

Exploring Biomass Conversion Technologies: From Raw Materials to Valuable Products

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Abstract: The global demand for eco-friendly energy has propelled biomass into the spotlight. This report delves into biomass conversion technologies, including biochemical and thermochemical processes, with a focus on hydrothermal conversion. It highlights challenges related to cost-effectiveness and commercial viability. Thermochemical conversion processes, such as pyrolysis and combustion, unlock energy from organic matter. Hydrothermal processing's three approaches and their efficiency are discussed, particularly in biofuels, chemicals, and biochar production. The review analyzes hydrothermal gasification, emphasizing its efficiency and minimal processing time. Carbon and hydrogen gasification efficiencies are crucial in determining gas yields in supercritical conditions. Yield distribution and the influence of feedstock nature and composition on product yield are examined. In conclusion, this report offers insights into biomass conversion technologies and their sustainability for energy and chemical needs.

Keywords: Carbon Gasification Efficiency; Gasification; Hydrothermal Process; Catalyst; Yield; Biomass

Introduction

In a world facing ever-increasing energy demands and environmental challenges, the exploration of sustainable and eco-friendly energy sources has become paramount. Biomass, a renewable and abundant resource derived from organic materials, has gained significant attention as a potential solution to these global challenges. Biomass conversion technologies represent a pivotal step towards harnessing the energy potential locked within organic matter, transitioning it from its raw form into valuable and versatile products. These products can range from biofuels, both in liquid and gaseous forms, to essential chemicals with applications in various industries (Yoganandham et al., 2020).

This comprehensive exploration delves into the diverse and evolving landscape of biomass conversion

technologies. Our journey begins with an overview of the available methods and processes used to transform raw biomass into valuable commodities. To set the stage, we focus on the hydrothermal conversion process and its significance as a promising approach. Before we dive into the intricate details of hydrothermal processing, we offer an insight into other fundamental routes for biomass conversion.

The first leg of our exploration ventures into biochemical conversion techniques, where the natural degradation of biomass occurs through biological processes. This section covers aerobic and anaerobic degradation, fermentation, and enzymatic hydrolysis reactions. These intricate biochemical pathways rely on microorganisms, enzymes, and bacteria to initiate the breakdown of biomass in carefully controlled environments. While these methods hold the potential for producing valuable biofuels and chemicals, they face

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challenges related to cost-effectiveness and commercial viability due to substantial capital investments.

Our journey continues with a discussion of thermochemical conversion processes, which have been a fundamental part of human civilization for centuries (Tekin et al., 2014). By subjecting biomass to high temperatures and various chemical reactions, thermochemical methods offer a means to unlock the energy stored within organic matter (Brown et al., 2010). This section highlights the subcategories of pyrolysis and combustion, shedding light on the transformation of biomass into valuable liquid, solid, and gaseous products. Temperature, time, and catalysts play pivotal roles in determining the composition of these products, making them an essential focus of study.

Finally, we shift our attention to hydrothermal processing, a domain of great significance within the realm of biomass conversion. This versatile process comprises three distinct approaches: hydrothermal liquefaction, hydrothermal gasification, and hydrothermal carbonization. Hydrothermal carbonization has gained recognition as an innovative technique, known for its ability to efficiently process wet biomass without the need for pre-drying (Funke & Ziegler, 2011). The operating conditions for hydrothermal processes include high temperatures and pressures, typically ranging from 250 to 374 °C and 4 to 22 MPa, all while in the presence of water. This unique feature of working with wet biomass at supercritical conditions leads to energy savings, making it a suitable option for managing high-moisture biomass generated by agriculture, food industries, and plants.

Intriguingly, hydrothermal conversion is not just about producing biofuels or chemicals; it also yields a solid product known as biochar (Brown et al., 2010). The composition and characteristics of this biochar can be finely tuned by altering parameters such as pressure, temperature, reaction time, and the presence of catalysts. Such flexibility offers a promising avenue for tailoring the output to meet specific requirements and applications.

