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A comprehensive review of chemical treatments for biomass feedstock to enhance briquette characteristics

Ronald Walozi[1,2*], George Samuel Onep[3], Yinka Sofihullahi Sanusi[1], Omer Eisa Babiker[1], Milon Selvam Dennison[1], Alphonse Candia[2] and Samuel Okurut[2]

*Correspondence:
Ronald Walozi
walozi.ronald@studwc.kiu.ac.ug; rwalozi@gmail.com
[1]Department of Mechanical Engineering, School of Engineering and Applied Sciences, Kampala International University, Western Campus, Ishaka-Bushenyi, Uganda
[2]Agricultural Engineering and Appropriate Technology Research Center (AEATREC)-Namalere, National Agricultural Research Laboratories (NARL), National Agricultural Research Organization (NARO), Entebbe, Uganda
[3]Department of Mechanical Engineering, School of Engineering and Applied Sciences, Kampala International University, Western Campus, Ishaka-Bushenyi, Uganda

Abstract

Converting biomass into briquettes offers a promising way to meet increasing global energy needs while reducing environmental issues. However, briquette performance is limited by low calorific value, high ash, and moisture contents. Materials such as corn cobs, groundnut shells, banana leaves, sugarcane bagasse, and rice husks contain ash levels exceeding the recommended 4%, resulting in slagging and reduced thermal performance. Chemical treatment with alkali, acid, and hydrothermal methods has become a practical approach to enhancing briquette quality. This review evaluates the effectiveness of these treatments by examining their influence on biomass characteristics. A structured narrative review methodology was applied, involving a comprehensive literature search of Google Scholar, Scopus, and other sources, covering peer-reviewed journals, grey literature, and case studies published in English between 2005 and 2025. Findings revealed sodium hydroxide as the most widely applied alkali, increasing calorific value by up to 16.2% in *celosia argentea*, cabbage, and banana leaf biomass. Among acids, sulphuric is the most effective, enhancing calorific value by up to 31.83% in rice stalks and watermelon biomasses, while hydrochloric achieves ash reduction of up to 96.26% in corn and soybean stalks. Briquettes for industrial application are classified according to DIN 51731 and ISO 17225 (class I1-I3 for industrial and B for standardized domestic heating) by ash content < 4%, moisture < 13%, volatile matter < 40%, net calorific value ≥ 14.5 MJ/kg, nitrogen < 0.6%, and sulphur < 0.8%. Despite demonstrated improvements, inhibitor formation, effluent disposal, and equipment corrosion hinder real-world application. Future research should optimize chemical treatment concentrations for heterogeneous biomasses and conduct post-treatment briquette analysis, including environmental and techno-economic implications.

Keywords Biomass briquettes, Energy conversion, Chemical pretreatment, Alkali treatment, Acid treatment, Briquette quality improvement

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1 Introduction

The world faces significant energy challenges that impact both developed and developing nations. Key among these challenges is the high energy demand, which is projected to increase by 47% between 2008 and 2035 [1], and 34% between 2022 and 2050 [2]. This has resulted in millions of people lacking access to sufficient energy, especially in developing countries. Particularly in Sub-Saharan Africa, about 630 million people lack access to electricity, and 790 million squarely depend on traditional biomass for household energy needs, especially cooking [3]. In the process of producing and consuming energy to meet this growing demand and improve access, Greenhouse Gas (GHG) emissions are generated. The world's carbon dioxide emissions reached 37.8 Gt CO_2 in 2024, contributing to the growing effects of climate change [4]. Of these emissions, about 3% is contributed by Sub-Saharan Africa, a region that suffers severely from the negative effects of climate change, especially crop and livestock failures, prolonged water stress, droughts, and persistent low economic growth [5].

To address these challenges, alternative and sustainable energy sources must be explored. Biomass briquetting has emerged as a promising solution, converting waste into solid fuel. This process involves sourcing, collecting, transporting, drying, size reduction, and compacting biomass feedstock such as sawdust and agricultural residues into densified briquettes [6]. The adoption of briquetting technology is gaining traction in Sub-Saharan Africa, including Uganda, as it offers multiple advantages. Briquettes are easier to transport, provide high strength and heat density, and serve as an effective waste disposal method. Briquettes further generate less emissions of CO_2, and CO amounting to 2 ± 0.212 g/MJ delivered and 0.79 ± 0.014 g/MJ delivered compared to wood charcoal at 129 ± 1.41 g/MJ delivered, and 7.43 ± 0.063 g/MJ delivered [7]. Compared to solar and wind energy sources, briquettes are produced in any locality using simple technologies, are not dependent on weather, require a small space, and have low investment for production, thus improving energy access. These attributes align with the United Nations (UN) Sustainable Development Goals (SDG), Goal 7 of improving access to affordable and clean energy [8].

Although briquettes present a viable alternative to address energy shortages and promote cleaner energy, they still face critical technical and performance-related challenges that limit their competitiveness with conventional fuels. These include a low calorific value and high ash content, which reduce energy output per unit input, combustion efficiency, and necessitate frequent fuel replenishment. For instance, the calorific value of briquettes from bagasse ranges from 14.6 to 17.01 MJ/kg with clay binder and 16.58 to 18.58 MJ/kg with molasses binder, which is lower than that of tropical wood species that range from 18.929 to 21.075 MJ/kg [9, 10]. Similarly, the calorific value of charcoal from conventional wood is 33 MJ/kg, which is still higher than that of briquettes [11]. Additionally, briquettes have ash contents exceeding the $\leq 4\%$ classification for industrial applications according to DIN 51731 and ISO 17225. This is evidenced by briquettes made from groundnut shells and corn cobs, which have ash content levels of 4.8% and 4.9%, respectively, leading to fouling and slagging [12]. These limitations have resulted in a high rate of briquette consumption per unit output, with shattering during handling, fouling, and low thermal efficiency, all of which affect the adoption rate [13].

Bridging this performance gap is central to making briquettes a sustainable and scalable energy solution, particularly in Sub-Saharan Africa, where the energy challenge

remains acute. One promising approach to overcoming these challenges is through chemical treatment of biomass feedstock, which enhances the thermal properties[14]. Chemical treatment involves soaking and washing biomass feedstock with water, sulphuric acid, nitric acid, acetic acid, hydrochloric acid, and sodium hydroxide to improve heat energy through the removal of microelements such as zinc, copper, iron, and macro elements that include magnesium, calcium, and potassium [15]. Treatment of biomass feedstock reduces the ash content, thereby improving the interparticle bonding during densification and enhancing the thermal properties of the briquettes [14, 16]. By lowering ash content and improving interparticle bonding during densification, chemical treatment directly enhances combustion efficiency and calorific value, two key properties that determine the energy performance and usability of briquettes.

In this treatment process, the complex cell wall structure breaks down, resulting in the reduction of lignin and hemicellulose during alkali and acid treatments, respectively [17, 18]. This leads to an increase in cellulose and sugars, which consequently improves the thermal properties [19]. The process is influenced by feedstock type, treatment reagent type, concentration of reagent, treatment temperature, and reaction time [14–16, 20]. Treatment methods, such as torrefaction, improve calorific value, among other combustion characteristics; however, they introduce non-combustible materials, such as ash content, as well as increase the energy requirement for the treatment process compared to chemical treatment methods [21]. In essence, chemical treatment transforms locally available low-grade biomass feedstock, such as crop residues, into a higher-efficiency renewable fuel, making briquettes a more practical and sustainable energy source capable of reducing dependence on conventional wood fuels. This, in turn, contributes to mitigating energy challenges in Sub-Saharan Africa through enhancing energy availability and reducing GHG emissions, key steps towards improving access to energy globally.

Some review studies have been conducted on briquettes-related aspects; however, the focus has been on: densification [22], material processing techniques and product characteristics [23], biomass feedstocks and their characteristics, and economic and potential markets [24, 25], parameters for quality briquettes and experimental variables [26]; and binders [6]. However, studies on the role of chemical treatment in enhancing briquette production are still limited. This may be due to the high costs, the complexity and precautionary nature of handling, as well as the safety-related aspects of reagents, and environmental concerns associated with waste disposal of the effluent. To address this gap, a comprehensive review was conducted to evaluate the effectiveness of chemical treatments in enhancing briquette energy conversion efficiency by analyzing the characteristics of treated biomass feedstock. By reviewing existing studies, this research aims to identify effective chemical treatment processes that improve briquette quality characteristics. This research focuses on identifying biomass feedstocks used in briquette production, clarifying the different chemical treatment methods and their effects on briquette quality, examining properties that measure briquette quality, identifying challenges and limitations of chemical treatment methods for briquette production, and exploring future research directions to improve the efficiency and sustainability of treated biomass feedstock briquettes production. This review offers a unique contribution by synthesizing current studies, identifying gaps, and proposing a future direction for research in chemical treatment aimed at enhancing biomass feedstock characteristics for improved briquette performance. Although several studies focus on the chemical treatment of

biomass feedstock for sugar yield, easing enzymatic activities, and biofuel conversion, a significant gap remains in understanding how chemical treatment improves key briquette properties such as ash content, calorific value, ignition, mechanical stability, strength, and fixed carbon. Moreover, these studies typically concentrate on a single type of material, leaving the potential benefits of blending two or more materials (heterogeneous), which respond differently to chemical treatment and can provide unique characteristics to briquettes.

This review broadens the scope by shifting focus from chemical treatments for sugar, enzymatic activities, and biofuel conversion to enhancing briquette performance, applying heterogeneous biomass feedstock, and ensuring the sustainability and efficiency of briquetting technology. The sustainability of briquetting technology should emphasize environmental impact assessment and techno-economic analysis.

The general structure of this paper consists of 8 sections, described as follows: Sect. 1 provides the study's introduction and outlines the methodological approach used in the review process. Section 2 describes the key factors for biomass feedstock for briquette production with emphasis on feedstock availability, density, calorific value, moisture content, ash content, and lignocellulose, as well as pretreatment of feedstock for briquette production. Section 3 discusses chemical treatment methods and their impact on combustion-related properties of biomass feedstock. Sections 4 and 5 cover the properties used to measure briquette quality and the challenges associated with the chemical treatment of briquettes, respectively. Section 6 outlines the limitations of the study. Finally, Sects. 7 and 8 outline the future direction for the quality and sustainability of chemically treated biomass briquette production and present the conclusions drawn from this study, respectively.

