.3 ± 2.0^{Aa}**	8.2 ± 0.5^{B}	**70.4 ± 1.5^{Aa}**	7.4 ± 0.1^{Bb}	**67.2 ± 0.2^{Aa}**	7.7 ± 0.3^{B}
	2	**41.3 ± 0.7^{Ab}**	7.6 ± 0.3^{B}	**47.6 ± 1.9^{Aa}**	7.8 ± 0.5^{B}	**61.5 ± 4.0^{Ab}**	7.1± 0.2^{Bb}	**53.4 ± 3.5^{Ab}**	7.3 ± 0.4^{B}
	4	**47.8 ± 2.5^{Aa}**	8.2 ± 0.3^{B}	**45.5 ± 1.2^{Ab}**	8.2 ± 0.1^{B}	**40.6 ± 2.6^{Ac}**	8.6 ± 0.2^{Ba}	**53.0 ± 1.8^{Ab}**	8.0 ± 0.4^{B}
500	1	**28.4 ± 0.8^{Ba}**	10.3 ± 0.0^{A}	**27.0 ± 0.3^{Ab}**	9.7 ± 0.3^{A}	**26.2 ± 1.2^{Bb}**	9.4 ± 0.1^{A}	31.1 ± 1.4^{B}	9.8 ± 0.2^{A}
	2	**26.1 ± 0.3^{Ba}**	10.9 ± 0.7^{A}	**26.2 ± 0.9^{Ba}**	10.0 ± 0.7^{B}	**32.4 ± 0.3^{Ba}**	10.1 ± 0.1^{A}	33.2 ± 1.7^{B}	9.9 ± 0.4^{A}
	4	**23.7 ± 0.4^{Bb}**	10.6 ± 0.7^{A}	**24.2 ±1.3^{Bb}**	9.8 ± 0.6^{A}	**25.2± 1.6^{Bb}**	10.5 ± 0.2^{A}	34.1 ± 0.2^{B}	9.5 ± 0.0^{B}
700	1	**24.1 ± 1.4^{Ca}**	10.5 ± 0.6^{A}	27.5 ± 0.7^{Ba}	10.2 ± 0.3^{A}	**25.7 ± 0.9^{Ba}**	10.7 ± 0.1^{A}	**28.8 ± 1.5^{Ba}**	10.8 ± 0.7^{A}
	2	**21.4 ± 0.9^{Cb}**	10.8 ± 0.6^{A}	17.2 ± 0.5^{Bb}	10.8 ± 0.7^{A}	**25.2 ± 0.2^{Ca}**	10.9 ± 0.1^{A}	**25.1 ± 0.7^{Ca}**	10.6 ± 0.1^{A}
	4	**21.4 ± 1.3^{Bb}**	10.8 ± 0.5^{A}	14.5 ± 0.6^{Cc}	10.7 ± 0.1^{A}	**19.7 ± 0.1^{Cb}**	10.7 ± 0.1^{A}	**20.6 ± 1.0^{Cb}**	10.3 ± 0.6^{A}

Note: Results are presented with the mean (n = 3) and the standard deviation. Different letters indicated significant difference among different samples ($p < 0.05$), the difference among biochars produced at different temperature are presented by big letters, and the difference among biochars produced with different residence time are represented by small letters.

Figure 2. Results of temperature and residence time studies of pyrolysis conducted on biochars derived from corn stalks, rape straw, wheat stalks, and peanut shells. Image and text adapted from Wang et al., 2020 [27].

A knowledge gap exists in understanding what exact correlations exist for the pyrolysis variables: temperature, temperature gradient, residence time, and furnace design. There is a correlation which projects product yield, but more comparative studies are required to gain a clearer understanding of how changing the pyrolysis variables affects the physiochemical properties such as pH, specific surface area, higher heating value, and chemical composition of the biochar. More comparative studies should also be conducted on pre- and post-pyrolysis treatment, such as chemical impregnation and leaching of the biomass/ biochar for the addition of specific functional groups or for the removal of metals in the biochar.

