

Review

# Production of Biocoal from Wastewater Sludge and Sugarcane Bagasse: A Review

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**Abstract:** The rising volume of wastewater sludge and sugarcane bagasse is becoming a prominent concern globally. Furthermore, the growing demand for fuel coupled with the depletion of fossil fuel reserves in South Africa demonstrates the need for alternative energy sources. To minimize the reliance on fossil-based energy sources, a renewable resource such as biomass can be optimized as an energy source. Wastewater sludge and bagasse have the energy potential to produce high-calorific-value biocoal; this will contribute to the supply of energy in South Africa. The synthesis of biocoal from wastewater sludge and bagasse through an artificial synthetic coal production process, i.e., hydrothermal carbonization (HTC), is preferred over other thermal conversion techniques as HTC is capable of handling feed having a high (75–90%) moisture content. This article focuses on the production of biocoal from wastewater sludge and sugarcane bagasse as an alternative to sustainable bioenergy supply and as one of the potential solutions for reducing net CO<sub>2</sub> greenhouse gas (GHG) emissions from fossil-fuel power plants, and addresses the use of different thermochemical technologies, previous studies on the composition of wastewater sludge and bagasse, and the benefits of hydrothermal carbonization.

**Keywords:** hydrothermal carbonization; biocoal; sugarcane bagasse; wastewater sludge



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## 1. Introduction

The current energy crises and the rising volume of wastewater sludge and sugarcane bagasse are becoming prominent concerns globally. This is due to the rapid increase in population and urbanization growth, which have resulted in higher demands on resources such as energy and land space [1]. The disposal of this sludge and bagasse has also intensified environmental challenges, which include pollution and waste management issues [1]. These issues are quite detrimental to the global goal of sustainable development, and hence have ignited global interest in sustainable strategies for energy utilization, production, and waste management. Therefore, the study of valorizing biomass (wastewater sludge and bagasse) is a viable conversion process for energy recovery from sludge and bagasse.

South Africa is facing environmental sludge and bagasse disposal problems and is severely challenged by an energy crisis, with widespread inaccessibility to clean energy still being an issue. In Africa, only about 30% of the sub-Saharan African population has access to electricity and roughly 70% must gather fuel wood [2]. Therefore, the conversion of biomass energy sources such as sludge and bagasse to bioenergy can provide a solution to these problems. This may not only solve environmental sludge and bagasse disposal problems, but it will also reduce CO<sub>2</sub> emissions in the atmosphere, which is the main source of climate change and global warming by the greenhouse effect [3]. The modern use of biomass is notable for its conversion into high-quality energy carriers such as electricity [4]. Energy recovery from waste and sustainable sources such as sludge and bagasse can play a role in mitigating energy shortages and diversifying the energy supply.

South Africa's energy needs are provided by fossil-based coal, and 53% of the coal produced in South Africa is used to generate electricity [5]. According to the World Bank

Development Indicators [6], electricity production from coal in South Africa was reported at 92.7%. While the industry (Eskom) is beneficial in providing electricity, substantial CO<sub>2</sub> emissions occur during the process.

As global energy demands are gradually growing with time, the number of research projects on various, large-scale biomass processes increases. Biomass is being converted into a renewable energy source through the global application of numerous industrial technologies and processes [7]. Thermochemical conversion processes include gasification, pyrolysis, and hydrothermal carbonization (wet pyrolysis) [7]. These treatment methods have been developed for improving energy efficiency with various optimistic commentaries [7].

Hydrothermal carbonization (HTC) was selected as the process for converting sludge and biomass to biocoal. Hydrothermal carbonization is a thermochemical process that converts organic feedstock into a carbon-rich solid product [8]. The process is especially suitable for biomass waste with a high moisture content (75–90%) [7]. This singular advantage of the HTC process eliminates the predrying requirement of wet biomass, which is a huge energy-intensive process and a financial load in biomass preprocessing, especially when performed under conventional thermal pretreatments such as slow pyrolysis or dry torrefaction [8].

This review focuses on research and evaluation of the HTC process to produce biocoal from wastewater sludge and sugarcane bagasse. The main objective is to produce biocoal and examine the use of HTC operating parameters as a sustainable development approach in converting biomass to bioenergy, as well as to address the use of various thermochemical techniques by different researchers.

## 2. Biomass as an Alternative Energy Resource

The importance of energy for a nation's development cannot be overemphasized. This is because energy is the cornerstone of economic and social development. Globally, 140 billion metric tons of biomass are generated every year by agriculture [9]. This volume of biomass can be converted into an enormous amount of energy. Agricultural biomass is waste that, when converted to energy, can replace fossil fuels, reduce greenhouse gas emissions, provide renewable energy, and achieve carbon neutrality. Carbon neutrality refers to net-zero carbon dioxide (CO<sub>2</sub>) emissions attained by balancing the emission of CO<sub>2</sub> with its removal so as to stop its increase in the atmosphere that causes global warming [10]. Biomass takes the form of residual stalks, roots, leaves, husks, shells, and animal waste. Waste biomass is a valuable resource. It is widely available, renewable, and virtually free.

### 2.1. Biomass

Biomass is a lignocellulosic material derived from living or recently living organic materials such as wood and agricultural residuals. In a broad vision, nonlignocellulosic materials, such as animal and municipal solid wastes (MSWs), are also termed biomass [11]. Biomass is the fourth-largest source of energy, followed by coal, oil, and natural gas, and provides about 14 percent of the world's total energy consumption [12,13]. Biomass is the only renewable energy resource that can be converted into any form of fuel, including solid, liquid, and gaseous fuels [14]. Biomass is widely used to meet a wide variety of energy requirements, such as heat and electricity generation, and produce biofuels for fueling vehicles. Moreover, its non-edible nature, ability to grow relatively quickly even on infertile land, and abundant availability on earth nominates it as a potential energy resource for sustainable energy production, which is the overall goal of the vision of bioenergy development [15]. Using biomass as a fuel can also be an opportunity to empower rural communities.

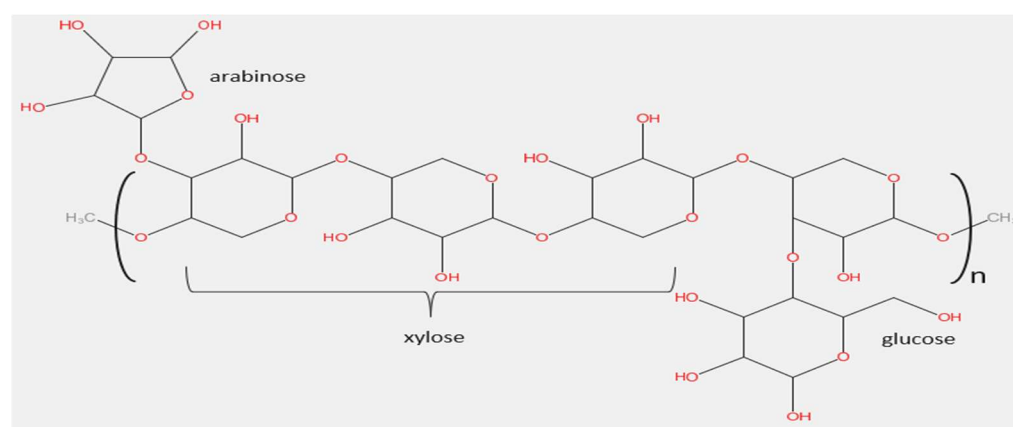
As an energy source, biomass can either be used directly via combustion to produce heat or indirectly after being converted to various forms of biofuel. There are two major biomass groups, and the subclassifications are presented below [16]:

1. Virgin
  - Terrestrial: cultivated crops, forest biomass, energy crops, and grass.
  - Aquatic: water plants and algae.
2. Waste
  - Municipal: MSW, biosolids, sewage, and landfills.
  - Agricultural: livestock and manure, agricultural crop residue.
  - Forestry residues: bark, leaves, and floor residues.
  - Industrial wastes: demolition wood, sawdust, and waste oil or fat.