Throughout our exploration, we will unravel the intricacies of these biomass conversion technologies and the factors that influence their outcomes. The knowledge and insights gained from this journey will not only expand our understanding of how to efficiently utilize biomass resources but also contribute to the ongoing efforts to establish a more sustainable and environmentally responsible approach to meeting our energy and chemical needs.

Method

In this study, a literature review methodology is utilized, concentrating on a range of international

journals investigating gasification and hydrothermal processes to convert biomass. The research delves into the effects of different parameters which optimized the carbon gasification efficiency and yield.

Result and Discussion

Different Routes of Biomass Conversion

There are various pathways for the conversion of biomass from its raw state into valuable products, potentially including biofuels (in liquid or gaseous form) and valuable chemicals utilized in various industrial processes (Hashaikeh et al., 2005). Our examination primarily centers on the hydrothermal process, and before delving into the intricacies of hydrothermal biomass conversion, we provide a concise survey of the existing technologies employed for the generation of these valuable products (Kong et al., 2008).

Biochemical Conversion Techniques:

This process involves the natural degradation of biomass through biochemical reactions that occur organically. These reactions encompass both aerobic and anaerobic degradation, fermentation, and enzymatic hydrolysis processes rooted in the principles of biochemistry (Saxena et al., 2009). In a simplified perspective, it can be described as the initiation of biomass degradation by microorganisms, enzymes, or bacterial organisms within a controlled environment (Awasthi et al., 2023).

In anaerobic degradation, bacteria consume the oxygen contained within the biomass rather than relying on atmospheric oxygen. This consumption leads to the decomposition of biomass into CH₄, CO₂, and solid byproducts. Conversely, aerobic degradation involves microorganisms breaking down biomass, resulting in the production of CO₂, energy, and solid residues while utilizing atmospheric oxygen (Manikandan et al., 2023).

Fermentation represents another biochemical pathway for biomass conversion, yielding products in liquid form. In this process, yeast plays a pivotal role in chemically transforming biomass into sugars and ethanol. Nonetheless, these techniques, despite their effectiveness, face significant challenges related to their cost and limited commercial viability due to the substantial capital investment required (Davis & Bartling, 2023).

Thermochemical conversion process

The fundamental principle of this conversion pathway revolves around the breakdown of biomass into valuable products through the application of thermal energy (L. Zhang et al., 2010). This process boasts a long historical legacy, having been employed

since the early days of human civilization to meet energy needs (Kabir et al., 2019). Throughout history, biomass has found application in generating heat, cooking food, and producing coke. The Subcategories of thermochemical conversion method is elaborate in coming section.

Pyrolysis:

A subcategory within the realm of thermochemical techniques is pyrolysis, which involves the thermal decomposition of organic materials or biomass within an inert environment (Shafizadeh, 1982). Pyrolysis holds particular significance within the broader thermochemical conversion process due to its advantages in terms of product storage, transportability, and ease of handling (Paz-Ferreiro et al., 2018). This method yields a spectrum of products, including liquids, solids, and gases (Cai et al., 2018). Various factors can influence both the quantity and composition of these end products.

When focusing specifically on biomass, researchers have identified two primary streams of output: condensable gas (liquid) and non-condensable gas (primary gas) (French & Czernik, 2010). Among the condensable gas products, substances such as tar and bio-oil, characterized by their heavy molecular compositions, are noteworthy. These products include oxygenated hydrocarbons like phenolic ethers, alkyl phenolics, heterocyclic ethers, polyaromatic hydrocarbons, and a significant proportion of water, which result from the decomposition of biomass (Bridgwater, 2012). The specific products obtained are contingent upon factors such as the type of biomass, the configuration of the pyrolysis reactor, heating intensity, temperature, time, and the presence of a catalyst. One of the most critical determinants of the product yield is the compositional makeup of the initial biomass.