4. Biomass Selection

Many different sources of biomass can be converted into biochar, such as agricultural waste, fruit waste, woody biomass, algae, and municipal solid waste. For biomass conversion, the most important aspects are the composition, and the microstructures present in the biomass [30–33].

Lignocellulosic biomass is the most abundant readily available biomass in the form of agrowaste. Lignocellulose contains the compounds lignin, cellulose, and hemicellulose, which are most important when considering biomass since they each influence the production of biomass [33,34].

Cellulose is a major compound found in biomass that stabilises the structure of plant cells. Cellulose is made up of glucose monomers bound by β-1,4 linkages [35]. Hemicellulose, unlike cellulose, is made up of multiple branched polysaccharides, which are made up of glycosyl monomers such as glucose, mannose, xylose, and glucuronic acid. Hemicellulose compounds are made up of monomer chains up to 200 monomers long [36]. Lignin is a polymer formed using the three aromatic monomers p-hydroxyphenyl, guaiacyl, and syringyl. Lignin is formed using ether-like (COC) or carbon-carbon (C-C) bonds between monomers [37].

Understanding the composition of biomass is important, as lignin, cellulose, and hemicellulose decompose at different temperatures. Hemicellulose breaks down at temperatures between 200–320 °C; cellulose decomposes in a temperature range between 314–500 °C, and lignin up to temperatures of 900 °C. Understanding the composition will help decide the optimal pyrolysis temperature for biochar production [33,38]. Fruit peels and shells are produced in large quantities during the fruit production process. Fruit waste has high contents of basic nutrients such as carbon, oxygen, and hydrogen, and the content of lignin, cellulose, and hemicellulose varies from fruit to fruit [39].

Wood residues fall under lignocellulosic biomass, and large amounts are produced in the wood's processing. At its most basic level, wood is made up of fibrous cells called tracheids, which are made up of lignin and cellulose [40]. Wood is divided into two subclasses; the first subclass is softwood, and the second class is hardwood. Softwoods are generally composed of 40–44% cellulose, 25–29% hemicellulose, 25–31% lignin, and 1–5% of extractives. Hardwoods are composed of 42–46% cellulose, 23–33% hemicellulose, 20–28% lignin, and 1–7% extractives [41].

Algae are a great source of biomass and are already used to produce food products, soil additives, homoeopathic medications, and animal feed [30]. Algae are considered a good feedstock due to their availability, their strong ability to absorb carbon dioxide, and their high nutrient content [42].

The algae in waste are made up mainly of lipids, proteins, and carbohydrates; their compositions will vary from species to species, and they are affected by the environment in which they are grown [43]. Chen et al. conducted experiments on three different species, including Chlorella vulgaris ESP-31, Nannochloropsis oceanica CY2, and Chlamydomonas sp. JSC4, and found that the carbohydrates present in all three samples decomposed in a temperature range of 164–467 °C, proteins in a range of 209–309 °C, and lipids in the range of 200–635 °C, which are close to the samples' true decomposing temperatures [44].

More than 1.3 billion tons of municipal solid waste (MSW) are produced each year around the world. Municipal solid waste consists of household and commercial waste, which can consist of biodegradable waste, recyclable waste, biomedical waste, electrical waste, and chemical waste [45]. Most of the municipal solid waste is dumped into a landfill; this method releases greenhouse gases and toxic compounds into the ground and surrounding environments. Landfills emit pollutants in the form of leachate that are absorbed by local sources of water [46]. Examples of biochar derived from the above-mentioned biomasses are tabulated in Table 3 below.

Table 3. Biochars derived from various feedstocks, their production conditions, and applications.