1.1 Methodology

The review methodology involved examining existing literature while ensuring care, precision, and attention to detail in selecting the appropriate studies. This study employed a structured narrative methodological approach, involving a comprehensive search and selection process to identify relevant studies on chemical treatment for enhancing briquettes production. The procedure began with a preliminary search of the Scopus database and Google Scholar using strategically selected keywords to enhance relevance. The search query included the following keywords: Chemical treatment of biomass, pretreatment of biomass, chemical pretreatment of biomass, biomass feedstocks, bio briquette production, and biomass briquettes. Boolean operators AND, "", and OR were used for key searches of the most relevant articles for the subject. The keywords were selected based on the research objective to encompass a broad range of studies related to the use of the chemical treatment concept in briquette production. Articles from 2005 to 2025 were included; those before 2005 were only considered if they were necessary to support or oppose other studies, and their content is unique and noteworthy. Furthermore, an inclusion criterion was applied to refine the selection. The criteria included peer-reviewed original and review journal articles; publications in English; studies discussing the chemical pretreatment processes such as acid, alkali and hydrothermal of biomass feedstocks, particularly focusing on lignocellulose and thermal-related properties; conference proceedings and grey literature supporting the subject under study; case studies; and studies from various geographical locations. The exclusion criteria encompassed

articles that directly addressed briquetting or chemical treatment, non-peer-reviewed articles other than reports, duplicates, and articles with inconsistent methodologies. This was followed by the filtering process, which included title and abstract screening to eliminate irrelevant papers, duplicate removal through manual checking of article titles and the use of Mendeley referencing management software, and full-text review of the remaining articles to assess methodological depth and relevance to the topic.

The potential biases during the review process include deviations from true scientific findings caused by conflicts of interest, flawed study design, data extraction errors, inconsistent data interpretation, selection bias from choosing favorable studies, language limitations to English in journals, heavy reliance on highly cited studies, restrictions to specific years of study, limitations to certain databases, and reporting bias due to selective reporting of studies. To mitigate these biases, the study employed various procedures throughout the literature search and selection process. The search was conducted across various databases, including Scopus, to gather a wide range of studies, such as articles, reviews, and case studies. This was to ensure that all relevant findings and perspectives on biomass feedstock chemical treatment and briquetting are incorporated. The review also considered studies from different geographical regions to diversify the viewpoints on the subject. Implementing this approach reduced publication bias during the synthesis of research on biomass chemical treatment and briquetting. After selecting the final papers, data extraction and analysis were conducted to identify patterns, new trends, and gaps in the research. Important information such as problems, study objectives, methodologies, key findings, innovative approaches, and useful recommendations was extracted from the selected papers. This process provided unbiased insights into the current state of research on biomass chemical treatment and briquetting for further investigation. The research methodology is depicted in the flow chart in Fig. 1.

2 Briquette production biomass feedstocks

Feedstock refers to the biomass feedstock used to produce briquettes. This section covers the factors to consider when selecting biomass for briquette production, reviews commonly used feedstock, and discusses pretreatment methods for feedstock.

2.1 Factors for selection of feedstock

The factors for the selection of biomass feedstock for use in briquette production are availability, density, calorific value, moisture content, ash content, and lignocellulose composition of biomass feedstock. Selecting biomass feedstock types for briquette production is reported to be easy when based on the calorific value, moisture content, ash content, costs, and availability, among other parameters [27]. These are explored in the following sections.

2.1.1 Availability of feedstock

Feedstock should be readily available in reasonable quantities for the sustainability of the briquette production enterprise [28]. Ajimotokan et al., [29] reported the use of materials such as charcoal particles, sawdust, and cassava peel for briquette production due to their availability. Falemara et al., [12] selected groundnut shells, corn cobs, and *Ageissus leiocapus* sawdust for use in briquette production due to their relative abundance. In Brazil, a study found that rice husks, wood residues, and coffee husks are among

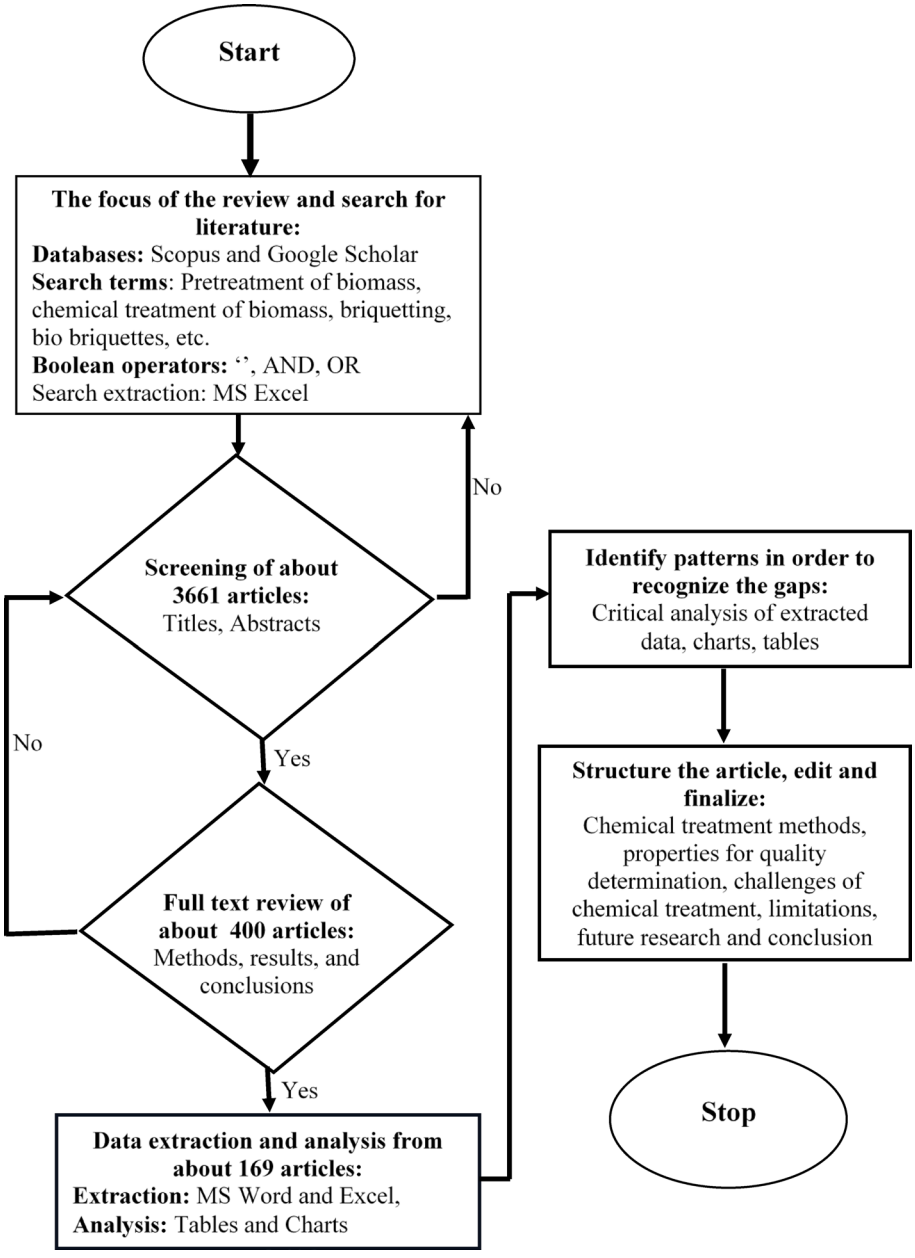


Fig. 1 Methodological flowchart

the most promising materials for briquette production due to their ready availability [30]. This was determined by estimating the amount of residues produced annually by the rice, coffee, and wood industries. The data showed that wood residues, primarily sawdust, totaled 30,000 Mg; rice husks totaled 45,000 Mg; and coffee husks reached 54,500 Mg in a case study conducted in São Paulo State, Brazil.

In India, the materials mostly used for briquette production are sawdust, sugarcane bagasse, groundnut shells, cotton stalks, maize stalks, rice husks, coffee husks, sunflower stalks, mustard stalks, coir pith bagasse, paper waste, wood chips, and forest residues, among others, partly because they are readily available [27]. These examples show that availability depends on proximity and seasonal stability of biomass sources, which are

essential for reducing feedstock procurement costs and maintaining continuous briquette production.

2.1.2 Feedstock density

Density affects stiffness and strength, and it varies depending on the material [31]. It also impacts the costs associated with transporting feedstock to the processing plant. Low-density feedstock results in higher transportation costs. A good example is that the bulk density of rice straws is 50–120 kg/m^3; this is relatively low compared to woody biomass, which is 170–600 kg/m^3 [32]. The bulk density of grass biomass, at 40–150 kg/m^3, is lower than that of commercial woodchips, which range from 15 to 200 kg/m^3 [33]. The low bulk density of biomass feedstock makes it challenging to handle, transport, and store [34]. The distances between production sites of biomass feedstocks, such as forests, agricultural land, and processing centers, and the points where these biomasses are needed for briquette production are always long, requiring high transport and storage logistics, calling for biomass with better density [33]. Therefore, high-density feedstocks are more economically and technically advantageous for briquette production.

2.1.3 Feedstock calorific value

The amount of energy released after the complete combustion of feedstock material determines the heat content of the resulting briquettes [35]. The calorific value of the resulting briquettes heavily depends on the carbon content of the biomass feedstock [9]. Calorific value is therefore the most critical factor when selecting biomass feedstock for use in briquette production [36]. Table 1 shows the calorific values of some biomass feedstock as extracted from a study by Akpenpuun et al. [39] and were converted into MJ/kg.

From Table 1, it is observed that biomass feedstock with low calorific value includes tobacco waste, rice husk, and paddy stalks, while those with high calorific values include paper, wood chips, and groundnut shells. These biomass feedstocks with higher calorific

Table 1 Calorific value of some biomass feedstock [37]

Biomass feedstock	Calorific value (MJ/kg)
Bagasse	18.326
Bamboo dust	17.405
Caster seed shells	16.159
Coffee husk	16.924
Coir pitch	17.347
Jute waste	18.527
Groundnut shells	18.928
Paper	20.255
Paddy straws	14.514
Palm husks	16.318
Rice husks	13.389
Sawdust	16.309
Sunflower stalks	17.991
Soya bean husk	17.447
Sugarcane	16.719
Tobacco waste	12.175
Tea waste	17.728
Wheat straw	17.154
Wood chips	20.020

value are preferred for briquette production because they provide better-burning efficiency [37].