The temperature required for the decomposition of different biomass components varies. For instance, hemicellulose typically decomposes at approximately 220°C (Wu et al., 2009), while lignin degradation occurs within a range of 200 to 500°C, and cellulose decomposition typically takes place around 280°C (Seah et al., 2023). Temperature exerts a significant influence on product yields, with higher temperatures resulting in increased quantities of liquid and gaseous products. This effect is attributed to the accelerated breakdown rate of lignocellulosic samples at elevated temperatures.

Combustion

This thermal conversion process represents a distinct category primarily employed for energy generation. It entails subjecting the compositional constituents of biomass to high temperatures in the presence of air, resulting in the generation of heat

(Nussbaumer, 2003). Widely recognized for its simplicity and extensive application in the production of heat and electrical energy, the energy content, or heating value, of lignocellulosic biomass plays a pivotal role in determining energy yield under specific process conditions (Allangawi et al., 2023).

An overall assessment of the energy potential of any biomass sample reveals that carbon-carbon (C-C) bonds possess the highest energy content when compared to carbon-oxygen (C-O) and carbon-hydrogen (C-H) bonds (Nhuchhen & Afzal, 2017). In general, lignocellulosic biomass, particularly woody biomass, can yield approximately 20,000 kJ/kg of energy when the ash content is minimal, typically around 1% (Galhano dos Santos et al., 2018).

Hydrothermal processing:

The hydrothermal process, particularly hydrothermal gasification, is a topic of interest. Within the realm of the hydrothermal process, this presents an alternative route to produce bio-based products from raw biomass. Three fundamental hydrothermal processes are recognized, namely hydrothermal liquefaction, hydrothermal gasification, and hydrothermal carbonization (Yoganandham et al., 2020). Typically, this process operates within the temperature range of 250–374°C and at pressures of 4–22 MPa, with water as a key component. It is possible to use self-generated pressure for this process, provided that the required temperature conditions are maintained (Tekin et al., 2014). One notable advantage of this approach is its ability to process wet biomass without the need for prior moisture removal. Consequently, it is an efficient method for dealing with high-moisture biomass residues commonly generated by agriculture, food industries, and plants. The hydrothermal process exhibits diversity and is categorized into two branches based on the reaction conditions: Subcritical conditions, Supercritical water conditions (Sinag et al., 2012).

The essential steps involved in the hydrothermal process during the biomass disintegration encompass: At around 100°C, water-soluble biomass components dissolve, and at or above 150°C, hydrolysis initiates; Biopolymers such as cellulose and hemicellulose begin to break down into their constituent units in a chain-like manner (Kong et al., 2008; Sinag et al., 2012; X. Zhang et al., 2016).

The solid biomass transforms into a slurry when the conditions reach 200°C and 1 MPa. Liquefaction takes place at 300°C and 10 MPa, leading to the production of an oily product. In addition to the production of an oily product, the hydrothermal process also yields a solid product known as biochar. Adjusting various parameters such as pressure, temperature, reaction time, and the presence of catalysts can influence

the desired product yield. Before delving into the two branches of the hydrothermal process, it is imperative to explore the behavior of water at subcritical and supercritical conditions.

Subcritical and supercritical water

The critical point of water is situated at 374°C and 22.1 MPa. The subcritical region, on the other hand, encompasses temperatures below the critical point, spanning from 100°C to 374°C, under sufficient pressure to maintain a liquid state (Sasaki et al., 1998). Both subcritical and supercritical conditions of water offer various advantages due to the alterations in their properties. Water, being a universal solvent, exhibits the capacity to modify its solvent properties as required by adjusting temperature and pressure (Kabyemela et al., 1997). As water's temperature transitions from ambient to the critical region, there is an escalation in the generation of ionic products. Viscosity, conversely, decreases with rising temperature, approaching a similar magnitude to that of water vapor as it nears the critical point. Notably, water exhibits characteristics such as heightened diffusion, rapid solvation, and increased reaction rates when its viscosity is low (Adschiri et al., 1992). Moreover, at these elevated temperature conditions, water functions as a reactant, particularly in the context of hydrothermal reaction mediums. At the critical point, water molecules act as a source of hydrogen during the hydrolysis of biomass (Sun et al., 2020).