## 2.2. Sugarcane Bagasse

The selection of feedstock for energy production purposes is dependent upon certain criteria such as potential yield per hectare, feedstock properties, and potential uses. However, the value of sugarcane bagasse as a fuel for energy production largely depends on its calorific value, which in turn depends on its composition, especially its moisture content, and the calorific value of the sugarcane plant, which mainly depends on its content of sucrose.

Sugarcane bagasse is a solid waste obtained after the crushing of sugarcane in sugarcane mills. It proves to be a very efficient raw material in the production of renewable energy. In comparison with the other agricultural crop residues, sugarcane bagasse is the most abundant and high-yielding material. In general, 1 ton of sugarcane generates 280 kg of bagasse. About 54 million dry tons of bagasse are produced annually throughout the world. In South Africa, approximately 6 million tons of raw bagasse are produced annually [17]. Most large and medium-sized mills can use up to 75% of this bagasse onsite to generate heat and electricity. Sugarcane bagasse has proven to be a great source of fuel for the downward gasifier to produce electricity. Sugarcane bagasse is one of the most important lignocellulosic, or plant biomass, materials utilized in the field of power generation. Lignocellulosic materials do not contain readily accessible monosaccharides and chemicals, but rather polymers that need to be hydrolysed to release the desired compounds. Lignocellulosic material is determined by its fibrous nature and the structural framework of which the plant cell is composed. Figure 1 illustrates a simplified structure of bagasse. Bagasse has ash content and a correspondingly high heating value of the order of  $4400 \text{ Kcal} \cdot \text{kg}^{-1}$  [9].



**Figure 1.** Simplified structure of bagasse.

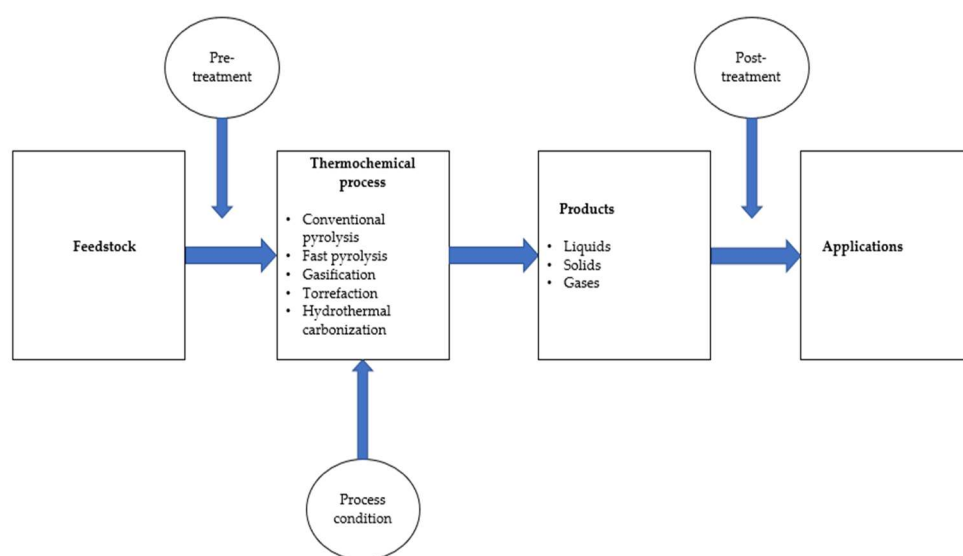
## 2.3. Wastewater Sludge

A direct and easily overlooked consequence of increasing waste globally is the escalating volume of urban wastewater, especially sewage sludge [1]. Sludge can be described as any solid, semisolid, or liquid waste generated by a wastewater treatment facility. This waste can be sourced from municipal, commercial, or industrial processes. The solid phase in sludge is made up of a homogenous mix of proteins, carbohydrates, oils, inor-

organic matter, and micro-organisms. This combination of organic, inorganic, and living organisms produces an unstable, volatile, and putrid matter containing toxic elements. Its volatile organic contents range from 21–48%, and the energy content of dried sewage sludge reported in past literature varies between 11.10–22.10 MJ·kg<sup>−1</sup>, which indicates higher calorific values in comparison to lignite and various other biomass samples [1]. This heating value is one of the core determinants of the suitability of sludge as a solid fuel, as well as the need to effectively eliminate the high organic matter from sludge before disposal. Energy recovery from sludge is regarded as the most attractive for utilizing the increasing quantity of sludge for eliminating volatile organic matter, reducing waste volume with the possibility of recovering nutrients, and providing bioenergy.

### 3. Thermochemical Energy Conversion Processes

As global energy demands grow exponentially with time, the number of research projects into various large-scale biomass processes also increases. Biomass is being converted into a renewable energy source through the global application of numerous industrial technologies and processes as shown in Figure 2. Besides thermal conversion of biomass (combustion), there are currently three main process technologies available: biochemical, thermochemical, and physicochemical. Biochemical conversion encompasses two primary process options: anaerobic digestion (to biogas) and fermentation (to ethanol), where enzymes or microorganisms break down the biomass into liquid fuels. The physicochemical conversion consists principally of extraction (with esterification), where oilseeds are crushed to extract oil. Thermochemical conversion processes include gasification, torrefaction, pyrolysis, and hydrothermal carbonization (wet pyrolysis). The main reason behind the recent interest in bioenergy production is the potentially unlimited supply of biomass available due to its renewability. Thus, biomass is the only naturally occurring carbon resource that is available in large enough quantities to substitute for the world's primary energy-containing resources (fossil fuels) [7].



**Figure 2.** Factors that affect how char is produced and used.

#### 3.1. Conventional Pyrolysis

This process describes the thermal decomposition of organic material under anaerobic conditions. During a pyrolysis operation, the biomass feed decomposes under high temperatures and pressures to produce an energy-dense and carbon-rich stream [7]. Slow pyrolysis is a process that has been traditionally used for thousands of years to produce charcoal. Organic material is heated over relatively long periods at temperatures of around 400 °C. Slow pyrolysis is more tolerant at a moisture content of 15–20%. The main yield is solid char, although tar-like substances and gases (the first being CO/CO<sub>2</sub> and the second one

being  $\text{CH}_4/\text{H}_2$ ) are also produced [18]. Reaction temperatures and residence times can be adjusted to promote the desired product yield. In general, lower temperatures and longer residence times will yield higher amounts of solid products. As temperatures rise and residence times decrease, higher yields of gaseous and liquid products are achieved [19]. However, the main concern associated with slow pyrolysis is the effect of longer residence time on the process energy requirement.

### 3.2. Fast Pyrolysis

Fast pyrolysis involves rapid heating (500 °C–1000 °C) and devolatilization of organic fuels by thermochemical processes in the presence of little or no oxygen [19]. The products of the process are primarily small amounts of char and relatively large amounts of vapour, which contain tars and volatile gases that are rapidly quenched into liquid form. These liquids can then be further refined as useful fuels [19]. The focus of fast pyrolysis is generally on the yield of liquid products (up to 75%) [20]. At very high temperatures and very low residence times, one can distinguish fast pyrolysis from flash pyrolysis [18].