2.1.4 Feedstock moisture content

Moisture content is a vital factor for both the briquetting process and the resulting fuel [38]. When the moisture content of feedstock is high, densification becomes very difficult, resulting in loosely packed briquettes [39]. In addition, high moisture content makes burning low, as extra energy is required to combust the fuel [35]. Moisture content significantly influences mechanical abrasion resistance, density, calorific value, and burning efficiency [40]. Furthermore, low moisture prevents decomposition and rotting [41]. Biomass feedstock, therefore, should be maintained at a moisture content below 13% for successful briquetting [42]. A case of briquette production in India favored using rice husks, coffee husks, and sawdust because they showed low moisture content of less than 15%, unlike sugarcane bagasse, which had a moisture content of 50% and required extra energy to reduce it to acceptable levels [27, 30]. Moisture content impacts durability; for example, rice husks tested at 12%, 14%, and 16% moisture showed a decline in durability from 100 to 99%, 100% to 98%, and a 1% reduction each day over the 7-day study respectively. While the calorific value of briquettes made from rice husks at the specified moisture contents ranged from 13.10 to 17.67 MJ/kg, with one at 16% moisture being the lowest, this indicates that higher moisture content reduces the calorific value of the briquettes [43]. These findings demonstrate that maintaining moisture content at acceptable levels is a crucial step for sustaining briquette quality.

2.1.5 Feedstock ash content

Ash content is one of the most important factors to consider while selecting biomass feedstock for combustion [38]. Woody biomass has an average ash content of 0.5 wt%, while crop residues have up to 25 wt% [44]. Care has to be taken when selecting crop residues for use in the production of briquettes to avoid problems associated with high ash content [38]. The ash content is preferred at levels of up to 4% for energy production to prevent slagging issues. Some biomass feedstock used for briquette production in India have ash contents of: bagasse 1–4%, wood chips 1.2%, cotton stalks 3%, groundnut shells 3.8%, and paper 1.5% [27]. The ash content affects the specific heat of combustion as reported for briquettes made from *Anogeissus leiocarpus* with an ash content of 3.4% which was at 34.40 MJ/kg, groundnut shells with an ash content of 4.8% were at 32.12 MJ/kg, and corn cob with an ash content of 4.9% was at 32.98 MJ/kg [12]. This indicates that high ash contents of biomass feedstock reduce the specific heat of combustion of the generated briquettes. These cases reinforce ash content as a key determinant of both technical performance and end-user acceptability of briquettes.

2.1.6 Feedstock lignocellulose

Lignocellulose consists of lignin, cellulose, and hemicellulose. Generally, the composition of lignin, cellulose, and hemicellulose in biomass is (15–20) %, (40–50) %, and (25–35) %, respectively [45]. Cellulose is the main component of the plant wall and is an insoluble substance, while hemicellulose is a complex carbohydrate. Lignin is responsible for binding biomass during densification to form briquettes [46, 47]. Therefore, the higher the lignin content, the better the briquette in terms of densification. At higher

temperatures, lignin exhibits thermoplastic behavior that enhances densification and also functions as a lubricant during compression [47]. Also, both cellulose and lignin produce a hydroxyl group, which helps in bonding through the formation of hydrogen bonds [48]. In addition, materials with high lignin levels yield more energy during combustion than cellulose.

Overall, the effectiveness of briquette production depends on the interaction of multiple feedstock characteristics, not just a single factor. Each of these factors contributes to effective briquette production. Abundant availability supports sustainability and economic viability; physical properties like density and moisture content affect logistics, the efficiency of the densification process, and the durability of the briquettes. At the same time, calorific value and ash content determine the quality of combustion, the satisfaction of users, and the performance of densification equipment. Case studies cited above demonstrate that successful briquette enterprises balance these factors, in most cases prioritizing readily available feedstocks while applying pretreatment methods to optimize energy yield as well as minimize ash-related problems. This approach underscores the need to align biomass feedstock selection with both technical and local socioeconomic aspects.

2.2 Biomass feedstock for briquette production

Biomass feedstocks presented in Table 2 for different types of briquettes were extracted from the reviewed studies. These feedstocks are primarily classified based on the type of briquettes produced. The classifications include homogeneous and heterogeneous feedstocks. Homogeneous feedstocks are used to produce briquettes (homogeneous briquettes) of a single feedstock type. In contrast, heterogeneous feedstocks are used to produce briquettes (heterogeneous briquettes) from two or more feedstock types. The data shown in Table 2 indicates that 67.6% of materials have been explored for the production of Homogeneous briquettes, compared to 32.4% of materials used for heterogeneous briquettes, as illustrated in the pie chart in Fig. 2. Table 2 shows that rice husks and sawdust are the most commonly used biomass feedstocks in briquette production. This is likely due to their relative abundance.

2.3 Pretreatment of biomass feedstocks for briquette production

The pretreatment of biomass feedstocks includes cleaning, drying, size reduction, and sieving to prepare it for briquette production. Each of these steps significantly contributes to the quality of the briquettes produced. These steps are discussed in the subsequent sub-sections.

2.3.1 Cleaning

Cleaning involves removing unwanted materials and particulates, such as dirt, plastic strings, metal particles, and stones, from the biomass feedstock to ensure maximum cleanliness [72, 82, 83]. This is done by hand-picking [29, 42], washing with water or mild solvents [25], and using equipment such as sieves and magnetic conveyors [23]. Washing reduces inorganic impurities such as ash content and sintering formation, making it paramount in the production of quality briquettes [84].

Table 2 Biomass feedstock for different briquette types

Biomass feedstock	Type of briquette	Sources
Groundnut shells	Homogeneous briquettes	[49]
Dried sewage sludge	Homogeneous briquettes	[50]
Rattan waste, coconut shells, sugarcane bagasse, banana peels	Homogeneous briquettes	[51]
Tannins from stem backs of *Acacia mangium*, *Anacardium occidentale*, *Azadirachta indica*, *Mimosa caesalpiniaefolia*, and *Mimosa tenuiflora*	Homogeneous briquettes	[52]
Glued wood waste	Homogeneous briquettes	[53]
Cotton stalks and wood sawdust	Homogeneous briquettes	[54]
Eucalyptus bark and sewage sludge	Homogeneous briquettes	[55]
Watermelon peels	Homogeneous briquettes	[56–58]
Oil palm trunk	Homogeneous briquettes	[14]
Corn cob and bean straw	Homogeneous briquettes	[59]
Corn and soy biomass	Homogeneous briquettes	[15]
Spent coffee grounds	Homogeneous briquettes	[60]
Raw watermelon waste	Homogeneous briquettes	[61]
Corn cob	Homogeneous briquettes	[62]
Celosia argentea waste	Homogeneous briquettes	[63]
Banana leaves	Homogeneous briquettes	[64]
Rice husk	Homogeneous briquettes	[65]
Bamboo, sawdust, pine needle, corn stalk, sugar cane bagasse, soya bean residue, and rapeseed de-oil cake	Homogeneous pellets	[66]
Rice straws	Homogeneous briquettes	[65, 67, 68]
Amaranthus hydridus waste	Homogeneous briquettes	[69]
Pine needles	Homogeneous briquette	[70]
Tea processing plant residues, pruning residues of persimmon, tomato stalk, pruning residues of peach	Homogeneous briquette	[71]
Sawdust	Homogeneous briquettes	[72]
Shredded forest residue and wood shavings from coniferous trees	Heterogeneous briquettes	[73]
Vegetable market waste and sawdust	Heterogeneous briquettes	[74]
Macadamia shell, passion fruit skin, *digitaria sanguinalis* grass, and coffee paste	Heterogeneous briquettes	[75]
Goat dung, lontar shell, lontar male fruit; Goat dung, lontar shell, rice husk; Goat dung, lontar shell and lamtoro twig; all in charcoal form	Heterogeneous briquettes	[76]
Corncobs and bark of oil palm trunk	Heterogeneous briquettes	[77, 78]
Carbonized cassava peel and sawdust	Heterogeneous briquettes	[79]
Maize stalk and neem leaves	Heterogeneous briquettes	[80]
Orange peels and corn cobs	Heterogeneous briquettes	[81]
Groundnut shells, rice husk, sawdust, and waste paper	Heterogeneous briquettes	[37]
Coffee husks, rice husks, and groundnut shells	Heterogeneous briquettes	[42]
Terminalia ivorensis charcoal particles and pinewood sawdust	Heterogeneous briquettes	[29]

2.3.2 Drying

Drying of biomass feedstock is done either naturally with sunshine or using a mechanical dryer, such as an oven or a rotary dryer [41, 81, 85]. The natural drying period is dependent on the weather, type, and size of feedstock, while mechanical drying is dependent on the type of dryer, type and size of the biomass feedstock. The dependence of the drying period on the type of biomass feedstock is evidenced in studies by Orhevba et al. [43] where rice husk and maize cobs were dried for 8 days; Aliyu et al. [84] dried orange peels and corn cobs for 5 days; Lubwama et al. [44] dried coffee husks, groundnut shells, and rice husks for 8 days; and Lubwama et al. [89] dried coffee and rice husks for 6–8 h. Drying is responsible for the attainment of the recommended moisture content of 10–15%

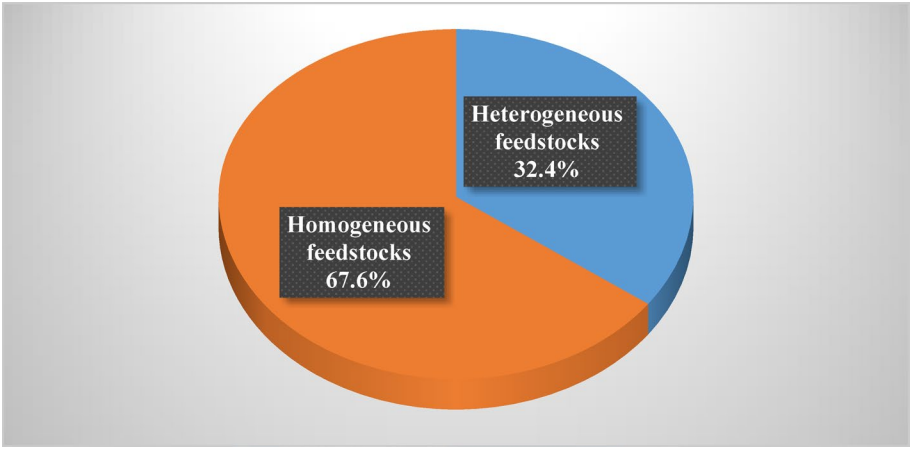


Fig. 2 Proportion of biomass feedstocks for homogeneous and heterogeneous briquette production

for proper briquetting [87]. In a study to investigate the effect of moisture content on the briquette characteristics of the impact resistance index, it was realized that impact resistance increases with decreases in moisture content of 12, 10, and 8% [72]. Drying, therefore, ensures the attainment of the required moisture content for quality briquettes.