Biomass	Treatment	Temperature (°C)	Residence Time	Application	Reference
Rambutan fruit peel	Microwave slow pyrolysis	328	30 min	Catalyst support for catalyst in pesticide removal from soil	[47]
Plum and apricot kernels	Slow pyrolysis	500	60 min	Removal of chromium and lead from wastewater	[48]
Mixed sawdust	Slow pyrolysis	400, 500	60 min	Air treatment and CO_2 adsorption	[49]
Birch tree chips	Slow pyrolysis	300, 500, 650	480 min	Pulverised coal, fuel, energy	[50]
Chlorella-based algal residue	Slow pyrolysis	300, 400, 500, 600, 700	20, 40, and 60 min	Nitrogen-rich minerals, soil treatment	[51]
Rhizoclonium riparium algae	Hydrothermal carbonisation	180	240 min	Removal of uranium (VI) from water	[52]
Organic fraction of MSW from the Gohagoda dumpsite	Slow pyrolysis	450	30 min	Removal of benzene from landfill leachate	[53]
Paper, grass, and hardwood mixture	Slow pyrolysis	300, 500, 750	120, 240, 360 min	Soil amendment and treatment	[54]

Biomass selection for biochar production is still a very new topic, and biochar itself is still a novel topic. The need to understand that feedstock is primarily based on proximate and ultimate analysis will prove very important, as it will help tailor the desired characteristics of the final product. The current focus in terms of feedstock selection is heavily based on which biomasses are produced in large quantities, such as agricultural waste; however, in the coming years, the topic of biomass selection will only continue to grow as there as many untapped biogenic feedstocks that have not been investigated.

5. Application of Biochar

The application of carbon-based materials is one of the largest areas studied in material sciences, and this is due to the strong conductive, optical, and mechanical properties they possess [55]. Biochar is the latest of the carbonaceous materials to gain attention for widespread application due to its large specific surface areas, highly functionalised surfaces, and strong absorptive properties (Figure 3) [56].

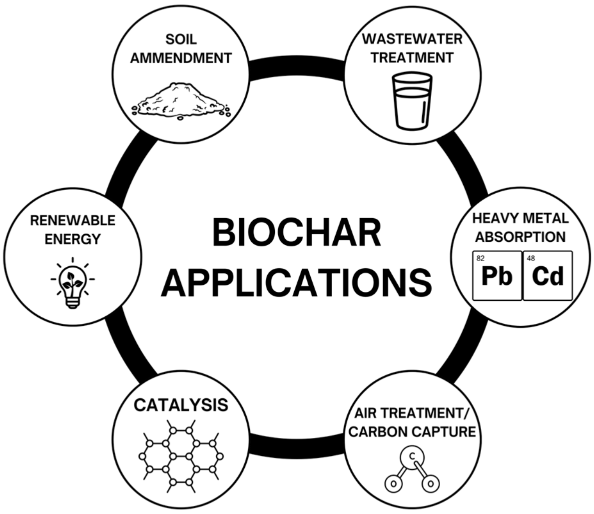


Figure 3. Diagram of biochar's various applications.

Soil remediation is a large area of application for biochar due to its high nutrient content and strong absorptive properties. Biochar is used to improve soil quality by increasing moisture content, moisture retention, available nutrients, and promoting microorganism activity [57].

Biochar is also used for the removal of toxic chemicals, heavy metals, and metalloids from the soil. Soil contamination can lead to poor agricultural produce and human health risks, as most contaminants are carcinogenic. These soil contaminants are often present in the water used to water the soil and crops and are carried into the soil [58]. Zhang et al. (2016) used biochar produced from sewage sludge to remove cadmium, a very toxic heavy metal to humans, from the soil of rice paddies. The field study showed that the application of 1.5–3 tons per hectare of soil reduced the amount of cadmium found in the rice grains and improved the crop yield [59].