### 3.3. Gasification

Gasification is similar to pyrolysis in that it involves the heating and devolatilization of organic fuels. In this case, enough oxygen is present so that partial combustion may occur. Temperatures remain high (approximately 800 °C) throughout the process to encourage high yields (up to 85%) of gaseous products, or syngas, which are typically used directly [19]. Alternatively, they can be purified and used as gaseous fuels, such as synthetic natural gas (SNG), or in the subsequent production of liquid fuels. As temperatures are generally higher than during pyrolysis and residence times are generally short (10–20 s), gasification yields very little char (10%) and even less liquid product (5%) [20].

### 3.4. Torrefaction

Torrefaction is a thermal process that involves the processing of biomass in a torrefied way to produce a “charred” product that can be used as fuel. Torrefaction is the heating of an input material within an engineered reactor where heat is added from an external fuel source that is directly or indirectly applied to the input biomass undergoing conversion into a “torrefied product” [21]. It is also known as “mild pyrolysis” and occurs at relatively low temperatures (200–300 °C) over moderate residence times (1–3 h). Importantly, the torrefaction process begins with stages of initial heating, predrying, postdrying, and intermediate heating designed to facilitate the evaporation of water and attain a target torrefaction temperature [19]. These stages may involve the consumption of external energy or the autoconsumption of gaseous products to generate heat. The main products of torrefaction are fairly high levels of char (70%) and torrefaction gas (30%). It can yield char that has an improved mass and energy balance over the original feedstock, resulting in improved heating values [19].

### 3.5. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is a thermochemical conversion technique that uses subcritical liquid water as a reaction medium for the conversion of wet biomass and waste streams into a valuable carbon-rich solid product called hydrochar. Figure 3 demonstrates the HTC reactor. Biocoal is a stable, hydrophobic, friable solid product that has a fuel value similar to that of lignite coal. It is usually performed at temperatures ranging from 180 °C to 280 °C, at pressures slightly higher than water saturation pressure to ensure water is in a liquid state, and under an inert atmosphere [22]. HTC temperatures aid the decomposition of biopolymers and the reformation of new compounds. The transformation starts at 100 °C with the dissolution of water-soluble compounds, followed by hydrolysis where monomeric bonds are broken; this occurs at temperatures greater than 150 °C [23]. Reactions occur within the first 20 min to several hours (1–12 h). Reaction time plays a role in increasing carbon and ash content while decreasing oxygen [15]. During

hydrothermal pretreatment, hemicelluloses and cellulose are hydrolysed into oligomers and monomers, while lignin is mostly unaffected [7].



**Figure 3.** The hydrothermal carbonization reactor.

#### 4. Review of the Use of Various Energy Conversion Processes

In the 21st century, research on biomass being converted into a renewable energy source through the global application of numerous industrial technologies and thermochemical processes is being conducted, as shown in Table 1.

**Table 1.** Comparison of thermochemical treatments and typical product yields.

| Process                    | Process Conditions |                        |                                                     |                                               | Approximate Product Yield (Weight %) |       |     | Recommendations |
|----------------------------|--------------------|------------------------|-----------------------------------------------------|-----------------------------------------------|--------------------------------------|-------|-----|-----------------|
|                            | Heating Rate       | Temperature Range (°C) | Pressure                                            | Residence Time                                | Liquid                               | Char  | Gas |                 |
| Fast pyrolysis             | Fast               | 450–550                | Depend on the desired distribution of product yield | Seconds                                       | 75                                   | 12    | 13  | [18]            |
| Slow pyrolysis             | Slow               | 250–450                | Low                                                 | Hours to weeks                                | 30                                   | 35    | 35  | [18]            |
| Torrefaction               | Moderate           | 200–300                | Atmospheric                                         | Several hours                                 | 0                                    | 70    | 30  | [24]            |
| Gasification               | Fast               | 900–1500               | Depend on the desired distribution of product yield | 10–20 s                                       | 5                                    | <10   | >85 | [20]            |
| Hydrothermal carbonization | Moderate           | 180–250                | High Autogenous                                     | Processing time from minutes to several hours | 5–20                                 | 50–80 | 2–5 | [20]            |

Cruz [25] assessed the slow pyrolysis of different biomasses (maple wood and birch bark) to produce a solid pyrolysis product (biocoal) with promising properties and potential use in traditional fossil-coal applications. Batch pyrolysis experiments were carried out in a mechanically fluidized reactor (MFR) having an inside diameter of 9 cm, a height of 13 cm, and a volume capacity of 815 mL. Experiments were conducted at various reaction temperatures (143 °C, 190 °C, 238 °C, 285 °C, 333 °C, 380 °C, 428 °C, 475 °C, 570 °C, and 665 °C), with a heating rate of 12 °C·min<sup>−1</sup> and holding times of 30 and 50 min.



The results showed a decrease of 35% in mass yield between 190 and 238 °C, followed by a decrease of 26–21% between 238 and 285 °C. At 285 °C, the biocoal mass yield decreased by 6% to 3%, reaching a final value of 22.3% at the highest evaluated reaction temperature of 665 °C. The decrease in biocoal mass yield resulted from the fact that further reactions occurred at an increased holding time of 30 to 50 min. The effect of reaction temperature on the high heating value (HHV, on a dry basis) of the biocoal produced with a holding time of 30 min showed that HHV increased with reaction temperature up to 380 °C, while the percentage energy recovery in the biocoal (i.e., energy yield) decreased with increasing reaction temperature. Energy recoveries for biocoal produced at 238 and 665 °C were 83.7% and 32.8%, respectively. The biocoal produced was characterized by ultimate (elemental) analysis, ash analysis, calorific analysis (high heating value), Fourier transform infrared spectroscopy (FTIR), and hygroscopicity. All tests were performed after predrying samples for over 2 h in an oven at 100 °C.

Fialho et al. [26] also investigated the potential use of four agroforestry biomasses (sugarcane bagasse (*Saccharum* sp.), bamboo (*Dendrocalamus giganteus*), straw bean (*Phaseolus vulgaris*), and eucalyptus wood chips (*Eucalyptus* sp.)) to produce biocoal. The pyrolysis of biomass was conducted in an electric laboratory oven using a container with approximately 0.003 m<sup>3</sup> volume capacity. The heating control was conducted manually in increments of 50 °C every 30 min, which corresponds to an average heating rate of 1.67 °C·min<sup>−1</sup>. The initial reaction temperatures were 100 °C, with the final temperatures being 400, 550, and 700 °C. Findings revealed that at 700 °C bamboo and eucalyptus biocoal had the highest heating values, with 30.43 and 29.33 MJ·kg<sup>−1</sup>, whereas sugarcane bagasse and straw bean had the lower heating values, with 27.37 and 28.25 MJ·kg<sup>−1</sup>, respectively. It was observed that bamboo and eucalyptus contained high lignin content, which resulted in them having a higher HHV when compared to the other biomasses. Cheng et al. [27] also recorded high heating values (25.4 to 28.2 MJ·kg<sup>−1</sup>) of biocoals from representative biomasses that were comparable to those of commercial coals. Five common renewable biomass wastes (rice husk, sawdust, wheat straw, bagasse, and soybean straw) were selected as representatives to produce biocoals. The renewable biomass was first fast-pyrolysed at 500 °C in an anaerobic atmosphere in a quartz tubular reactor to produce bio-oil and biochar. Then, the bio-oil was distilled under an air atmosphere from room temperature to approximately 240 °C to obtain the liquid chemicals and biocoal. Results demonstrated the five types of biocoals obtained from the different biomass wastes exhibited yields derived from the bio-oil of 45.2, 37.2, 33.9, 41.8, and 34.3%, respectively. In addition, the estimated mass–energy densities of the rice husk, sawdust, wheat straw, bagasse, and soybean straw-derived biocoals were 25.4, 28.0, 28.2, 26.3, and 27.6 MJ·kg<sup>−1</sup>, respectively.