Hydrothermal liquefaction.

As demonstrated previously, hydrothermal processing represents another method by which lignocellulosic biomass can be effectively converted into liquefied products with high energy content. This process is typically conducted in the subcritical region under high pressure and offers the advantage of rapid liquid fuel production, often within the span of an hour or even minutes (Toor et al., 2011). The appeal of this technique can be attributed to several compelling reasons: environmentally friendly solvent utilization, Capability to process moist biomass without the need for additional steps, and lower temperature requirements compared to pyrolysis.

Moreover, this process boasts remarkable energy efficiency. The production of bio-products within this method is marked by intricate reactions owing to the complex polymeric structure of biomass (Li et al., 2021). The disintegration of biomass components in the subcritical region leads to various products through the following degradation mechanisms: depolymerization of the biomass, degradation of monomers involving cleavage, dehydration, and decarboxylation reactions,

binding of fragmented components (Gollakota et al., 2018).

The process starts with hydrolysis in water, breaking down biopolymeric structures into oligomers and monomers (Gollakota et al., 2018). Water disrupts hydrogen bonds, leading to glucose monomers from cellulose. Rapid hydrolysis produces various products, including acetic acid and furfural derivatives (Brown et al., 2010). Hemicellulose yields sugar monomers, such as xylose, which can transform into different structures, like furfural (Gollakota et al., 2018). Lignin disintegrates into lower-weight compounds, including phenolic ones under hydrothermal conditions. In summary, bio-oil yield increases at 300-350°C, while exceeding 350°C enhances bio-gas yield (Elliott et al., 2015). High oxygen content in biofuel reduces its higher heating value (HHV), making it unsuitable as a vehicle fuel. Methods like dehydration, biomass decarboxylation, and hydro-deoxygenation can reduce the oxygen content, increase HHV, and enhance stability for better biofuel characteristics (Gollakota et al., 2018).

Hydrothermal carbonization (HTC).

This conversion technique garnered considerable attention from researchers for the evaluation of its process and conditions. The fundamental principle of this method is to convert biomass into valuable products, and it is known for its cost-effectiveness and environmentally friendly nature (Reza et al., 2014). In a nutshell, the hydrothermal carbonization (HTC) process involves treating a biomass sample at 200°C and pressure for several hours in the presence of water, resulting in high product yields in a relatively short time frame. HTC offers several advantages, including a low carbonization temperature, reactions in an aqueous phase, utilization of cost-effective feedstock, access to renewable sources of carbon, and the potential incorporation of significant chemicals such as nanoparticles or functional monomers into the product structure (Libra et al., 2011). Numerous studies have been conducted to transform carbohydrates, cellulose, and other biomass materials into carbon-rich substances through HTC. Hydrothermal carbonization reactions occur in three sequential steps, primarily utilizing carbohydrates as the biomass source: dehydration of carbohydrates into compounds like 5-HMF or furfural, polymerization processes that result in the formation of poly-furans, and carbonization through intermolecular dehydration (Seah et al., 2023).

The carbons derived from HTC of carbohydrates typically manifest as spherical micron-sized particles, featuring numerous polar functional groups. These functional groups contribute to the product's hydrophilic nature and enhance its solvation rate in water (Sivaranjane et al., 2023). The particle size of the

resulting product can vary and is influenced by process duration and precursor concentration. Consequently, carbons obtained through HTC exhibit distinctive characteristics, which have driven the growing interest in hydrothermal carbonization studies.

Hydrothermal Gasification (HTG)

Conventional gasification involves introducing oxygen or steam into a gasifier to oxidize carbon, producing CO₂, CO, and H₂. The energy released maintains the gasifier temperature, and adding steam promotes hydrogen production (Paidá et al., 2019). However, these methods require feedstock pre-treatment to reduce moisture. Unconventional subcritical and supercritical water-based gasification methods offer solutions (Luterbacher et al., 2009). Hydrothermal gasification (HTG) in supercritical water is particularly effective for biomass, yielding gaseous products like CO₂, CO, H₂, and CH₄. These gases, called syngas, can be used for energy or further processed for hydrogen production and synthetic liquid fuels using the Fischer-Tropsch process.