2.3.3 Size reduction

Biomass feedstock is reduced in size by chopping, shredding and grinding. The reaction of biomass occurs at the surface; therefore, the smaller the particle size, the more preferred it is so that the more reactive chemical bonds are exposed to attack during treatment [88]. Different feedstock sizes influence briquette quality characteristics. Particle size less than 10 mm screen size produces briquettes with enhanced quality [89]. Chopping, as a method of size reduction, involves cutting feedstock into manageable sizes in various orientations to ensure homogeneity [23]. Size reduction is also achieved through grinding, a high-intensity preprocessing option that yields a favorable particle size distribution for densification. The use of grinding is a suitable method for particle size reduction [81, 85, 90]. It produces small particles in size ranging from 0.19 to 12.7 mm [91]. Hammer mill screen sizes of 0.8–3.2 mm are reported to be an effective parameter for the density of pellets made from barley straws, corn stover, and switch grass, but not on wheat straws. This is demonstrated by rice husk briquettes made from particles of 1.8 mm, which have better density and mechanical strength compared to briquettes made from 5 to 15 mm particle sizes [92].

The shredding size-reduction mechanism involves the separation of fiber, laterally leaving an isotropic fiber that is thin and long. This generates fibrous material that can be compacted at the same pressure as other treatment methods to create good interlocking bonds. The pellets produced have good durability and strength [93]. Sugebo [96] reported better physicomechanical and energy characteristics at particle sizes less than 1.2 mm when examining the effect of particle sizes from 1.2 to 1.8 mm for briquettes made from coffee husks at a densification temperature of 120 °C, a compaction pressure of 15 MPa, and a residence time of 15 min. It also indicated that briquettes made from particles of 0.3 mm had a higher density of 605 kg/m^3 compared to briquettes from 0.9 mm particles, which had a density of 506 kg/m^3.

2.3.4 Sieving

Sieving is done to generate feedstock particles of uniform size. Tumuluru et al., [87] reported that using different screen sizes of 4.8, 12.7, and 19.05 mm affects bulk density at moisture contents above 12% (w.b.), with 4.8 mm exhibiting the highest bulk density. Aliyu et al. [81] used a sieve of size 2.32 mm to generate feedstock for heterogeneous briquettes of rice husk and corn cob. Ajimotokan et al., [26] used sieves of 0.25, 1, and 1.75 mm to generate feedstock for densification into heterogeneous briquettes from charcoal fines and pine sawdust. Briquettes from the sieve size of 0.25 mm exhibited the highest compressive strength, while those from the sieve size of 1.75 mm exhibited the least. The screen size, therefore, determines the particle size distribution of biomass feedstock and, hence, the briquette quality.

3 Chemical treatment methods and effects on combustion-related properties for biomass feedstock

Chemical treatment involves processing biomass feedstock with alkalis, acids, salts, and steam. During this process, cell walls are broken down and carbohydrates are hydrolyzed through an integrated liquefaction and saccharification process in a single step [95]. The breakdown of cellulose and lignin in biomass into sugars is used for wider biomass applications, including the production of quality briquettes [19, 96]. The chemical structure of cellulose, syringyl unit, guaiacyl unit, and a combination of syringyl and guaiacyl units of lignin are shown in Fig. 3 [97]. The dominant connection between lignin monomers is alkyl aryl ether $C_{\propto} - O - C_4$ $(\beta - O - 4)$ linkage. There is lignin recondensation due to the chemical treatment of biomass, resulting in the formation of new linkages through cleavage. The presence of a phenyl propane linkage of C–C or C–O–C leads to the formation of a resistant condensed structure of $\beta - 5'$, $\beta - 6'$, $5 - 5'$, and $4 - 0 - 5'$.

Treatment of the biomass feedstock improves combustion characteristics, which is crucial in the improvement of the briquette production [14, 15, 98]. Although chemical treatment positively influences combustion characteristics, it is also impacted by factors such as solvent type, concentration, biomass feedstock type, treatment temperature, and retention time. To clarify this further, the various chemical treatment methods,

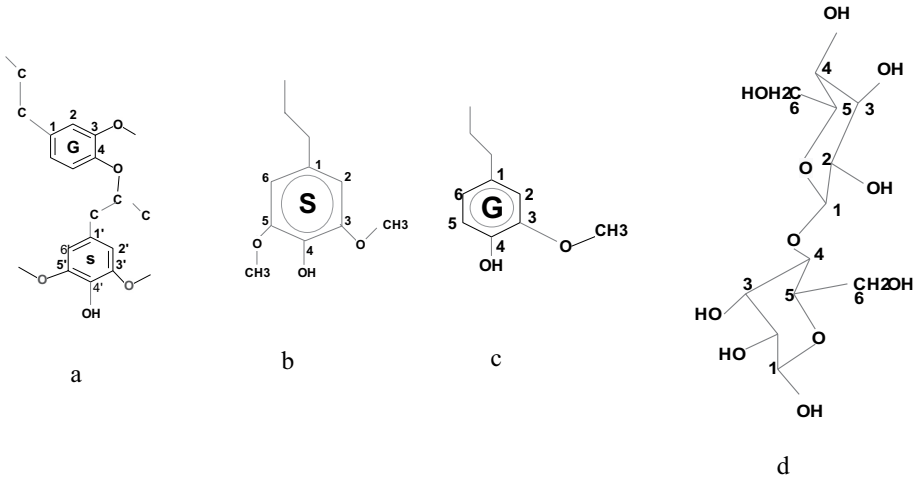


Fig. 3 Structure of **a** lignin linkage, **b** syringyl unit, **c** guaiacyl unit, and **d** cellulose

including acid treatment, alkali treatment, and hydrothermal treatment, are discussed in the following subsections.

3.1 Alkaline treatment

This involves treating biomass feedstock with sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium oxide (CaO), ammonia (NH3), ammonium salts, calcium hydroxide ($Ca(OH)_2$), and urea [69, 99]. Treating biomass with alkali causes swelling, which reduces polymerization, increases the separation of structural linkage of carbohydrate and lignin, and destroys the lignin structure due to an increase in its internal surface area [100]. It results in the effective removal of lignin biomass by disrupting its structure, breaking the bonds between cellulose and hemicellulose, and thereby delignifying the biomass [17]. Alkali treatment is typically performed at low temperatures and pressures, targeting the hemicellulose acetyl group and lignin-carbohydrate ester linkages [101]. Treatment of biomass feedstocks improves the briquette quality, including combustion due to delignification [69, 102]. An illustration of the alkali treatment process is presented in Fig. 4.

The calorific values of untreated and treated biomass feedstocks are shown in Table 3.

The percentage improvement was calculated by subtracting the calorific value of untreated biomass feedstock from that of treated biomass feedstock, dividing the result by the original value, and multiplying by 100%, as shown in Table 3. From this table, there is a noticeable increase in the calorific value of biomass feedstock when treated with NaOH. There is also a significant statistical difference between the calorific values of chemically treated and untreated biomass feedstocks, since the p-values are less than

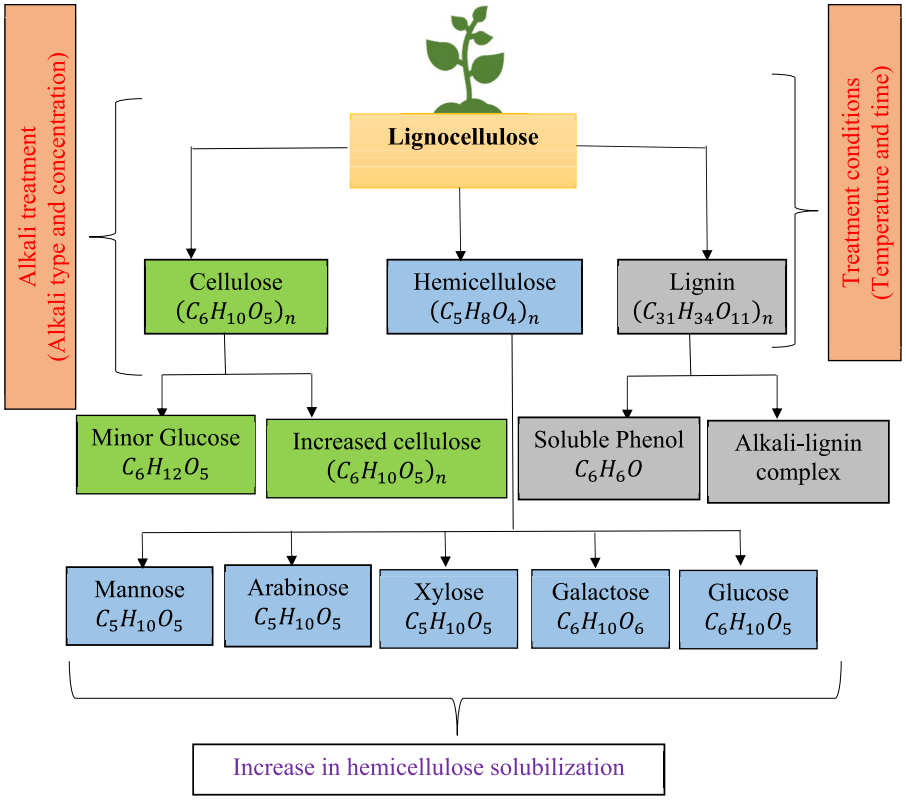


Fig. 4 Flowchart of the alkali treatment process for biomass feedstock

Table 3 Effect of NaOH on the calorific value of different biomass feedstock

Biomass feedstock	Calorific value (MJ/kg)		Statistical values	Improvement (%)	References
	Untreated	Treated			
Celosia argentea waste	10.13 ± 0.01	11.29 ± 0.05	n = 3 p = 0.0001 Significant	11.5	[63]
Cabbage waste	10.20 ± 0.12	11.52 ± 0.10	n = 3 p < 0.05 Significant	12.9	[102]
Banana leaves	11.37 ± 0.23	13.21 ± 0.01	n = 3	16.2	[64]

0.05 for *celosia argentea* waste and cabbage wastes, as indicated in Table 3. The increase in calorific value when banana leaves are treated with NaOH is more pronounced at 16.2% with a 3% concentration for 3 h at ambient temperature, compared to cabbage waste at 12.9% under the same conditions and Celosia argentea waste at 11.5% under the same conditions. In conclusion, alkali treatment with NaOH significantly enhances calorific value, and the extent of improvement depends on the biomass feedstock.

Besides calorific value, alkali treatments with NaOH decrease briquettes' combustibility from 5.25 ± 0.02 to 4.93 ± 0.1 g/min, increase compression strength from 6.1 ± 0.01 × 105 to 6.6 ± 0.24 × 105 Pa, and raise bulk density from 550 ± 0.35 to 590 ± 0.20 kg/m^3, as well as extend burning time to ash from 11.68 ± 0.52 to 12.71 ± 0.12 min for *celosia argentea* biomass briquettes [63]. A similar trend was observed for briquettes made from cabbage, with an increase in compression strength from 0.62 ± 0.03 to 0.69 ± 0.20 N/mm^2, a decrease in combustibility from 5.48 ± 0.20 to 4.20 ± 0.01 g/min, and an increase in burning time to ash from 12.11 ± 0.01 to 13.34 ± 0.11 min [102].