Muhammad et al. [28], developed a modified vacuum pyrolysis reactor to convert sugarcane bagasse to syngas. The pyrolysis of bagasse was conducted in a stainless-steel fix batch reactor (lab-scale reactor) using a modified vacuum pyrolysis reactor. Experiments were conducted at reaction times (20, 30, 40, 50, and 60 min) and reaction temperatures (210, 230, 250, 270, and 290 °C). An electromagnetic field was applied as a function of current, starting from 1, 2, 3, 4, and 5 Ampere (A) in the second method. The results showed that 0.12 ng·μL<sup>−1</sup>, 0.85 ng·μL<sup>−1</sup>, and 0.31 ng·μL<sup>−1</sup> of hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), and carbon monoxide (CO) gases, respectively, started forming in the first 20 min at 210 °C. At 60 min and 290 °C 20.98, 14.86, 14.56, and 15.78 ng·μL<sup>−1</sup> of H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and CO were generated, respectively. The application of the electromagnetic field demonstrated a significant improvement, in which applying current 3A improved the gas product to 33.76, 8.71, 18.39, and 7.66 ng·μL<sup>−1</sup> of H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and CO, respectively, with an H<sub>2</sub>/CO ratio above 2.

Research by Manyuchi et al. [29] to produce a high-calorific-value biocoal from sugarcane bagasse as an alternative use of coal was experimentally investigated using a stainless-steel reactor with a length of 200 cm and a width of 150 cm. Bagasse was subjected to carbonization at 250–400 °C for 1–7 days. The findings indicate that the amount of ash content in the biochar produced significantly decreased by about 69%. The amount of

moisture content in the biocoal decreased as high as 49%. As the carbonizing temperature increased from 250 °C to 400 °C, the fixed carbon content in the biochar increased by 385%. The biocoal had a calorific value of 28.2 MJ·kg<sup>-1</sup>, a moisture content of 6.3%, a fixed carbon of 74.6%, and an ash content of 1.4%. The biocoal also had carbon dioxide and carbon monoxide emissions of less than 0.9% and 0.02%, respectively.

Tan et al. [30] used microwave-induced torrefaction to synthesize and characterize biocoal from lemongrass (*Cymbopogon citrates*) residue. A modified benchtop microwave oven (model R374AST, Sharp, Malaysia) was purged with nitrogen gas to maintain an inert environment as well as to prevent combustion [4,31]. The microwave power level (100, 300, 500, 800, and 1000 W) and reaction time (30 and 40 min) were varied to obtain the desired torrefaction temperature. Findings revealed that changes in elemental composition were most significant at a torrefaction temperature of 300 °C. The carbon content increased by 0.49, 2.29, and 3.96%. At torrefaction temperatures of 200, 250, and 300 °C, the hydrogen content decreased by 3.12, 8.77, and 8.92%. The oxygen content also experienced a reduction in amount by 2.08, 1.84, and 58.79%, respectively, at the three torrefaction temperatures, studied. A high heating value of 19.37 MJ·kg<sup>-1</sup> was achieved by lemongrass residue torrefied at 300 °C. The H/C and O/C ratios were reduced by 14.3% and 60.0%, respectively. The mass and energy yield of the torrefied lemongrass residue was 61.20–81.50% and 66.11–83.85%, respectively.

In the study of processing and valorizing elephant dung by torrefaction to produce fuel with improved qualities for cooking. Stepien et al. [32] conducted lab-scale experiments at six different temperatures (200, 220, 240, 260, 280, and 300 °C), and three process durations of torrefaction (20, 40, 60 min) using a muffle furnace (Snol, model 8.1/1100, Utena, Lithuania) with CO<sub>2</sub> gas supplied to the furnace, ensuring nonoxidative conditions occur. Results showed a downward trend in the mass yield (MY) for elephant dung biocoal with the increase in process temperature. The highest mass yield value of 90% was obtained at 200 °C. The lowest MY value of 66% was achieved at 300 °C. In this case, the mass yield decreased. The energy yield (EY) of the biochar from elephant dung also decreased with the increase in temperature and did not change with time. When compared to raw material, the biocoals produced at 200 °C yielded more than 105% EY. However, the EY dropped below 68% due to torrefaction at 300 °C. A decrease in the HHV of the biocoals produced from the elephant dung was observed, along with an increase in temperature and time. The highest average HHV of 27.20 MJ·kg<sup>-1</sup> for the biocoal generated was obtained at 280 °C for 60 min.

Chen et al. [33] analysed the torrefaction of sugarcane bagasse at 200–300 °C for 1 h using a reaction tube that was situated in a tube furnace. Nitrogen was continuously blown into the reaction tube to keep the samples in a nonoxidizing environment and to remove volatiles produced from the thermal degradation of bagasse. The flow rate of nitrogen was controlled at 100 mL·min<sup>-1</sup> (25 °C). Results from the research showed that solid and energy yields go down with increasing heating time, and the solid yield is always lower than the energy yield. In examining the HHV, the value rises from 17.1 (raw bagasse) to 22.3 MJ·kg<sup>-1</sup> (torrefied at 290 °C). To produce torrefied pellets, Agar [34] assessed European beech wood using a torrefaction temperature of 270 °C and a residence time of 40–45 min in a rotary-drum reactor. The data obtained revealed a low heating value of 18.28 MJ·kg<sup>-1</sup>, moisture content of 5.0%, and an energy density of 12.84 GJ·m<sup>-3</sup>.

Van der Stelt et al. [24] investigated wood biomass upgrading by torrefaction to produce biofuels at a temperature range of 250–300 °C and a reaction time of 30–10 min. Thus, results showed that at 250 °C and 30 min, carbon was 51.3%, hydrogen 5.9%, oxygen 40.9%, nitrogen 0.4%, ash 1.5%, and LHV 17.6 MJ·kg<sup>-1</sup>. At 300 °C and 10 min, carbon was 55.8%, hydrogen 5.6%, oxygen 36.3%, nitrogen 0.5%, ash 1.9%, and LHV 21.0 MJ·kg<sup>-1</sup>. Kambo and Dutta [4] assessed lignocellulosic biomass to produce a solid biofuel. The experiment was carried out in a reactor, which consisted of a small, perforated basket made of stainless steel fitted with a ceramic crucible attached to the balance to hold the sample at 260 °C with a heating rate of 10 °C·min<sup>-1</sup> for 30 min. The reactor was continuously purged



with nitrogen gas at a rate of  $10 \text{ mL} \cdot \text{min}^{-1}$  to maintain an inert atmosphere as well as to prevent the combustion of feedstock. Findings showed at  $260^\circ\text{C}$  and 30 min, hemicellulose (%) was  $21.5 \pm 3.1$ , cellulose (%)  $36.2 \pm 3.2$ , lignin (%)  $35.1 \pm 3.9$ , and ash (%)  $0.94 \pm 0.04$ .

Barskov et al. [21] studied the torrefaction of three types of biomasses (agricultural wastes, food wastes, and nonlignocellulosic wastes). The experiments were conducted at  $200\text{--}350^\circ\text{C}$ . The results showed that the energy yield for agricultural waste was 71.9%, the oxygen/carbon (O/C) ratio was 0.60, the hydrogen/carbon (H/C) ratio was 0.10, and the heating value was  $21.1 \text{ MJ} \cdot \text{kg}^{-1}$ . Food waste has an energy yield of 78.2%, an oxygen/carbon (O/C) ratio of 0.49, a hydrogen/carbon (H/C) ratio of 0.23, and a higher heating value of  $24.5 \text{ MJ} \cdot \text{kg}^{-1}$ . The nonlignocellulosic waste energy yield was 83.3%, the oxygen/carbon (O/C) ratio was 0.61, the hydrogen/carbon (H/C) ratio was 0.13, and the heating value was  $22.2 \text{ MJ} \cdot \text{kg}^{-1}$ .