Hydrothermal gasification offers several advantages over conventional methods, including: water serving as both a reactant and a reaction solvent, greater stability due to the use of water as the primary reactant, high reactivity, elimination of the need for pre-treatment of biomass, reduced processing time compared to other methods, gaseous state of the final product, and limited formation of byproducts such as tar and coke (Kipçak et al., 2011; Kruse et al., 2010; Luterbacher et al., 2009; Selvi Gökaya et al., 2020). These attributes make hydrothermal gasification an attractive and efficient alternative for converting biomass into valuable gaseous products.

SCWG Products analysis

The products of SCWG were evaluated easily the analysis of CGE and HGE. Because the gas yield is a function of CGE and HGE at supercritical condition. Carbon Gasification Efficiency (CGE) it is define as the ratio of the amount of carbon in the gas phase products to the amount of carbon in the feedstock (Matsumura et al., 2006). Hydrogen Gasification Efficiency (HGE) is defined as the ratio of the hydrogen in the gas phase products to the amount of hydrogen in the feedstock.

Carbon and hydrogen gasification efficiency have also been calculated from elemental analysis and the yields of gaseous products. CGE and HE have several factors, which can be responsible for fluctuating these efficiencies. Some of these factors are feedstock composition, temperature, pressure, heating rate, catalyst, Water to biomass ratio, etc (Lu et al., 2012; Matsumura et al., 2006). Briefly, it is stated those factors which lead to enhance the gas yield composition also

enhance the CGE as well HGE. Like heating rate enhances the yield of all gas yield except CO yield, similarly it enhances the CGE as well HGE. Increment in temperature and pressure leads to enhance the gas yield by depleting the liquid as well solid yield, similarly it also enhances the CGE as well HGE (Arun et al., 2020; Paidá et al., 2019). As the catalytic effects has tremendous role on yield enhancement, these catalytic effects also enhance the CGE, HEG and dramatically enhancement in HS by Nickle catalyst observed (Youssef et al., 2010).

Feedstock nature and its microstructure and composition influences on gasification and efficiencies like the more complex the structure, CGE and HGE decreases (Wang et al., 2023).

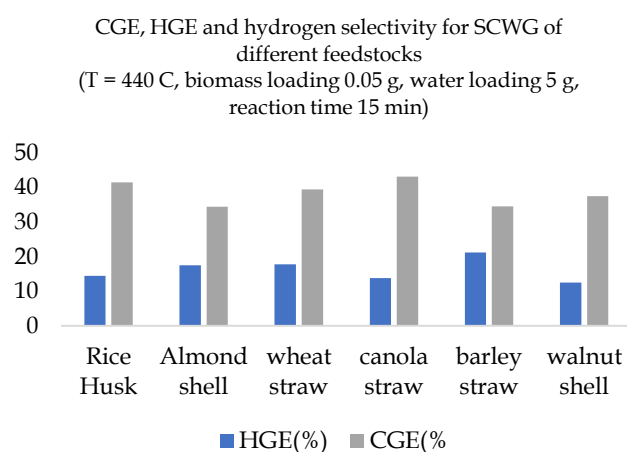


Figure 1. Biomass Gasification (Kurian et al., 2022; Safari et al., 2016, 2018; Wang et al., 2023; Zhang et al., 2022)

Figure 1 showed the comparative outcomes of some selected biomass. Canola showed the maximum CGE whereas the barley shows the maximum HGE because Canola likely has a higher carbon content and a more favorable composition for efficient gasification. Factors such as the ratio of carbon to other elements, the presence of moisture, and the overall structure of the biomass can affect the CGE. Canola's specific properties make it more efficient in converting its carbon content into gas products during the gasification process (Sarker et al., 2022). The HGE is influenced by the hydrogen content in the biomass, and barley straw likely has a higher inherent hydrogen content. This higher hydrogen content can lead to a more efficient conversion of hydrogen into gas products during the gasification process (Ljunggren et al., 2011).