Water security and water quality are a global concern. Wastewater from the commercial and private sectors is contaminated by a wide variety of materials, including organic and inorganic substances, pharmaceuticals such as antibiotics, pesticides, and heavy metals known as emerging contaminants. The cleaning of wastewater is important due to the scarcity of fresh drinking water [60]. Currently, there is a wide arsenal of methods to remove contaminants from water, such as microbial, adsorption, electrochemical, and oxidative methods. Adsorption is considered the most effective method since it is the most environmentally friendly and cost-effective [61].

Biochar has seen increasing research applications in wastewater treatment because of its strong absorptive properties, pore structure, pore volume, and tunability. Biochar has been found to be effective in removing many emerging contaminants [62]. Magnetic biochar has been used to remove heavy metal ions such as cadmium, lead, zinc, and copper [63]. Pradhananga et al. (2017) conducted research into the use of biochar derived from bamboo cane for the adsorption of carpet dyes from wastewater. The results showed that the biochar was successful at removing the dye from the water due to its high surface area. It was found that the absorbance capacity of the biochar was 3.04×10^3 $\text{mg}{\cdot}\text{g}^{-1}$ for Lanasyn gray [64].

Carbon emissions, global warming, and greenhouse gases are three linked areas that have attracted the world's attention due to the need for solutions to the problems they pose [65]. The rise in carbon dioxide concentration in the atmosphere is a concern, as it is the primary driver of global warming. A large portion of carbon dioxide is produced from anthropogenic activities, such as burning fossil fuels for energy production. Reducing the concentration of CO_2 in the atmosphere and limiting the amount of CO_2 emitted into the environment are of the highest importance [66].

Carbon capture is one method to remove CO_2 from the environment. Biochar, being a carbonaceous material, possesses the ability to absorb carbon dioxide, and biochar's stability is a large determining factor of the material sequestrating characteristics. Along with its soil remediation application, biochar in soil also largely contributes to the reduction of greenhouse gasses [67]. The strong absorptive quality of biochar means that some variants of biochar can absorb up to 870 kg of carbon dioxide per metric ton of dry biochar [68]. A biochar's stability can be determined using its H/C molar ratio, as the H/C ratio is an indicator of the biochar's aromaticity, and O/C molar ratio is an indicator of the expected half-life. An O/C ratio of <0.2 indicates the most stable of biochars, which has a half-life of >1000 years. An O/C ratio between 0.2 and 0.6 has a half-life between 100 and 1000 years, and an O/C ratio > 0.6 has an expected half-life of less than 100 years [67]. Deng et al. (2014) conducted experimentation with a biochar derived from pine nut shells. The research showed that at room temperature, the pine nut biochar absorbed 5.0 mmol/g [69].

Biofuels are considered a more environmentally friendly alternative to fossil fuels, as they are non-toxic and renewable. Biochar is used as a heterogeneous catalyst in the production of biodiesel because of its high surface areas, the high presence of surface functionalisation, and its ability to withstand highly acidic and basic environments. This technology has been applied to the conversion of cooking oil waste into biodiesel and has seen conversion efficiencies of up to 90% [70]. Mardhiah et al. (2017) conducted experimentation with biochar derived from Jatropha curcas for the conversion of Jatropha curcas oil into biodiesel. The research showed that the biochar-supported catalyst used for the esterification of the oil converted 99.13% of the free fatty acids [71].

Biochar has been applied to supercapacitors for energy storage. Supercapacitors require a carbonaceous material with a high surface area specifically composed of a pore structure adequate for the absorbance of the electrolyte, high conductivity, and high presence of oxygen-containing functional groups. Biochar offers a high surface area with a tunable pore structure, high electron conductivity, and functional groups containing oxygen. The high surface area biochar testing showed that the biochar possessed high specific capacitance and maintained almost 90% of its capacitance after 5000 cycles [72].

Energy generation and energy storage are two fields in which biochar can have a large impact. Currently, a large percentage of global energy is generated by burning fossil fuels, which is the largest contributor to CO_2 and other greenhouse gas emissions [55]. Biochar has been applied in microbial fuel cells as an electrode and as a catalyst in the production of fuels such as biodiesel and hydrogen [73].