A study was conducted by Van der Stelt et al. [24] on biomass (wood) gasification in a circulating fluidized bed (CFB) at operating temperatures of  $950\text{--}1200^\circ\text{C}$  and atmospheric pressure to avoid problems with ash softening and melting. Air was used as a gasifying medium. The steam was exported at  $280^\circ\text{C}$  and 45 bar. Results showed that the integration of torrefaction and gasification resulted in higher energy efficiency than stand-alone gasification. Torrefaction at  $300^\circ\text{C}$  integrated with gasification at  $1200^\circ\text{C}$  conserves the highest amount of chemical energy in the product gas. Couhert et al. [35] carried out gasification experiments using torrefied beech wood in an entrained flow (EF) reactor. It was confirmed that torrefaction reduces the O/C ratio in biomass, and the quality of syn-gas is improved. The gasification of torrefied wood produces 7% more hydrogen, 20% more carbon monoxide, and approximately the same amount of carbon dioxide as the original wood.

## 5. Advantages of Hydrothermal Carbonization

The main advantages of HTC over other thermochemical conversion technologies (such as pyrolysis, gasification, and incineration) are its ability to convert wet feedstock to become carbon-rich solid products (hydrochar) at relatively high yields without preliminary dewatering and drying [20,36], and consequently, requiring less energy. The energy required for the HTC process is expected to be substantially lower than that required for the pyrolysis of such wet feedstock (moisture content of 75–90%) [20].

HTC technology provides a sustainable and eco-friendly approach to producing bio-coal from wastewater sludge and bagasse. This process is cost-effective (costly drying processes are not required), environmentally friendly (net  $\text{CO}_2$  emissions released to the atmosphere are reduced), and capable of producing biocoal with characteristics approaching those of low-rank natural coal. HTC products are mostly in the solid phase, accompanied by gaseous (mainly  $\text{CO}_2$ ) and aqueous (containing bio-oil) by-products. The percentage and properties of final products of HTC processes are affected considerably by process conditions, mainly temperature, which is the main parameter [37].

HTC has been applied to a great variety of lignocellulosic biomasses, with variable composition in hemicellulose (20–40%), cellulose (40–60%), and lignin (10–25%); as well as nonlignocellulosic ones, such as animal manure, food, sewage sludge, and municipal solid wastes, among others, which have significant differences in composition [8]. Along with the numerous benefits that hydrothermal carbonization can provide, identifying potential hurdles to overcome is required to ensure its deployment in future projects. However, HTC will face some obstacles in overhauling the current process, notably among which are the fact that the procedure has numerous unknown mechanisms because it is a novel technology. It also must compete with existing waste disposal processes and other renewable energy technologies. Due to its complexity, the logistics system can be both time-consuming and expensive.

### 5.1. Reaction Mechanisms

Hydrolysis is the first step of the HTC reaction. Hydrolytic reactions occur on the surface of solid biomass, where water reacts with extractives, hemicellulose, or cellulose and breaks ester and ether bonds (mainly  $\beta$ -(1-4) glycosidic bonds), resulting in a wide range of products, including soluble oligomers such as (oligo-) saccharides from cellulose and hemicellulose [38]. Liquid water enters through surface pores and hydrolyses the components, after which the hydrolysed products may proceed to exit through the same pore. Components such as extractives, which are monomeric sugars (mainly glucose and fructose), along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are very reactive in hydrothermal media. With increased reaction time, the oligomers further hydrolyse into simple monosaccharides or disaccharides [38]. At HTC temperatures above 180 °C, hemicellulose starts hydrolysing, and cellulose hydrolysis starts above 230 °C. A very small portion of lignin reacts at a higher HTC temperature (200–260 °C) and releases phenol and phenolic derivatives [7]. Furthermore, inorganic components are very stable and probably remain unchanged by HTC at 200–260 °C. However, the degradation of polymeric components might release inorganics from the solid structure into the liquid [7].

Dehydration of biomass is the formation of water molecules via the elimination of branched hydroxyl (–OH) groups, also known as dihydroxylation [7]. The products resulting from the hydrolysis of cellulose and hemicellulose are dehydrated to form 5-hydroxymethylfurfural (HMF) and furfural, respectively. At temperatures above 150 and 200 °C, respectively, dehydration of water during the cleavage of both phenolic monomers and hydroxyl functional groups may occur during HTC [7]. The dehydration of catechol, formed from the hydrolysis of lignin, may also occur [39].

Usually, decarboxylation refers to the reaction of carboxylic acids with carbon atoms, removing a carbon atom from a carbon chain. Degradation of carbonyl (–C=O) and carboxyl (–COOH) can be associated with the formation of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), respectively [38]. Carbonyl and carboxyl degradation occur rapidly at temperatures above 150 °C and produce minor concentrations of the gases mentioned previously [7]. The carbonyl functional group is present on both 5-HMF and furfural molecules, and a likely source of the carboxyl functional group is the formation of both formic acid and levulinic acid (the hydrolysis products of furfural and 5-HMF, respectively) [7].

Lignin is naturally composed of many stable aromatic rings; these aromatic structures exhibit high stability under hydrothermal carbonization conditions and are the basic building blocks of the resulting biocoal [7].

### 5.2. Production of Biocoal Using the Hydrothermal Carbonization Process

In a study conducted by Bevan et al. [7] on the HTC of paper sludge over an experimental range of 180–300 °C, the temperature of 210 °C produced the highest heating value (9.7 MJ·kg<sup>−1</sup>) and the highest energetic recovery efficiency (90.12%) in the experimental trials. This implies that the final application of the hydrochar as a fuel source would be most optimally produced at this temperature. However, this study further found that hydrochar had lower nitrogen and sulphur content as the reactor temperature was increased. This implies that a lower reactor temperature would be preferred for hydrochar that is to be applied as a soil conditioner (for a paper sludge feedstock). Furthermore, the nitrogen content in hydrochar has been shown to have a significant impact on its specific applications.

Research has shown that the ideal reactor conditions can be determined by identifying the application of the hydrochar and by analysing the composition of the feedstock. Kiran and Ross [40] recorded biocoal with fuel properties similar to those of lignite coal in the hydrothermal treatment of swine manure. Hydrothermal processing of the swine manure was performed in an unstirred 600 mL Parr reactor (Parr, Moline, IL, USA), at temperatures ranging from 120 to 250 °C for 1 h in either water alone or reagents, including 0.1 M NaOH, 0.1 M H<sub>2</sub>SO<sub>4</sub>, and 0.1 M organic acids (CH<sub>3</sub>COOH and HCOOH). The heating rate was approximately 10 °C·min<sup>−1</sup>. The findings revealed that pH has a strong influence on ash

chemistry, with decreasing pH resulting in increased removal of ash. The reduction in mineral matter influences the volatile content of the biocoal and its energy content. As the ash content in the final biocoal reduces, the energy density increases. Treatment at 250 °C results in a more “coal-like” biocoal with fuel properties similar to that of lignite coal and a higher heating value (HHV) ranging between 21 and 23 MJ·kg<sup>−1</sup> depending on pH. Processing at low pH results in favourable ash chemistry in terms of slagging and fouling. Operating at a low pH also appears to influence the level of dehydration during HTC. The level of dehydration increases with decreasing pH, although this effect is reduced at higher temperatures. At higher temperatures of processing (250 °C), operating at a lower pH increases the yield of biocoal. However, the lower yields obtained below 200 in the presence of acid may be due to the acid hydrolysis of carbohydrates in the manure.