The heating rate enhance the yield of all gas yield except CO yield, similarly it enhances the CGE as well HGE (Heeley et al., 2023). Increment in Temperature and pressure leads to enhance the gas yield by depleting the liquid as well solid yield, similarly it also enhances the CGE as well HGE (Mishra et al., 2023) . As the

catalytic effects has tremendous role on yield enhancement as discuss in detail previously, these catalytic effects also enhance the CGE, HEG and dramatically (Heeley et al., 2023; Reddy et al., 2014)

Yield Distribution:

In this section we discussed the yield of gasification at SCW. In above sections, it has been cleared the factors which influences on yield. The yield of biomass is classified into three major streams same as the state of matters. From the literature it is seemed the major work on SCWG focused on gas yield and its distribution due to its direct usability without any further processing that is why its demand enhance as the usability (D. et al., 2015). Here we focused on liquid and gas yield distribution by quoting different experimental

outcomes of different biomasses. But the solid product, i.e tar or tarry materials was not examined by most researchers. Different researchers investigate the liquid as well as gas yield of different biomass, but it is not possible to show all these outcomes. The yield distribution of liquid when popular wood dust was gasified at P= 25 MPa (Selvi Gökkaya et al., 2019). This experimental investigation defines that phenol behaves as intermediate for tarry materials that cause to block the tubes of tubular reactor, but its yield decreases with enhancement of temperature from 300 °C to 500 °C. Product yields (aqueous product/kg C in biomass) of major organic compounds identified in liquid product from the gasification of poplar wood dust in relation to catalyst.

Products Yield distribution of different feedstocks where as gas distribution in mmol/gm (T = 440 C, biomass loading 0.05 g, water loading 5 g, reaction time 15 min)