The improvement in combustion-related characteristics, such as calorific value, is due to soaking biomass feedstock in NaOH, which causes surface modification, especially in the cell wall. The cell wall comprises neutral detergent fiber, acid detergent fiber, and acid detergent lignin, which contribute to hemicellulose, cellulose, and lignin [103]. An equation showing the reaction between the fiber and NaOH is presented in Reaction 1. In this chemical process, the hydroxyl group of the cellulose molecule in the fiber reacts with NaOH to produce sodium cellulose (alkali cellulose) and water. This alteration of the hydroxyl group in cellulose is significant because it changes the fiber's internal structure and physical properties, thereby influencing crystallinity and mechanical strength, enhancing water absorption resistance, and increasing the tensile and impact strength of the briquettes [103]. The enhanced water resistance of the briquettes prevents water absorption during long-term storage, thereby maintaining moisture levels below 13%, in accordance with DIN 51731 and ISO 17225 classifications I1-I3 for industrial and B for standardized domestic heating applications, thereby improving combustion performance. Additionally, the increased tensile and impact resistance help the briquettes withstand abrasion and shattering during storage and transportation.

$$Fiber - OH + NaOH \rightarrow Fiber - O^{-}Na^{+} + H_2O \quad (1)$$

NaOH increases the cellulose content in feedstock materials by dissolving non-cellulose components like hemicellulose and lignin; this positively impacts briquette development, as seen in the improved calorific values (Table 3). The solubilization of hemicellulose and lignin can reach levels of up to 37% and 75%, respectively, with a reduction in ash content from 3.8 ± 0.5% to 3.4 ± 0.3% for corn stover at an NaOH concentration

of 1%, temperature of 90 °C, and a retention time of 1 h [104]. High cellulose content also enhances the mechanical properties such as Young's modulus, elongation at break, water absorption resistance, and tensile and impact strength. NaOH reduces lignin, wax, and resins in biomass feedstocks, leading to decreased water absorption and improved thermal stability of the briquettes [103]. The carbohydrate-lignin structure consists of hydrogen and ester bonds, which are weakened and broken by the hydroxyl group (OH-) produced during alkali treatment. This structure is made up of cross-links between lignin and hemicellulose that cover the D-glucose. This occurs due to a saponification reaction, leading to the breakage of ester bonds. The carbohydrate-lignin structure varies depending on the type of biomass feedstock. The structural changes in hemicellulose are determined by the degree of branching, which is proportional to the arabinose to xylose ratio, resulting in increased solubility of polysaccharides during alkali treatment [105]. Lignin consists of syringyl S, guaiacyl G, and p-hydroxyphenyl H, which are affected during alkali treatment. The H-lignin component is attached to macromolecules by unstable ester bonds in an alkaline environment, which destroys the H-lignin structure during alkali treatment. This results in S-unit and G-unit lignin being connected by the β-O-4 bond instead of the normal β-O-4, β-β, β-5, and β-1; therefore, alkali treatment dissolves the β-β, β-5, and β-1 bonds, hence depolymerization [105]. The cellulose in biomass contains both amorphous and crystalline regions. During alkali treatment, the amorphous region is targeted, which increases the crystallinity, measured by the crystallinity index. This region is more vulnerable to attack because its hydrogen bonds are weaker than those in the crystalline region. Evidence of this can be seen in apricot shells, which showed a crystallinity index of 47% after treatment with 1.0 L of 1.0 mol/L NaOH, compared to 39% in untreated samples [106].

The optimal conditions for maximum lignin removal are 62 mg NaOH/g of dry biomass at 130 °C and 47 mg NaOH/g of dry biomass at 160 °C for corn stover biomass treatment with NaOH [107]. Lignin removal increases rapidly above 100 °C up to 130 °C, and after this, the increment is gradual. Xylan, a hemicellulose component, was found to solubilize with an increase in NaOH, whereas glucan, a cellulose component, showed no effect with temperature change. Alkali treatment is essential in that the hydroxyl group is destroyed, exposing the cellulose and hemicellulose, a significant effect that reduces moisture absorption by the briquettes, hence improving the mechanical and thermal properties of the briquettes [86].

García-Negrón et al., [110] reported the effect of treating sweet sorghum bagasse with alkalis, specifically sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), in ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 at temperatures of 85 °C and 150 °C for a retention time of 1 h. The average cellulose, hemicellulose, and lignin contents after treatment at 85 °C were 58%, 22%, and 11%, respectively, while at 150 °C, these increased to 64%, 19%, and 5%. In comparison, the untreated sample had 5%, 24%, and 24% for these components. The increase in cellulose from 58% at 85 °C to 64% at 150 °C was attributable to enhanced solubilization, delignification, and further hemicellulose extraction. Samples treated with 100% NaOH had higher cellulose content than those with higher Na2CO3 ratios, although the latter had higher hemicellulose content. The solubilization of hemicellulose, cellulose, and lignin was also observed in treatments of barley and bean straws using an alkali reagent of NaOH at 5% dry basis of biomass [18]. Alkali treatment using sodium hydroxide or calcium hydroxide in water at 1%w/v and 2%w/v,

combined with microwave heating of rice husks, demonstrated better performance with sodium hydroxide, producing pellets with a tensile strength of 11.02 MPa, a bulk density of 1344.96 kg/m^3, and specific energy requirements of 33.14 MJ/T, although the calorific value was lower compared to untreated and other treatment methods [109]. Solubilization of cellulose, hemicellulose, and lignin in wheat straws increases with higher concentrations of NaOH and $Ca(OH)_2$ under microwave treatment, from 1 to 2%, compared to ash content, which behaves differently; however, NaOH is more effective at dissolving hemicellulose than $Ca(OH)_2$ [100]. Similarly, bulk density and tensile strength increase with both alkali treatment and concentration. The char mass of aspen biomass increases during pyrolysis when treated with KOH at concentrations of 0.24% and 0.48%, rising from 16.2% to 22.3% and 25.2% respectively [110].

NaOH is the most commonly used alkali in biomass feedstock treatment because it effectively breaks ester and ether bonds in lignin and hemicellulose, thereby dissolving lignin without impacting cellulose. This enhances the enzymatic digestibility of the biomass for further processing into products such as bioethanol. Additionally, NaOH is readily available and relatively inexpensive compared with other options, such as KOH.

On the other hand, lignin plays a critical role in bonding, thereby ensuring mechanical durability; therefore, it should be maintained within an appropriate range by increasing its levels through the use of external binders in cases of partial or severe delignification. The relationship between delignification and external binder is quantitatively inverse, implying that as the lignin level decreases, the binder proportion required to achieve acceptable mechanical durability increases [8]. Densification of biomass with native lignin content of 18–20% dry matter yields mechanical durability above the ISO 17831–2 threshold of ≥ 90% [34]. Partial delignification to lignin content levels of 12–14% requires 3–5%, severe delignification to 9–11 lignin levels requires 8–12% binder, while less than 8% lignin level requires over 12% binder to restore durability [6, 8]. This underscores the role of lignin as an intrinsic thermoplastic binder in briquetting.

3.2 Acid treatment

Acid treatment is a chemical process that breaks down the complex structure of lignocellulose biomass into simpler components, which can then be converted into bioenergy products. During this process, inorganic impurities in the form of mineral elements are removed. This treatment eliminates mineral elements such as potassium, magnesium, calcium, zinc, copper, and iron, which are responsible for ash in biomass, thereby improving the combustion characteristics of biomass feedstock [14, 15, 98]. Other mineral elements reduced by acid treatment include titanium, silicon, phosphorus, and aluminum, which contribute to ash that is undesirable in combustion [15].

The acids used include sulphuric acid, hydrochloric acid, hydrogen peroxide, nitric acid, acetic acid, and phosphoric acid [15, 95]. Acid treatment is classified into dilute, with high temperature, and concentrated, with lower temperature treatments. Dilute acid treatment is preferred in an industrial setting because concentrated acid treatment causes equipment corrosion, is toxic, and is not economically feasible [111, 112]. The acid hydrolyzes and breaks down the polymer molecules, leading to the disintegration of the cellular matrix and the destruction of cellular crystallinity [113]. This is achieved by breaking down bonds in the lignin-carbohydrate complex, which condenses the lignin and removes the hemicellulose, although the extent depends on the treatment

conditions [18]. Acid treatment is aided by the presence of the more mobile C_3 and C_5, which creates an ether linkage in the combined two-unit lignin structure, as in Fig. 3 [97]. A flowchart illustrating the acid treatment process is shown in Fig. 5.

Acid treatment efficiency depends on biomass feedstock size, solid-to-liquid ratio, treatment time, acid concentration, and temperature [111]. Concentrated sulphuric and hydrochloric acids have been reported to achieve at least 90% conversion efficiency to glucose at concentrations of 72% and 44%, respectively, at low temperatures. Meanwhile, dilute sulphuric acid, used at concentrations of 0.4 to 2% and temperatures ranging from 160 to 220 °C for a few minutes, has been successfully employed to hydrolyze hemicellulose into sugars with high yields [112]. In dilute acid use, hydrolysis of hemicellulose and cellulose occurs due to the attack of their amorphous regions by hydrogen ions [111].