In the study of hydrothermal carbonization of chemical sludge from a pulp and board mill at 180–260 °C, using a 0.28 L Büchi Limbo (Büchi AG) reactor fitted with a magnetic stirrer, by Mäkelä et al. [41], results indicated that carbonization increased the carbon content of chemical sludge from 49% to 55–65% depending on the experimental conditions. Char solid and carbon yields were in the range of 63–77% and 64–81%, respectively, and showed an increase in the dissolution of organic compounds at higher temperatures and higher sludge moisture contents. Char ash contents were in the range of 43–53%, with respective ash yields of 75–86%. Filtrate properties were mainly governed by the moisture content of the sludge feed, as a higher moisture content generated a more diluted filtrate. Nonaka et al. [42] found a more hydrophobic solid product and a 91% mass yield with an energy density of 140%. When forest mangrove (*acacia magium*) was hydrothermally treated at 300 °C for 30 min in a batch reactor, Reza et al. [38] investigated the effects of HTC on the agricultural residues of corn stover and rice hulls at 200–260 °C with a 5 min reaction time and reported mass yields of 75–90%. Chen et al. [33] performed HTC on sugar cane bagasse at 180 °C for up to 30 min. The mass yield was reported to range from 61% to 70%, but HTC had an insignificant effect on energy densification, which was 110%. Kambo and Dutta [4] also assessed the potential of using hydrothermal carbonization (HTC) on miscanthus feedstock to produce a carbon-rich solid fuel, referred to as hydrochar, whose physicochemical properties are comparable to those of coal. HTC of biomass was conducted in a 600 mL Parr benchtop reactor (Moline, IL) fitted with the glass liner (762HC3), at different reaction temperatures (190, 225, and 260 °C), residence times (5, 15, and 30 min), and feedstock-to-water ratio (1:6 and 1:12). Results documented revealed that with an increase in the reaction temperature from 190 to 260 °C at a solid load ratio of 1:6, the mass yield of hydrochar decreased from 83.5% to 47.8% and from 72.5% to 44.9% at 5 min and 30 min residence time, respectively. Similarly, at the solid load ratio of 1:12, with an increase in the reaction temperature of 190 to 260 °C, the mass yield of hydrochar decreased from 82.8% to 44.9% and from 66.6% to 42.8% at 5 min and 30 min residence time. The effect of reaction temperature on the HHV of hydrochar was found to be more prominent than the effects of reaction time and feedstock-to-water ratio. At the solid load ratio of 1:6, with an increase in the reaction temperature from 190 to 260 °C, the HHV of hydrochar samples was increased by 29.1% (from 19.9 to 25.7 MJ·kg<sup>−1</sup>) and by 42.9% (21.2 to 30.3 MJ·kg<sup>−1</sup>) at reaction times of 5 min and 30 min, respectively. On the other hand, at the same solid load ratio, with an increase in reaction time from 5 to 30 min, the HHV of hydrochar samples increased by 6.5% (from 19.9 to 21.2 MJ·kg<sup>−1</sup>) and by 17.9% (25.7 to 30.3 MJ·kg<sup>−1</sup>) at 190 and 260 °C, respectively. This shows that the effect of reaction time on the HHV of hydrochar samples is more pronounced at a high reaction temperature (260 °C) compared to a low reaction temperature (190 °C).

He et al. [43] reported that the husks of nuts contained extremely high levels of lignin, e.g., about 61% of the husks of *carya cathayensis* sarg (HCCS). The HHV of hydrochars from the HTC of HCCS under 180–260 °C ranged from 22.0 to 28.2 MJ·kg<sup>−1</sup>, which is even higher than some commercial coals. When assessing the hydrothermal carbonization of sugarcane bagasse via wet torrefaction in association with microwave heating, Chen et al. [33] also reported that the calorific value of bagasse can be increased by up to 20.3% from wet

torrefaction. The mixture of bagasse, deionized water, or sulphuric acid solution was transferred into a cylindrical reactor (50 mm i.d.  $\times$  318 mm length), which was a Teflon vessel. The reactor was placed in a microwave oven which was operated at a frequency of 2.45 GHz. The maximum power of the microwave oven was 900 watts, and the current output from the power controller was fixed at 10 A. The reaction temperature was kept constant at 180 °C. The carbon content in raw bagasse was 39.78 wt.%, but it could be increased to 52.35 wt.% under the conditions of SLR = 0.1 g·mL<sup>-1</sup> and 15 min heating time. This accounts for a 32% increment in carbon content. The values of atomic H/C and O/C ratios in raw bagasse were 1.605 and 0.961, respectively, and they were in the ranges of 1.003–1.325 and 0.528–0.824 when bagasse was pretreated by wet torrefaction. This implies that the chemical formula of bagasse was transformed from CH<sub>1.605</sub>O<sub>0.961</sub> to CH<sub>1.003–1.325</sub>O<sub>0.528–0.824</sub>. The HHV obtained was 16.495 MJ·kg<sup>-1</sup>.

In Berge et al.'s [44] study, food waste, paper, and municipal sewage waste (MSW) were hydrolysed at 250 °C for 20 h in 160 mL stainless-steel tubular reactors. Each reactor consisted of a one-inch-diameter stainless-steel pipe nipple and endcaps (McMaster Carr). One of the end caps was equipped with a gas sampling valve (Swagelok, Inc.) to allow for the controlled collection of gas samples. Findings indicate that at 250 °C and 20 h, the HHV obtained for paper, food waste, and MSW was 23,860, 29,100, and 20,010 KJ·kg<sup>-1</sup><sub>db</sub>, respectively. When assessing biocoal obtained upon hydrothermal carbonization of brewer's spent grain, Poerschmann et al. [45] also recorded high calorific values, indicating significant energy densification of biocoals as compared to the input substrate. The hydrothermal process was performed in an autoclave with a capacity of 200 mL (Roth; Karlsruhe, Germany) filled with 50 g of BSG (23.5% *w/w* dry mass) and 50 mL of distilled water at an operating temperature of 200 and 240 °C, a reaction time of 14 h, and 80 µg·mL<sup>-1</sup> of citric acid as catalyst. Results showed that increased HTC temperatures resulted in lower coal mass yields but higher OC content. The high yield of black-coloured carbon-rich precipitates and the high carbon content of the biocoal point to the good suitability of BSG for the HTC process and are expected to be beneficial for a prospective energetic application. Due to decarboxylation, dehydration, and condensation reactions, both HTC coals showed distinctively higher HHV values (29.9 MJ·kg<sup>-1</sup> at 200 °C and 31.8 MJ·kg<sup>-1</sup> at 240 °C) compared to the input feedstock and the aqueous HTC phase. The energy density of the coalification process as expressed by the HHV<sub>Biocoal</sub>/HHV<sub>Feedstock</sub> ratio amounted to 1.35 for the 200 °C biocoal and 1.43 for the 240 °C biocoal. The calorific values calculated for both aqueous product streams were 20.5 and 20.9 MJ·kg<sup>-1</sup>, respectively. Both biocoals had calorie data slightly higher than those of brown coal and lignin, and significantly higher than those of carbohydrates, but lower compared to those of anthracite and lipids. Findings demonstrate that the brewer's spent grain by-product is a good feedstock for hydrothermal carbonization to produce biocoal, the latter offering good prospects for energetic and soil-improving application fields.