6. Biochar and the Production of Green Hydrogen

The global energy demand continuously increases due to the increasing human population and the improvement in the standard of living. Energy demand is expected to increase by 50% by 2030, and currently, 95% of this need is met by burning fossil fuels [74]. Hydrogen has the characteristics to be a viable alternative to fossil fuels as an energy carrier.

Hydrogen is storable, renewable, versatile, and can be used in environmentally friendly methods of energy generation that are non-polluting and sustainable [75].

Hydrogen production methods have been classified into three classes: grey hydrogen, blue hydrogen, and green hydrogen. The main difference in the classification is determined by the level of carbon capture which takes place (Table 4) [76,77].

Table 4. Hydrogen colour classifications, their feedstocks, production technology, and carbon emissions [76].

Hydrogen Colour Classification	Feedstock	Production Technology	Carbon Emissions
Grey	Natural gas	Steam Methane Reforming (SMR)	High
Blue	Natural gas	SMR with carbon capture	Low
Green	Water	Water electrolysis	Free

6.1. Current Methods of Hydrogen Production

The current global demand for hydrogen is 70 megatons and is met predominantly using fossil fuels. Natural gas steam reforming, coal gasification, and oil reforming are the top three current technologies for producing hydrogen (Figure 4) [78].

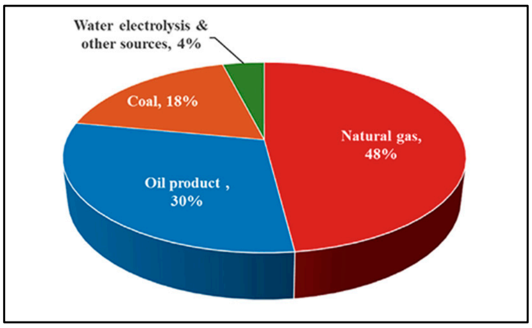


Figure 4. Percentage breakdown of current feedstocks used for hydrogen generation. Image from Ji, M. and Wang, J., 2021 [78].

6.1.1. Reforming of Natural Gas Steam

Natural gas steam reforming, also known as steam methane reforming (SMR), is the main method of hydrogen generation and represents over 45% of hydrogen products. Natural gas, of which 95% is methane, undergoes SMR in the presence of a precious metal or nickel-based catalyst at a temperature of 700 °C or higher. The reactions are discussed below [78–80].

6.1.2. Coal Gasification

Coal gasification is a process in which raw solid carbon-containing material is converted into syngas using gasification agents such as oxygen, H_2O, and carbon dioxide at elevated temperatures. The gasification process produces syngas and solids such as carbon monoxide, hydrogen gas, hydrogen sulfide, methane, ammonia, ash, and tar [81,82].

6.1.3. Oil Reforming

Oil reforming is a process in which oils with a high carbon-to-hydrogen ratio undergo partial oxidation to form hydrogen gas. The reaction requires high temperatures (>1000 °C) and pure oxygen. Oil reforming utilises catalysts to help accelerate the reaction rate and reach equilibrium faster. These catalysts are largely based on noble metals, metal oxides, and aluminium oxides. These catalysts have increased the yield of hydrogen gases over the uncatalyzed reaction [83,84].

Although natural gas steam reforming, coal gasification, and oil reforming make up a large portion of the world's hydrogen production, these methods release large amounts of carbon dioxide. The need for sustainable hydrogen production has gained widespread attention and led to research into green hydrogen technologies.

6.2. Green Hydrogen Technologies

Green hydrogen technologies such as water electrolysis have gained much attention due to the potential of hydrogen to replace fossil fuels in many commercial applications, such as oil refining, heating, energy storage, alternative fuels, and energy generation through technology such as the hydrogen fuel cell [85].