Organic acid treatment of rice husk has demonstrated high removal efficiencies for inorganic elements such as potassium, chlorine, calcium, magnesium, iron, aluminum, manganese, phosphorus, and sulphur at 97.8%, 94.3%, 51.2%, 92,5%, 27.7%, 43.0%, 81.1%, 74.9%, and 74.4% respectively [16]. The high removal efficiency of inorganic elements resulted in improved fuel characteristics, improving briquette production from rice husks. The effect of acid treatment using different types of acids on the ash content for different biomass feedstocks is extracted in Table 4. From Table 4, it is observed that the acid treatment of biomass for particle size $630–1000 \times 10^{-24}$ m at a 30-min retention time and concentration 1% is more effective on soybean stalks, with a maximum percentage reduction of 96.26% for hydrochloric acid and a minimum of 74.9% for acetic acid, than in corn stalks [15]. The percentage reduction of hydrochloric acid (96.26% for soybean and 48.74% for maize stalks) is higher than that of nitric acid (93.3% for soybean and 42.79% for corn stalks) and acetic acid (74.49% for soybean and 35.22% for

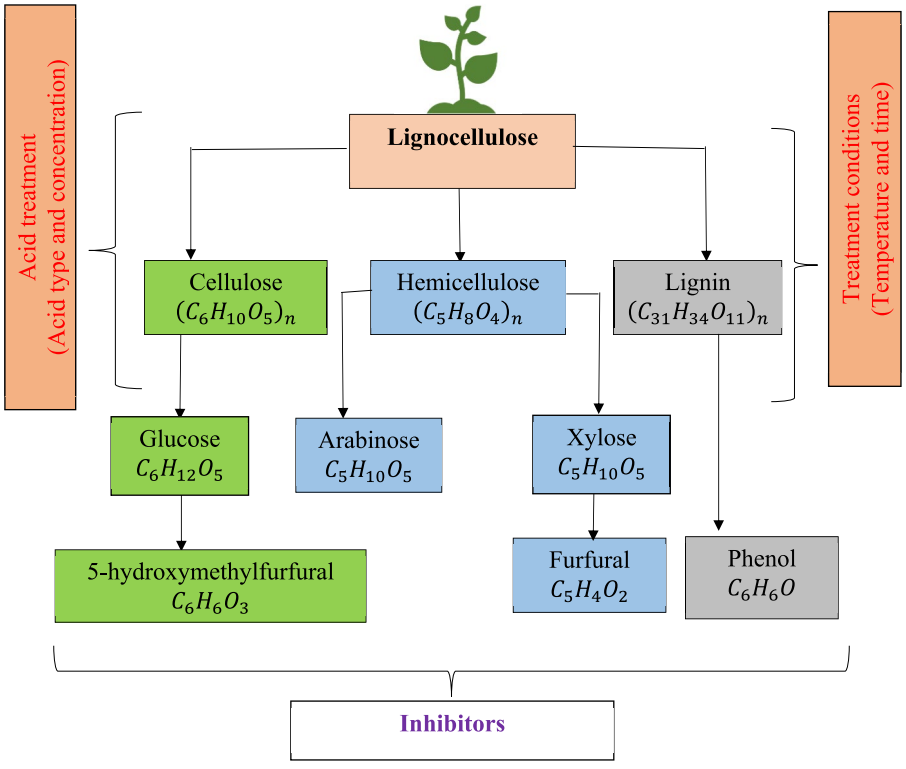


Fig. 5 Flowchart of the acid treatment process for biomass feedstock

Table 4 Effect of different acid treatment reagents on the ash content of different biomass feedstocks

Biomass feedstock	Ash content (%)											References
	Initial	Acetic acid		Hydrochloric acid		Nitric acid		Water		Ammonium acetate		
		Treated	Reduction (%)	Treated	Reduction (%)	Treated	Reduction (%)	Treated	Reduction (%)	Treated	Reduction (%)	
Soybean stalks	2.94 ± 0.77	0.75 ± 0.04	74.49	0.11 ± 0.02	96.26	0.18 ± 0.05	93.88	1.38 ± 0.06	53.06			[15]
Corn stalks	6.73 ± 0.03	4.36 ± 0.35	35.22	3.45 ± 0.13	48.74	3.85 ± 0.1	42.79	4.46 ± 0.1	33.73			
Willow	1.8			n.d	100*			1.7	5.56	1.1	35.25**	[114]
Eucalyptus	3.2			n.d	100*			1.0	68.75	0.6	40.00**	
Miscanthus	3.7			n.d	100*			1.4	62.16	1.1	21.43**	
Wheat straws	9.2			n.d	100*			7.0	23.91	4.3	38.57**	

n.d denotes non-detectable levels, assumed as zero for calculations.

soybean and maize stalks, $p < 0.05$.

* These are cumulative ash content reduction values after treating feedstock with water, followed by ammonium acetate, and then HCl.

** These are cumulative ash content reduction values after treating feedstock with water and later ammonium acetate.

corn stalks). This study further showed that the ash levels reduce with an increase in residence or reaction time as observed in the reduction in ash content from 2.94 ± 0.77% to 0.75 ± 0.75 at 30 min and 0.59 ± 0.13% at 240 min for acetic acid, 0.11 ± 0.02% at 30 min and 0.04 ± 0.01% for HCl, and 0.18 ± 0.05% at 30 min and 0.1 ± 0.04% for HNO_3 with soybean stalks biomass. The reductions in corn stalks were from 6.73 ± 0.03% to 4.36 ± 0.35% at 30 min and 3.62 ± 0.25% at 240 min for acetic acid, from 3.45 ± 0.13% to 3.35 ± 0.21% at 30 min and 3.35 ± 0.21% at 240 min for HCl, and from 3.85 ± 0.10% to 3.45 ± 0.12% at 30 min and 3.45 ± 0.12% at 240 min. As shown in Table 4, treating biomass with acid significantly reduces ash content, and the effectiveness of this treatment varies with the acid type, residence time, and biomass feedstock type.

Further from Table 4, HCl is still effective at removing ash from biomasses of willow, eucalyptus, *miscanthus*, and wheat straws, with a percentage ash reduction of 100% for all biomasses since its ash content after treatment was below detectable levels, which were assumed to be zero (0) during ash reduction computation. In this study, the three biomass feedstocks were first washed with ionized water, then with 1 M ammonium acetate, and finally with 1 M hydrochloric acid [114]. The ash reduction was computed by taking the difference between the initial and final ash contents, dividing by the initial ash content, and then multiplying by 100%. The ash reductions ranged from 5.56 to 38.89% at water treatment and 68.75% to 81.25% at ammonium acetate treatment for these biomasses. This demonstrates the gradual removal of ash at each treatment level, resulting in undetectable ash levels after the final wash with HCl. Inorganic acids such as hydrochloric acid have a higher ability to remove inorganic compounds and, consequently, enhance combustion-related parameters more than organic acids like acetic acid and formic acid, among others [115]. This is attributed to an increase in cellulose during acid treatment, like in the case where there is an increase in cellulose from 8.3 wt% in untreated palm kernel shells to 11.2 wt% after treatment with hydrochloric acid [115]. Treatment of melon seed husks with hydrochloric and sulphuric acid showed that sulphuric acid is more effective than hydrochloric acid [116]. The type of acid and material influence the effective removal of ash and hydrolysis of biomass feedstock, thereby affecting the calorific value. Sulphuric acid is one of the most commonly used acids in treating agricultural residues, including corn stover, switchgrass, poplar, and tidy [99]. This is because, at low concentrations, sulphuric acid is highly effective in hydrolyzing hemicellulose, and it limits the formation of inhibitors and equipment corrosion. Additionally, sulphuric acid is inexpensive and widely available, as protocols for safe handling are well established and understood.

Besides the acid type and feedstock material, acid concentration also significantly influences the effectiveness of ash removal from biomass. Research conducted by Wistara et al. (2021) [15] revealed that the ash content of oil palm biomass ranged from 0.62 to 4.27% when washed with 1% sulphuric acid, which is higher compared to 0.42% to 2.15% when washed with 5% acid. The calorific value was higher for oil palm biomass treated with 5% sulphuric acid compared to 1%, aligning with the fact that lower ash content leads to a higher calorific value [98]. Paper mill sludge treated with phosphoric acid at concentrations of 0%, 4%, 9%, 16%, and 20% showed an increase in cellulose from 48 to 58.5%, a reduction in volatile matter from 52 to 25–45%, a decrease in inorganic elements such as magnesium, potassium, aluminum, calcium, and sodium to less than 30 mg/kg (which contributes to ash), and an increase in carbohydrate concentration.

Additionally, char yield increased by more than 50% compared to 40% [117]. The severity of cellulose degradation increased with an increase in acid concentration. This is attributed to the high availability of H^+ ions in acid, which dissolves both water-soluble and water-insoluble elements present in biomass feedstock, thereby reducing the elements responsible for ash and, consequently, ash content in the treated biomass feedstock. An increase in calorific value was also observed in the treatment of watermelon peels with sulphuric acid, reaching 14.62 ± 0.21 MJ/kg, while the ash content decreased to 11.2 ± 0.13% [61]. The same trend is observed in an investigation of dilute sulphuric acid treatment at a concentration of 0.5%, a treatment temperature of 120 °C and reaction time of 3 h on watermelon waste feedstock, with a calorific value increase of 31.83% and an ash content decrease of 1.77% [57]. The effect of sulphuric acid treatment on rice stalks at concentrations of 29.5%, a retention time of 3 h, and a temperature of 120 °C revealed an increase in calorific value by 22.64% [65]. Similarly, Bamisaye et al. [61] reported that the calorific value of watermelon peels increased through sulphuric acid treatment. The importance of chemically treating biomass feedstock with acid was highlighted, as shown by the removal of alkali and alkaline earth metals that reduced ash-related problems during use [118]. However, the use of strong acids in biomass feedstock treatment damages the physicochemical structure. It produces inhibitors like furfural and 5-hydroxymethylfurfural, hence the need to explore the use of weak acids in biomass treatment [20]. Other than concentration, treatment conditions of high temperature and residence time introduce these inhibitors, which affect the destruction of the complex cell wall matrix to cellulose during acid treatment. Furfural and 5-hydroxymethylfurfural are generated from the pentose and hexose components of precursor sugars due to biomass feedstock treatment under high acid concentrations, prolonged residence time, and elevated treatment temperatures. The effects of these inhibitors on reducing enzymatic and biological activities are overemphasized in the literature; however, little is known about their effects on briquette-related characteristics.

Dilute acids, such as dilute sulphuric acid, used to treat biomass feedstocks, remove hemicellulose, which increases glucose yield from cellulose through hydrolysis and further breakdown of xylose [119]. It has been revealed that the optimal concentration for the hydrolysis of canola fine using sulphuric acid is 1.7% (v/v) [120]. The effect of hydrolysis temperature and residence time of wheat straws in saturated formic acid solution with 4% hydrochloric acid shows that wheat hydrolysis and glucose yield increase with temperature and residence time, with the rate of increase being higher before 7.5 h and at a temperature of 75 °C [121]. In this, the wheat hydrolysis velocities were 0.0190 h^{-1} at 60 °C, 0.0325 h^{-1} at 65 °C, and 0.0683 h^{-1} at 70 °C. Glucose degradation velocities were 0.00285 h^{-1} at 55 °C, 0.0448 h^{-1} at 65 °C, 0.1098 h^{-1} at 70 °C, and 0.0931 h^{-1} at 75 °C. The activation energy of wheat hydrolysis was 106.35 kJ/kg, while glucose degradation was 111.00 kJ/kg. It is further noted that glucose degrades faster than wheat hydrolysis. Additionally, the activation energy for glucose degradation is higher than that for wheat straw hydrolysis, indicating that treated wheat straws have greater thermal resistance, are thermally stable, and are suitable for controlled pyrolysis, storage, and transport [122].