In the study of hydrochar production from faecal sludge (FS) at temperatures of 180, 220, and 250 °C and reaction times of 0.5, 1.0, 5.0, and 10.0 h, using a 1 L high-pressure reactor made of stainless steel, equipped with a pressure gauge, thermocouple, and gas collecting ports by Fakkaew et al. [46], the results from three replicates of batch experiments indicated that high energy contents of 19.5 and 19.0 MJ·kg<sup>-1</sup> could be obtained when the moisture contents were varied at 80% and 90%. However, the energy content of the produced hydrochar decreased to 17.6 MJ·kg<sup>-1</sup> when the moisture content was reduced to 70%. At 95% moisture content, the energy content of the produced hydrochar also decreased to 18.0 MJ·kg<sup>-1</sup>. The range of energy content of the produced hydrochar was comparable to that of lignite and sub-bituminous coal (15.0 MJ·kg<sup>-1</sup> and 18.2 MJ·kg<sup>-1</sup>, respectively) [47], which can be used as a solid fuel in conventional combustion. The highest energy content of 20.3 MJ·kg<sup>-1</sup> was achieved at a temperature of 250 °C and a reaction time of 10 h, while the lowest energy content of hydrochar was found at a temperature and reaction time of 180 °C and 0.5 h, respectively. From the experimental results, increasing temperatures from 180 to 220 °C and from 220 to 250 °C resulted in about 4% and 10% increases in the



energy content of the produced hydrochar, respectively. Increasing the temperature in the HTC reactor would result in more dehydration and decarboxylation of the FS samples, resulting in increased energy content of the produced hydrochar. Concerning reaction times led to increased energy content, especially when operating the HTC at 250 °C. At HTC reaction times of 0.5 h, 1.0 h, 5.0 h, and 10.0 h, energy contents of 13.8 MJ·kg<sup>-1</sup> in the initial dried FS were increased to 18.2 MJ·kg<sup>-1</sup>, 18.8 MJ·kg<sup>-1</sup>, 19.7 MJ·kg<sup>-1</sup>, and 20.3 MJ·kg<sup>-1</sup> in the hydrochar, respectively. The normalized energy yields of the produced hydrochar were found to decrease with increasing reaction time, but the temperature of 250 °C still produced a higher normalized energy yield than those at 220 and 180 °C. It can be deduced from the results that the reaction time of 5 h was optimum in producing the highest normalized energy yield of 13.8 MJ·kg<sup>-1</sup>.

In 2015, Fakkaew et al. [46] studied the effects of hydrolysis and carbonization reactions on hydrochar production. The research was conducted in a reactor at a low-energy HTC process known as “Two-stage HTC”, which consists of hydrolysis and carbonization stages with faecal sludge as feedstock. The study stated that for the hydrolysis stage, increasing the hydrolysis reaction time from 20 to 200 min resulted in the increased energy content of the produced hydrochar. The energy content of the produced hydrochar was greater than 20 MJ·kg<sup>-1</sup> at hydrolysis temperatures and reaction times of 150–175 °C and 150–200 min, respectively. The effects of the carbonization temperature and reaction time on the energy content of the produced hydrochar indicated that increasing the carbonization temperature from 200 to 250 °C resulted in the increased energy content of the produced hydrochar. The energy content of the produced hydrochar was greater than 20 MJ·kg<sup>-1</sup> at the carbonization temperature range of 230–250 °C. Concerning the carbonization reaction time, the energy content of the produced hydrochar tended to decrease with the increase in the reaction time. If the energy content of the produced hydrochar was expected to be greater than 20 MJ·kg<sup>-1</sup>, the carbonization reaction times should be 100–250 min. The experimental results indicated the optimum conditions of the two-stage HTC to be a hydrolysis temperature of 170 °C, a hydrolysis reaction time of 155 min, a carbonization temperature of 215 °C, and a carbonization reaction time of 100 min. The hydrolysis reaction time and carbonization temperature had a statistically significant effect on the energy content of the produced hydrochar. Therefore, the two-stage HTC could be considered a potential technology for treating FS and producing hydrochar.

Khaskhachikh et al. [48] analysed the influence of hydrothermal carbonization parameters on the biomass to produce biocoal obtained from peat. Experiments were conducted in a stainless-steel batch reactor at operating temperatures of 160, 190, 210, and 230 °C with reaction durations of 1 h and 8 h. Results from the research showed that the mass yield of hydrochar samples was reduced with an increase in the reaction time and temperature. Hydrothermal treatment of peat at a relatively low temperature (160 °C) increased the carbon concentration to 60.5% compared to the initial peat, and an increase in the treatment temperature (230 °C) made it possible to increase it to 68.17%. At the same time, a decrease in the oxygen content of the sample by almost 10% was observed. It was established that with an increase in temperature and reaction time, the yield of hydrochar oxygen in it decreases (from 33.1% for initial peat to 19.47% for hydrochar obtained at 230 °C), but carbon increases (from 52.09% for initial peat to 68.17% for hydrochar obtained at 230 °C). With an increase in the reaction time, carbon increases (from 55.91% at 1 h to 64.84% at 8 h) and oxygen decreases (from 33.51% at 1 h to 22.13% at 8 h). It was further discovered that heating values depend on the carbon and oxygen content present in the material. With increasing amounts of carbon and decreasing oxygen, the calorific value will increase. As a result, the high heating values (26.77—LHV, 28.03—HHV) were obtained for a sample at 230 °C.

Mäkelä [49] investigated the carbonization of two different pulp and paper mill sludge residues (fibre reject and mixed sludge) with a laboratory-scale pressure reactor at reaction temperatures of 180–260 °C and retention times of 0.5–6.25 h. It was established that during the fibre reject experiments, the dry solids contents of filtered hydrochar samples



were in the range of 39–65%, with respective solid yields of 59–98% dry basis (db). The reaction temperature was correlated with the increasing ash content of dried hydrochar, ranging from 48 to 67% (db). The ash recoveries obtained ranged from 82 to 102% (db), with an inverse relationship with increasing reaction temperature. Carbon content, O/C ratio, higher heating value, and calculated energy densification of obtained fibre reject hydrochar did not change with reaction temperature, retention time, or liquid-to-solid ratio until respective corrections for increasing ash contents were made. The resulting corrected, dry-ash-free carbon content ranged from 37–87% with respective O/C ratios of 0.05–1.2. Heating values and energy densification ratios for the dry-ash-free hydrochars varied in their respective ranges of 19.9–30.7 MJ·kg<sup>−1</sup> and 1.0–1.6. In addition, the corrected dry-ash-free solid yields were in the range of 37–95%. Energy yields, derived from hydrochar mass yields and energy densification ratios, were in the range of 54–98%.

Results for the mixed sludge experiments indicated that the dry solids content of the filtered hydrochar samples was in the range of 23–53%, with respective solid yields of 64–96% (db). The reaction temperature was correlated with the increasing ash content of dried hydrochar, ranging from 35 to 48% (db). The recovered ash ranged from 81 to 99% (db), with an inverse relationship with increasing reaction temperature. Similar to fibre rejects, the carbon content, O/C ratio, higher heating value, and calculated energy densification of attained mixed sludge hydrochar showed no apparent change with reaction temperature, retention time, or liquid-to-solid ratio until respective corrections for increasing ash contents were made. The corrected, dry-ash-free carbon content ranged from 43–84%, with O/C ratios ranging from 0.01–0.9. Heating values and energy densification ratios for the dry-ash-free hydrochars varied in their respective ranges of 24.2–33.1 MJ·kg<sup>−1</sup> and 1.0–1.3. In addition, the corrected dry-ash-free solid yields were in the range of 54–95%. Energy yields, derived from hydrochar mass yields and energy densification ratios, were in the range of 65–97%.