Water electrolysis is the process of dissociating water (H_2O) into hydrogen gas and oxygen gas using an applied potential in a water electrolyser. A water electrolyser consists of three key components: the anode, cathode, and electrolyte. The anode is responsible for the production of oxygen through the oxygen evolution reaction (OER). The cathode is responsible for the production of hydrogen via the hydrogen evolution reaction (HER) [86].

There are four variants of water electrolysers: solid oxide, alkaline polymer exchange membrane (PEM), and anion exchange membrane (AEM). The main difference between them is the reaction pathways, electrolyte, electrode, separator, operating potential, useful life, and efficiency (Figure 5 and Table 5) [74].

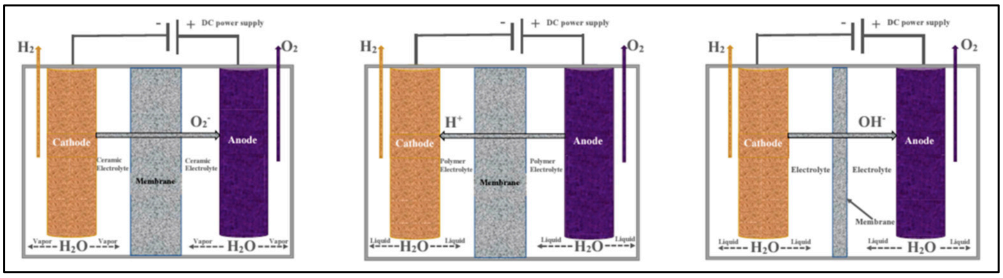


Figure 5. Schematics and operations of the solid oxide, alkaline water, and proton exchange membrane electrolysis techniques. Image from Anwar et al., 2021 [87].

Table 5. Components and technical characteristics of the four major water electrolysis technologies: alkaline, anions exchange membrane, polymer exchange membrane, and solid oxide, adapted from Kumar & Lim, 2022 [74,84].

	Alkaline	**Anion Exchange Membrane (AEM)**	**Polymer Exchange Membrane (PEM)**	**Solid Oxide**
Electrolyte	KOH, NaOH (5M)	DVB Polymer Support + 1M KOH/ NaOH	Solid Polymer Electrolyte (PFSA)	Yttria-Stabilised Zirconia (YSZ)
Anode (OER)	Nickel-coated stainless steel	Nickel or NiFeCo alloys	Platinum on Carbon	Perovskites (LSCF, LSM) (La, Sr, Co, FE) (La, Sr, Mn)
Cathode (HER)	Nickel-coated stainless steel	Nickel	Iridium Oxide	Nickle/Yttria-Stabilised Zirconia (YSZ)
Anodic reaction	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$	$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Cathodic reaction	$2H_2O + 2e^- \rightarrow H_2 + \frac{1}{2}O_2$	$2H_2O + 2e^- \rightarrow H_2 + \frac{1}{2}O_2$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Cell reaction	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$
Separator	Asbestos/Zirfon/Nickel	Fumatech	Nafion	Solid electrolyte YSZ
Potential range	1.4–3 V	1.4–2.0 V	1.4–2.5 V	1.0–1.5 V
Operating temperature	70–90 °C	40–60 °C	50–80 °C	700–850 °C
Life span	60,000 h	>30,000 h	50,000–80,000 h	20,000 h
Conversion efficiency	50–78%	57–59%	50–83%	89% (Lab only)

Based on the technologies listed above, ion exchange membranes and solid oxides are still being researched and developed. Alkaline and polymer exchange membranes have seen commercialisation and industrial applications [74]. The polymer exchange membrane water electrolyser offers greater benefits over alkaline technology, such as greater energy utilisation efficiency, increased hydrogen production, decreased ohmic loss, and increased rates of reactions, leading to higher system response and shorter start-up period, making it best for pairing with intermittent renewable energy generation methods such as solar [88].

6.3. Biochar's Current Application of Biochar in Hydrogen Production

Biochar can have active or passive participation in the production of hydrogen. Active involvement includes catalytic processes where it is used as a support material, while passive involvement includes processes where biochar is produced as a by-product, such as biomass gasification and gas reforming [89].