Washing biomass of willow, eucalyptus, *Miscanthus*, and wheat straws with HCl reduces ash content to accurately measurable levels, resulting in higher calorific values compared to treatment with ammonium acetate and water [114]. A significant increase

in higher calorific value and ash quality has been observed with the use of dilute acid treatment and water on spruce biomass [123]. The consequence of high reduction using hydrochloric treatment of biomass is the collapse of the cell wall due to the extraction of hemicellulose, amorphous lignin, and elements of calcium, potassium, sodium, and magnesium. This increases fiber brittleness and reduces the lignin content, hence lowering the mechanical properties of the biomass. From these studies, it is observed that the calorific value of chemically treated biomass feedstock increases with an increase in acid concentration as a result of reduced ash content and destruction of lignocellulose structure. However, high acid concentrations have negative effects on equipment corrosion and inhibitor formation.

Exploration of the effect of combined acid (sulphuric acid) and alkali (sodium hydroxide) treatment on vetiver grass at 0.5%v/v and 4%w/v, respectively, revealed a higher increase in sugar (32.6 g/L) compared to individual treatments with either sulphuric acid (13.5 g/L) or sodium hydroxide (24.1 g/L) [124]. Treatment of sugarcane bagasse with sulphuric acid at a concentration of 1% v/w, at 120 °C, for 30 min reduced 66.4% of hemicellulose, while cellulose and lignin increased [125]. These provide guidance for improving briquette production through acid treatment of biomass feedstocks; however, parameters such as acid type, treatment temperature, feedstock materials, optimal concentration, and cost should be considered. Comparison of sulphuric with hydrochloric acid shows that hydrochloric acid is more effective at hydrolyzing biomass. This is demonstrated by the high levels of cellulose in biomasses like mahogany sawdust, iroko sawdust, and palm kernel shells when treated with hydrochloric acid compared to sulphuric acid, both at 3 M. The cellulose levels increased from 8.4 ± 1.3 to 11.2 ± 1.2% for HCl, which is higher than that of H_2SO_4. Palm kernel shells increased with HCl, reaching 28.0 ± 1.4% for mahogany sawdust, whereas the range for mahogany sawdust was 27.5 ± 0.6% to 29.9 ± 0.3%. For iroko sawdust, levels increased from 25.0 ± 0.3 to 29.2 ± 0.1% for HCl, surpassing 27.7 ± 0.7% for H_2SO_4 [115]. Treating biomass feedstock with sulphuric acid introduces sulphur into the biomass, which, when burned, forms sulphur oxides. These oxides lead to sulphates condensing on heating surfaces and produce fly ash emissions, which pollute the environment [126, 127]. At the same time, treatment with hydrochloric acid introduces chlorine into the treated biomass, thereby facilitating ash deposition by lowering its melting point. The consequences of ash include reduced combustion efficiency and operational instability, leading to unplanned power plant shutdowns. The presence of chlorine further accelerates the corrosion of the combustion system at higher temperatures. This is because it leads to the formation of hydroxides and carbonates, which then react with hydrochloric acid to form alkali chlorides [127, 128].

3.3 Hydrothermal treatment

This is the process of pretreatment using water/aqueous solution or steam, in which value is extracted from biomass feedstock while improving the quality of the remaining solid material. Hydrothermal treatment is classified into subcritical water treatment, which is carried out at temperatures between 100 and 374 °C under sufficient pressure to maintain the liquid phase, and supercritical, where the treatment occurs above temperatures of 374 °C and pressure of 22.1 MPa [129]. The water dissociates at higher temperatures to produce hydroxonium and hydroxide ions, which hydrolyze the polysaccharide

in the biomass into sugars. The treatment involves removing extractives, hemicellulose, and metals from the feedstock biomass [20]. During hydrothermal treatment, depolymerization occurs due to the hydrolysis of cellulose to form glucose monomeric units, as illustrated in Reaction 2.

$$(C_6H_{10}O_5)_n + H_2O \rightarrow (C_6H_{10}O_5)_{n-1} + C_6H_{12}O_6 \quad (2)$$

In this hydrothermal treatment reaction, water at high temperatures and pressure breaks down cellulose into smaller glucose molecules. Additionally, hemicellulose reacts and decomposes faster than lignin. The final product has high lignin levels, which results in increased mass density, volumetric fuel value and calorific value [130]. The calorific value, mass density, and volumetric fuel value were reported to improve to 26.4 MJ/kg from 19.2 MJ/kg, 1468 kg/m^3, and 22.8 GJ/m^3 from 22.8GJ/m^3, respectively, on palletization of biochar produced from hydrothermally treated pine biomass at 260 °C [130]. Hydrolysis by steam treatment liberates the acetyl group in the xylan backbone of the hemicellulose to produce protons that are used for autohydrolysis, increasing the durability of the produced pellets [131].

This process is affected by the temperature at which the treatment occurs and the reaction time. The lignin removal was 6.2% at a reaction time of 60 min and water temperature of 180 °C, and 22.8% at a reaction time of 96 min and temperature 195 °C [132].

The calorific value of biomass feedstock treated with the hydrothermal method increases with an increase in treatment temperature, as reported in the treatment of sawdust at temperatures ranging from 200 to 330 °C. It was revealed that the calorific values at temperatures of 200 °C, 240 °C, 270 °C, 300 °C, and 330 °C were 22.90 MJ/kg, 24.51 MJ/kg, 25.56 MJ/kg, 25.87 MJ/kg, and 29.44 MJ/kg, respectively, from 21.67 MJ/kg [133].

The increase in calorific values is linked to greater depolymerization of biomass, breakdown of monomers such as through cleavage, dehydration, and decarboxylation reactions, and recombination of fragmented components. It was also reported that there is no significant difference in calorific value due to changes in treatment pressure compared to temperature. Although high reaction temperature and residence time increase calorific value, it has been reported that the optimal reaction temperature and residence time for treating kitchen waste are 265 °C and 3.5 h, respectively, to achieve a maximum calorific value of 30.933 MJ/kg [134].

Hydrothermal treatment eliminates alkali and alkaline earth metals from biomass, which cause ash formation during combustion [135]. The effect of hydrothermal treatment on alkali and alkaline earth metals in the form of the dissolution rate for Mg^{2+}, Ca^{2+}, and K^+ in eucalyptus is shown in Table 5 [20]. The dissolution rates for K^+, Mg^{2+} at 160 °C and Ca^{2+} at 150 °C and 160 °C were obtained by interpolation since the dissolution

Table 5 Effect of hydrothermal treatment temperature on dissolution rate of metals in eucalyptus biomass [20]

Element	Dissolution rate (%)				
	140 °C	150 °C	160 °C	170 °C	180 °C
K^+	51.81	51.81	75.26	98.7	98.70
Mg^{2+}	65.94	65.94	70.65	75.36	83.84
Ca^{2+}	35.5	39.37	43.24	43.83	44.42

rate for each of these metals increased by 46.89% and 9.42% from 150 to 160 °C for K^+ and Mg^{2+}, respectively, and 8.32% from 150 to 170 °C for Ca^{2+}.

From Table 5, the dissolution rate of K^+ is higher than that of Mg^{2+} and Ca^{2+}, with the dissolution rate of Ca^{2+} being the lowest. This is because almost all the K^+ content in the lignocellulose biomass exists in inorganic ion form, which can easily dissolve in water. While Ca^{2+} and Mg^{2+} are bound to the organic macromolecular substance, this results in low proportions of free Ca^{2+} and Mg^{2+} ions in the plant cell wall. The dissolution rate generally increases with an increase in hydrothermal treatment temperature. This is because of the decreased pH, resulting in increased degradation of the lignocellulosic cell wall [20]. This agrees with Antonopoulou et al. 2024 [135] where hemicellulose solubilization of sawdust woody biomass was enhanced at hot water treatment temperatures of 215 °C and 230 °C compared to hot water treatment temperatures of 130 °C and 180 °C. It is noted from Table 5 that hydrothermal treatment dissolves alkali and alkaline earth metals responsible for ash, and the dissolution rate depends on the temperature and metal type.

Hydrothermal treatment can also be conducted using saturated steam; in this process, lignocellulosic biomass is exposed to saturated steam at high pressure, decompressing the material and breaking down the lignocellulosic matrix. This procedure further removes the lignin and enhances the cellulose, thereby significantly increasing sugar recovery [137]. Rice husk properties such as tensile strength reaching 26 MPa (2.6 times that of untreated), fracture energy up to 1453 mJ (7.8 times untreated), and water uptake of 40 wt% (0.72 times untreated), have also been reported to increase through hydrothermal treatment with hot compressed water, which enhances the properties of cellulose, hemicellulose, silica, and lignin [138]. Steam explosion on switch grass at a temperature between 170 and 200 °C and a residence time between 5 and 15 min, revealed that the effect of temperature was more pronounced than residence time and that the saccharification yield was 88.3% at 200 °C and 10 min [139].

Treatment of wheat straw with liquid hot water at 180 °C for 1 h yielded carbohydrate contents of 17% in the large reactor and 38% in the small reactor. In comparison, treatment with ethanol organosolv yielded 2% and 10%, respectively [140]. Hydrothermal pretreatment of grass residues reduces ash content to below 3.9%, whereas slow pyrolysis and torrefaction increase it to above 6%. However, the high calorific value improves to 29.08 MJ/kg and 25.81 MJ/kg, respectively [141]. Hydrothermal treatment is one method to improve briquette production, and therefore, the parameters of temperature, hydrolyte, and pressure are crucial to ensure an effective process.

3.4 Comparative analysis of acid and alkali treatment of biomass feedstocks

Acid treatment breaks down the bond in the lignin-carbohydrate complex, removing the hemicellulose and condensing the lignin [18]. In this, there is cellular matrix disintegration and destruction of cellular crystallinity [113]. In alkali treatment, there is delignification due to a decrease in polymerization as a result of swelling of the biomass, which increases the internal surface area [100, 102]. The result of alkali treatment is an increase in cellulose as a result of the destruction of the lignin [103]. For acid treatment, there is an increase in sugar yield as a result of the hydrolysis of cellulose [119]. To ensure the conversion of cellulose to sugars in alkali treatment, additional sequential treatments are required, increasing the production cost as compared to acid treatment, which can

directly convert biomass to sugars [17, 142]. Generally, both acid and alkali result in ash reduction and calorific value increase [61, 104].

There is inhibition of complex cell wall destruction due to the production of furfural and 5-hydroxymethylfurfural at acid concentrations higher than 1.7% (v/v) for sulphuric acid [120]. Similarly, furfural and phenolic compounds and lignin-derived inhibitors, due to excess delignification in alkali treatment, reduce the conversion of treated biomass into sugars and biofuels [143]. These inhibitors are minimized by optimizing conditions such as concentration, reaction time, and temperature. They are also decreased by over-liming with high temperature and pH, and through the use of alkalis such as $Ca(OH)_2$ and NaOH [144].

Like in acid treatment, disposal of effluent requires neutralization and proper handling to avoid environmental consequences [142]. Acid treatment in concentrated form can cause equipment corrosion, be toxic to the environment during disposal, and may not be economically feasible [112]. Alkali treatment using treatment reagents like NaOH is less corrosive compared to acid treatment reagents using sulphuric acid and sulphites [17].