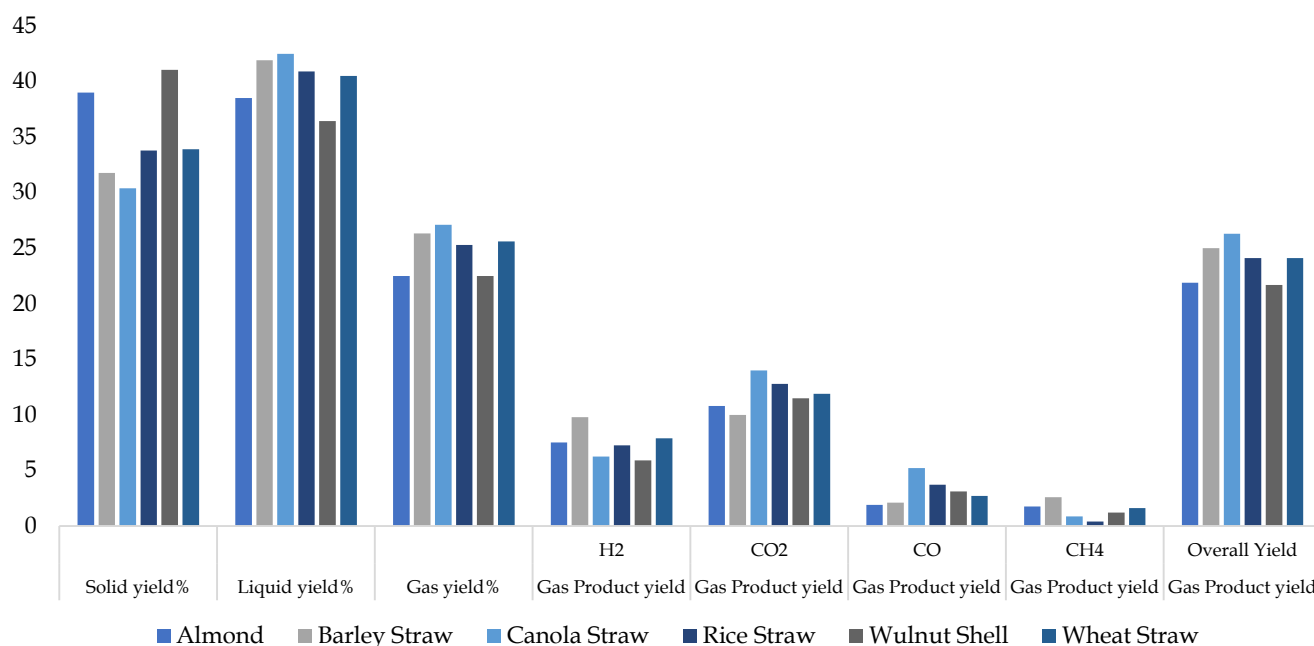


Figure 2. Product Yield Distribution of Different Biomass Feedstock

If we evaluate the total yield of different biomass samples then it presents the concept of structure effects like complexity in structure of biomass increases cause to enhance the tarry yield and deplete the gas yield of biomass (Mishra et al., 2023), it can be state that it causes to decrease the gasification efficiency of biomass. This effect has been proved by different researchers during their investigation of SCWG and its parametric evaluation. The results justify the statement of structure and the overall gas yield% define in order like canola stalk>wheat straw >rice straw>barley straw >almond shell>walnut shell as shown in figure 2. Except walnut shell, Walnut shell has a very high lignin amount in its structure because of its complex structure (Güngören

Madenoğlu et al., 2014), it resists during hydrolysis and postpones the completion of the process and decomposition in SCWG.

In addition, comparing the amount of hydrogen yield, barley straw had the highest yield because of the higher percentage of hydrogen in its initial form and walnut shell had the lowest. Furthermore, the solid yield% in order of walnut shell > almond shell> wheat straw > rice straw> canola stalk> barley straw and the trend of liquid yield as canola stalk> barley straw > rice straw >wheat straw >walnut shell > almond shell. (Kruse et al., 2010; Kumar et al., 2020; Liu et al., 2012; Luterbacher et al., 2009; Sims et al., 2010; Street, n.d.; Xiao et al., 2010).

Critical Discussion

The article explores biomass conversion technologies as a sustainable solution to global energy demands and environmental challenges. It covers biochemical and thermochemical conversion methods, emphasizing the significance of hydrothermal processing. While biochemical pathways rely on microorganisms, enzymes, and bacteria to degrade biomass, they face cost-effectiveness challenges. Thermochemical processes like pyrolysis and combustion play a crucial role in unlocking energy from organic matter, although their environmental impacts could be explored further. Hydrothermal processing, operating at high temperatures and pressures, efficiently converts wet biomass, and the discussion of subcritical and supercritical water conditions is informative. Hydrothermal gasification is highlighted for its efficiency and minimal processing time, and the analysis of carbon and hydrogen gasification efficiencies adds depth to the discussion. Yield distribution analysis reveals the complex nature of biomass conversion and emphasizes the role of feedstock composition. However, the article could provide more real-world applications and environmental considerations to make the concepts more tangible for readers.

Conclusion

In conclusion, the exploration of biomass conversion technologies in this overview highlights their potential to address global energy demands and environmental challenges. It covers biochemical and thermochemical conversion methods, with a focus on hydrothermal processing, which efficiently converts wet biomass. The analysis of carbon and hydrogen gasification efficiencies adds depth to the discussion, showcasing factors that influence conversion outcomes. However, the article could benefit from more real-world applications and addressing environmental sustainability aspects associated with these methods. Overall, this comprehensive overview contributes to our understanding of how to harness the energy potential of biomass resources in a more sustainable and environmentally responsible manner.

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Author Contributions

All authors had significant contributions in completing this manuscript

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Conflicts of Interest

The authors declare no conflict of interest.

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