Liu et al. (2014) discovered a benchtop method to produce hydrogen gas via the gasification of water hyacinth in a two-stage fixed-bed reactor. In the first stage of the reactor, water hyacinth was placed in the pyrolysis reactor at 650–700 °C to produce the hydrogen-rich syngas. The syngas then flows into the microwave reactor, which is the second stage. The microwave reactor uses a set temperature of 800 °C and a mix of silicone-carbide and the nickel/sepiolite catalyst placed on the fixed reactor to crack the syngas into 60–70% rich hydrogen gas [90].

Yao et al. (2016) conducted experiments on the method produced by Liu et al., 2014, using a biochar support material for the nickel catalyst. Yao et al. (2016) replaced the sepiolite support, a magnesium silicate-based material, with biochar produced from wheat straw, cotton stalk, and rice husk. The catalyst was produced using a 15% *w*/*w* nickel impregnation of the char followed by calcination at 800 °C in a tube furnace. The results showed that the cotton stalk biochar-supported catalyst had the highest catalytic activity in the production of hydrogen gas at 92.08 $\mathrm{mg \cdot g^{-1}}$ biomass [90,91].

Afolabi et al. (2021) converted bioethanol into hydrogen gas through catalytic steam reforming that utilised a nickel catalyst supported by Mallee wood-derived biochar. The biochar was synthesised using a two-stage pyrolysis and partial gasification process. The biochar was impregnated with 10 *w*/*w*% nickel using the incipient wetness impregnation method. The biochar-supported nickel catalyst performed on par with the commercial nickel catalyst supported by silicon oxide (Ni/SiO_2), which had an ethanol to hydrogen gas conversion efficiency of 30.8% and 30.0%, respectively, at 450 °C [92].

Sugiarto et al. (2021) conducted experimentation involving the addition of biochar to food waste to observe the effect it would have on the production of biohydrogen through anaerobic digestion. Pinewood-derived biochar was synthesised using slow pyrolysis at 650 and 900 °C. The biochar produced was then leached using a 0.5 mol/L citric acid solution to remove the metal and metalloid impurities found in the biochar. The unleached and leached biochars were then used in the anaerobic digestion of white bread in conjunction with a sludge serving as a microbe source, and it was found that the addition of unleached improved the hydrogen yield by 107% and the hydrogen production rate by 54% compared to the control experiment without biochar [93].

Many of these current biochar applications for hydrogen production are still at or are limited to the laboratory scale because of their novelty or issues with their scalability.

6.4. Biochar's Potential Application of Biochar in Hydrogen Production

Ninety-six per cent of the hydrogen produced around the world is still produced using grey hydrogen methods because of its mature technology and scalability. With green hydrogen technologies mostly favoured for smaller-scale applications, the focus should be on innovating grey hydrogen technology to be more environmentally friendly [78].

Steam reforming of methane accounts for 50% of grey hydrogen production [78]. A big issue that steam methane reforming faces is the deactivation of the nickel catalyst via coking and sintering. Sintering is the process of agglomeration of the nickel catalytic material because of the poor catalyst-support interaction. Coking is the process in which the nickel catalyst is coated by a coke-like material produced by side reactions. Both processes lead to the loss of active catalyst surface area and a decrease in catalyst conversion efficiency [94].

Biochar has great potential as a support material for nickel catalysts used in steam reforming applications, which can be seen in the work done by both Yao et al. (2016) and Affolabi et al. (2020). In both cases, the conventional support material was replaced by a biochar derived from agrowaste and showed on-par performance [91,92].

Other research works, such as the work by Chen et al. (2021), in which a biochar-supported nickel catalyst was used to reform CO_2 from tar, showed improved resistance to coking [95]. Meloni et al. (2020) research showed that support materials with a higher number of functional groups containing active oxygen led to higher resistance to coking [94]. Hence, the application of biochar, a material containing a high oxygen functional group, will be beneficial to the stability and durability of nickel catalysts [96].