Zvimba and Musvoto [50] investigated calorific values using a hydrothermal carbonization process, such as the polymeric carbon solid (PCS) process, at short processing times of 1 h and temperatures ranging from 180 °C to 240 °C. The results revealed that an optimal temperature of 210 °C is required to produce a high-quality product. The process increases the calorific value of primary sludge (18 MJ·kg<sup>−1</sup>) and waste-activated sludge (16 MJ·kg<sup>−1</sup>) to the level of low-grade coal (lignite and sub-bituminous), which makes the product a clean, useful biofuel with very low emissions compared to coal. However, the calorific value of digested sludge (11 MJ·kg<sup>−1</sup>) is generally low due to anaerobic digestion. The process reduces volatile and total solids by 62–40% and 37–22%, respectively, when processing sludge only. Nonetheless, the processing of combined sludge and screenings increased the calorific value of the product by up to 35%. In this regard, the process not only provides a single solution for sludge and screening handling at wastewater treatment plants, but it also offers the possibility of co-processing wastewater sludge with other biomass (e.g., municipal solid waste, food waste, agricultural waste, and so on). Scale studies have demonstrated that PCS technology can convert wastewater sludge into useful biofuels and commercial products.

Yang et al. [51] investigated hydrothermal carbonization for the conversion of organic residue from solid-state anaerobic digestion (SS-AD) of livestock waste to solid fuels. The experiments were performed using a 2000 mL reactor consisting of a reactor body, a heater, and a steam condenser that operated under nitrogen gas. The operating temperatures of the HTC reactor were 180–240 °C, and the reaction time was set to 30 min, with a 200 rpm agitation speed. The raw organic residue of SS-AD indicated 10.9% of fixed carbon content and 68.5% of volatile matter content. After the HTC process, the fixed carbon content increased to 13.5% and 14.8%, and the volatile matter content decreased to 59.3% and 54.2% at 200 °C and 220 °C, respectively. As a result, the fuel ratio (fixed carbon/volatile matter) increased due to the hydrothermal carbonization reactions of 0.16, 0.23, and 0.27 at 200 °C and 220 °C, respectively. Results also demonstrated that the carbon content of the hydrochar increased from 44.9% to 47.1% and 48.0% as the HTC reaction

temperature increased at 200 °C and 220 °C. The nitrogen content decreased from 1.4% to 0.8%, respectively. Furthermore, the atomic H/C and O/C ratios decreased from 1.3 and 0.5 to 1.1 and 0.3, respectively, as the reaction temperature increased from 180 °C to 240 °C. Moreover, the results of hydrochar showed properties approaching those of lignite and sub-bituminous coal as the HTC reaction temperature increased. The calorific values of the hydrochar from the organic residue of SS-AD were improved from 19.4 to 20.4 MJ·kg<sup>-1</sup> at 180 °C, 22.4 MJ·kg<sup>-1</sup> at 200 °C, 22.5 MJ·kg<sup>-1</sup> at 220 °C, and 23.1 MJ·kg<sup>-1</sup> at 240 °C, respectively. Therefore, these results confirm that the HTC process can improve the properties of hydrochar from the organic residue of SS-AD and that the elevated carbon and fixed carbon contents can be said to have a strong influence on the calorific value. As a result, the hydrothermal carbonization process can be said to be an advantageous technology in terms of improving the properties of organic waste as a solid-recovered fuel product. To produce solid hydrochar and process water rich in organic carbon, Kiran and Ross [40] compared the treatment of four dissimilar digestates from anaerobic digestion (AD) of agricultural residue (AGR); sewage sludge (SS); residual municipal solid waste (MSW); and vegetable, garden, and fruit waste (VGF). Hydrothermal reactions were performed in a 600 mL stainless-steel Parr 4836 bench-top reactor (Parr, Moline, IL, USA) at 150, 200, and 250 °C for 1 h using 10%, 20%, and 30% solid loadings of a fixed water mass. The results obtained for feedstock characterization indicated that digestate samples contained high levels of ash, ranging from 40–55 wt.%. The exception was the AGR digestate, which had a lower ash content of 16 wt.% and a corresponding higher carbon content. The calorific value of the dewatered digestates ranged from 15 to 17 MJ·kg<sup>-1</sup>, with the lower ash content (AGR) having a higher calorific value. The protein content was highest in the SS digestate (24.3 wt.%), followed by the AGR digestate (17.7 wt.%), then VGR (9.8 wt.%), and MSW (6.8 wt.%). It was recorded that as the temperature increased, the yield of hydrochar was reduced for all the feedstocks, but the most dramatic decrease was seen in the AGR digestate, which contained the largest lignin content and the lowest ash content. At 250 °C, there was significant energy densification from the feedstock of 17.8 MJ·kg<sup>-1</sup> to 24.2 MJ·kg<sup>-1</sup>. Energy densification was not observed for the other digestate samples, largely due to their high ash content. However, the yields of MSW, SS, and VGF hydrochar were higher, although the carbon contents of the hydrochars were significantly lower than that of AGR (44–57 wt.% for AGR to 24–34 wt.% for all other hydrochars).

The results showed that the effect of solid loading on solubilization is feedstock-dependent. Increasing solid loading lowers the solubility across all feedstocks treated, increasing hydrochar yield. The greatest reduction in solubility was found with AGR treated at 200 °C. However, an increase in temperature has been shown to favour an increase in carbon content and HHV. The AGR digestate produced the greatest higher heating value (HHV) of 24 MJ·kg<sup>-1</sup> at 250 °C. The effect of energy densification was greater with AGR due to its larger lignin content. SS hydrochar carbon content is uniform; therefore, there was little benefit to hydrochar quality when processed over 150 °C. Ash content in the hydrochar increased with both higher temperatures and solid loading, resulting in a decrease in inorganic content in the process water.

## 6. Conclusions

Hydrothermal carbonization is poised to compete against several thermochemical processes for biomass and waste that can produce new and more diverse solutions for waste management in addition to value-added products. Undoubtedly, there are obstacles to overcome. At the same time, energy security and climate change concerns have sparked an interest in innovation, experimentation, and motivation to look beyond traditional carbon-based materials toward new boundaries. By presenting new possibilities and a variety of new carbon-based solutions, HTC can provide a method of addressing the so-called carbon problem.

HTC is an effective technique for the treatment of sewage waste and biodegradable municipal waste. It can significantly reduce the emissions of dangerous gases as compared

to the conventional landfill and incinerator approaches. Additionally, the energy created is sustainable because it is generated with no net CO<sub>2</sub> emissions and is renewable. Implementing the HTC process is a viable solution in achieving the phasing out of subsidies to fossil-fuel industries, as well as reducing reliance on fossil fuels. This presents an opportunity to counteract climate change, global warming, and its detrimental effects. Additionally, using HTC as a substitute technique for disposing of biomass waste will prevent municipal biodegradable waste from going to landfills.

This study recognizes that the production of biocoal is highly affected by temperature, time, and solid loading. The capacity of carbon content and increased calorific value slowly increase at elevated temperatures. Furthermore, lower-temperature hydrothermal process waters typically have higher biodegradability than higher temperatures. Solid loading lowers the solubility of the feedstock increasing in hydrochar yield, carbon content, and calorific value. Furthermore, reaction time plays a role in increasing carbon and ash content while decreasing oxygen. Interestingly, more research is required to evaluate the long-term stability of the HTC process, and there are still some challenges for HTC replacing the current process:

- Due to the intricacy of the various biomass sources employed and potential contamination of the biomass feed, there may be considerable variability in the final quality of the hydrochar.
- Since HTC is a novel technology, there are numerous unidentified mechanisms.
- The HTC logistics system can be pricey and time-consuming.

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