Biochar recently found an application in carbon-assisted water electrolysis (CAWE), which is a process where a carbon-based electrode is used as a sacrificial anodic electrode in the production of hydrogen gas. The reactions take place as follows:

$$\text{Anode:} \quad C_{(s)} + 2H_2O_{(l)} \rightarrow CO_{2\,(g)} + 4H^+ + 4e^-$$

$$\text{Cathode:} \quad 4H^+ + 4e^- \rightarrow 2H_{2\,(g)}$$

$$\text{Overall:} \quad C_{(s)} + 2H_2O_{(l)} \rightarrow CO_{2\,(g)} + 2H_{2\,(g)} \qquad E^o = 0.21\ V$$

The theoretical standard potential of carbon-assisted water electrolysis, $E^o = 0.21$ V [97], is significantly lower than that of standard water electrolysis, $E^o = 1.23$ V. Therefore, this method of water electrolysis is more energy efficient as it requires a lower electricity input due to the chemical energy of carbon that replaces part of the electrical energy input needed [98].

It was found that the presence of mono and polycyclic aromatic hydrocarbons such as benzene and others further decreased the standard potential of water electrolysis than that of graphitic carbon. Therefore, the use of biochar, known for producing polycyclic aromatic carbons during its synthesis that is then retained in the biochar, is well suited for use in carbon-assisted water electrolysis [98,99].

Based on the above research work, the current focus of biochar's application in hydrogen production is as a catalyst support material. This is because biochar has many of the traits which a catalyst support needs, such as high surface area, tunable pore structure, and high stability in acidic and basic environments [100].

7. Future Outlook of Biochar Application in Hydrogen Production

The application of biochar in hydrogen production in the near future will progress very slowly as both the fields of biochar and green hydrogen are still establishing themselves. Therefore, the current focus of biochar's application in hydrogen production should be placed on improving the current well-established grey hydrogen methods, which have known shortcomings. Two ways in which biochar could be utilized for grey hydrogen production are by using biochar as a catalyst support material to improve reaction efficiency and by utilizing biochar as a method of carbon capture to decrease the impact these grey methods have on the environment. By implementing these two ideas, grey hydrogen methods would become more sustainable methods of production until green hydrogen methods mature further past their shortcomings and improve their scalability.

Once green hydrogen generation methods such as water electrolysis become more mature, the application of biochar will be guaranteed as there are many benefits to its utilisation, as seen in the literature above. The need for more affordable catalysts is a major factor that limits the widespread application of green hydrogen technologies. The implementation of biochar as a support material will lessen the cost of materials and improve the financial feasibility of these methods.

8. Conclusions

Based on the information put forward in this review and the referenced literature, Biochar holds a vast amount of latent potential. This potential will only grow larger as more research into synthesis methods and feedstocks is investigated, as there are many biogenic substances that remain untapped. The unexploited potential of biochar means that in the future, it could offer even more viable candidates for application in its wide array of fields.

Although the number of prospective applications of biochar is high, the realized application is low. This is attributed to the novelty of biochar and conflicting literature. However, with the push for a more circular economy in terms of how waste is processed, the conversion of waste into valorized products will become a more researched and applied field.

Author Contributions: Conceptualization, E.D.V. and N.S.S.; methodology, E.D.V.; software, L.K.; validation, E.D.V., N.S.S. and L.K.; formal analysis, E.D.V.; resources, L.K.; data curation, E.D.V.; writing—original draft preparation, E.D.V.; writing—review and editing, N.S.S.; visualization, L.K.; supervision, N.S.S. and L.K.; project administration, L.K.; funding acquisition, L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Research Foundation: 138079 and Eskom (South Africa): 2002/015527/0.

Data Availability Statement: All data that support the findings of this study are included within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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