The environmental toxicity aspects are a result of the disposal of effluent and sludge. Mechanisms such as membrane technology, including diffusion dialysis using anion exchange membranes, can be used to recover acids. This technology has been in industrial settings since 1984, because it consumes low energy, has a low cost of installation and maintenance, is simple to operate, and is environmentally friendly since no post-processing and chemical reagents are required. In this system, the anions in the acid sludge (SO_4^{2-}, Cl^-, and NO_3^-), as well as cations (H^+), migrate through the anion exchange membrane because of the positively charged elements in the membrane that create the activity gradient [145]. This presents a solid solution to address the challenge of environmental toxicity resulting from the disposal of sludge and effluent. On the other hand, alkali, including NaOH, can be recovered through evaporation, crystallization, and membrane separation. Recycling can be a sustainable solution for reducing reagent consumption, minimizing waste discharge, and lowering operational costs. However, optimal concentration ranges must be maintained, and residual biomass materials should be removed.

Corrosion of equipment can be overcome through the use of equipment made out of stainless steel with chromium levels of duplex grade, such as Type 2205, which has chromium content 22%, Type 2304, which has chromium level of 23% and Type 2507, which has chromium levels of 25% and Type 312 (UNS S31200) which has chromium levels of 22–28%. Corrosion is also prevented through the use of thermal spray coating with Alloy 625 (UNS N06625) coating material, employing the twin-wire arc spray process [146]. In a nutshell, the challenges of inhibitors are minimized by optimizing the treatment process, overliming with high temperature and pH, and the use of $Ca(OH)_2$ and NaOH. Furthermore, the use of membrane technology, specifically diffusion dialysis, overcomes the environmental toxicity associated with sludge and effluent disposal. The corrosion challenge is addressed by utilizing stainless steel with chromium levels of duplex grade.

Acid and alkali treatments for briquetting are primarily employed to reduce ash content and increase calorific value, thereby improving combustion efficiency. These treatments reduce lignin levels, which are critical in binding and mechanical durability. Lignin is the binding agent during biomass densification. Excessive lignin removal during chemical treatment reduces bonding, thereby compromising briquette strength. Low

briquette strength amounts to shattering during use, handling, transportation, and storage. Lignin degradation varies with chemical severity. Severity can be high or low. High severity results in high lignin degradation and high ash removal; therefore, such treated biomass requires the addition of high binder levels for proper densification and better strength, hence high mechanical durability. While low severity results in low lignin degradation, densification can be achieved without a binder, resulting in good mechanical durability. However, the literature surveyed concentrated on the reduction of ash and improvement of calorific value. This therefore calls for an investigation linking briquette mechanical durability in terms of strength and break resistance with optimal acid or alkali treatment parameters.

Technically, dilute sulphuric acid is the most suitable reagent for treating biomass materials to improve fuel quality and energy, including enhancing calorific value and reducing ash content. This is because these can be achieved at lower concentrations and at moderate temperatures, and they can be applied to various biomass materials. It is also inexpensive and widely available in Sub-Saharan Africa. However, it poses serious handling and safety risks, especially in rural and small-scale briquetting enterprises where protective equipment and effluent treatment infrastructure are limited. This leaves alkali, mostly NaOH, as the most recommended treatment method, as its safety protocols are similar to those already familiar in agricultural settings.

For blending biomass feedstocks for alkali or acid treatment, the criteria should account for hemicellulose and amorphous cellulose levels, as these are reactive components during chemical treatment and should be avoided to prevent over-degradation. Accordingly, biomass feedstocks with similar reactive compounds should be blended. In addition to reactive components, lignin levels should be considered, as lignin degrades less readily under acid and alkali treatments than hemicellulose. Feedstocks with higher lignin content are recommended to be blended with lower-lignin feedstocks to reduce the use of external binders and enhance briquette durability. Generally, ash content leads to emissions and ash-melting characteristics, such as fouling and slagging, which negatively affect combustion. It is therefore recommended that the feedstock of lower ash content should be blended with that of higher ash content to balance the ultimate ash content in the blend, since in the event of reducing high ash during alkali or acid treatment, consequences of overdegradation of cellulose and lignin may arise, compromising the structural integrity of the briquettes. Therefore during the selection of biomass feedstock for alkali or acid treatment, reactive compounds, lignin and ash content should be considered.

3.5 Comparative matrix of alkali, acid, and hydrothermal pretreatment

A comparative matrix of alkali, acid, and hydrothermal treatments with respect to performance gains is summarized in Table 6. The performance gains indicated is the calorific value improvement and reduction in ash content.

From the reviewed studies, the studies that examined briquettes after treatment include Bamisaye et al. [63], Bamisaye et al. [102], Bamisaye et al. [64], Kashaninejad et al. [100] and Jayakumar et al. [109] for alkali treatment, Kukuruzović et al. [15], Adeleke et al. [57], Bamisaye et al. [61] for acid treatment and Reza et al. [130], Tang et al. [131], and Wang et al. [138] for hydrothermal. While studies on biomass feedstock treatment without briquetting include Yiga et al. [103], Veksha et al. [110], Roy et al. [65], Karp

Table 6 Comparative performance matrix of alkali, acid, and hydrothermal treatment

Treatment type	Biomass type	Performance gain
Alkali (NaOH), concentration: 3%, reaction time: 3 h at ambient temperature	*Celosia argentea* waste, Cabbage waste, Banana leaves	Calorific value improvement *Celosia argentea* waste: 11.5% Cabbage waste: 12.9% Banana leaves: 16.2%
Acid (H_2SO_4), reaction time: 3 h, concentration: 29.5%, temperature: 120 °C	Rice stalks	Calorific value Improvement: Rice stalks: 22.64%
Acid (H_2SO_4), reaction time: 3 h, concentration:0.5%, temperature: 120 °C	Watermelon waste	Calorific value Improvement: Watermelon water:31.83%
Acid (HCl), reaction time: 30 min, concentration:1%	Soybean, maize stalks	Reduction in ash Soybean: 96.26% maize stalks: 48.74%
Acid (HNO_3), reaction time: 30 min, concentration: 1%	Soybean, maize stalks	Reduction in ash Soybean: 93.3% maize stalks: 42.79%
Acetic acid, reaction time: 30 min, concentration: 1%	Soybean, maize stalks	Reduction in ash Soybean: 74.49% maize stalks: 35.22%
Hydrothermal carbonization at 260 °C	Pine wood	Calorific value enhancement: 34%
Hydrothermal treatment	Sawdust	Calorific value enhancement: 5.68%, 13.11%, 17.95%, 19.38% and 35.86% at 200 °C, 240 °C, 270 °C, 300 °C, and 330 °C

et al. [107], Šoštarić et al. [106], and Geng et al. [104] for alkali, Saddawi et al. [114], Nwosu-Obieogu et al. [116], and Roy et al. [65], for acid and Oktaviananda et al. [133], Shi et al. [134], Ge et al. [20], and Poucke et al. [141] for hydrothermal treatments.

Hydrothermal treatment relies on heat and water, unlike alkali and acid treatments, which require repeated chemical inputs and effluent treatment. Therefore, hydrothermal treatment is more sustainable than dilute acid and alkali treatments under decentralized, small- to medium-scale briquetting conditions, where chemical, handling, and effluent treatment costs are prohibitive, and where energy for heat and water costs are moderate to low.

3.6 Economic and environmental impact of briquettes from chemically treated biomass feedstock

3.6.1 Economic analysis of briquettes from chemically treated biomass feedstock

Net present value, payback period, internal rate of return, and benefit–cost ratio are the main parameters that determine whether investing in any business enterprise is profitable. The net present value is an indicator of a business's profitability. It is determined by a discounting method where the total present value of the cost streams is subtracted from the total present value of the benefit streams[126, 147]. The enterprise is worth investing in when its net present value is positive. Payback period, on the other hand, measures how long it takes to recoup the initial investment and is determined by dividing the initial investment by the average cash flows [147]. The shorter the payback periods, the more valuable and worth the enterprise. The internal rate of return is the discount rate that makes the net present value of an enterprise zero. At this point, the total present value of the cost streams is equal to the total present value of the benefit streams [126, 147]. An enterprise is profitable when the internal rate of return is more than the discount rate [126]. The benefit–cost ratio is the ratio of benefits accrued to

costs incurred in running an enterprise, and when it is greater than one, the enterprise is profitable [126].

The net present value, internal rate of return, payback period, and benefit–cost ratios in the production of briquettes from treated biomass feedstock are therefore significant in exploring its scalability in real-world applications. However, the literature searched does not provide information on these essential aspects of briquette production from chemically treated biomass feedstock. The limited literature found, for instance, on alkali treatment was only on costs incurred during cellulose extraction, which include milling costs, manpower costs, feedstock costs, alkali chemical costs, and utilities, accounting for 7%, 2%, 4%, 46% and 41% respectively, indicating that the chemicals are the costly item during alkali treatment [142].

Similarly, for biomass feedstock treatment using acids, economic analysis for briquettes has been given no attention in the reviewed studies. The focus has been on the cost-related parameter for the conversion of biomass using acid treatment to bioethanol and sugars, hence limiting the following discussions to these aspects as an indicator. The costs of equipment for the treatment and fermentation of the biomass of spruce wood are 135.1 million dollars, using dilute acid treatment in a solvent-to-solid ratio of 5:1. Other capital costs were associated with equipment erection, piping, instrumentation and control, design, and engineering. The power consumption for this set was 13.2 kW/kg of bioethanol, totaling to 213.8 MW of energy [148]. Interestingly, the cost values depend on the solvent-solid ratios, like in lignocellulosic biomass pretreatment using dilute sulphuric acid at solvent solid ratios of 10/1, 20/1, and 30/1, the operational costs were 1,101 k USD, 1,990kUSD, and 2,879kUSD, investment cost was 11,765kUSD, 11,778kUSD, and 12,387kUSD, and total cost per year was 2,277kUSD, 3,167kUSD, and 4,118kUSD respectively, indicating increasing cost with increase in solvent used [149]. Simulation of the bioethanol refinery process using software showed that the dilute acid treatment has the largest economic margin, amounting to 39.2 million USD, compared to that of steam explosion, a hydrothermal process, which is 25% that of dilute acid. A comparison of the cost of dilute sulphuric acid and ethanol treatment methods revealed that the cost of treatment using dilute sulphuric acid is not different from that when using ethanol; hence, dilute acid treatment is one of the main methods used in the industrial setting [149]. Prediction of the energy and economic gains in the treatment of rice stalks for energy recovery using sulphuric acid at 29.5% concentration and a treatment temperature of 120 °C revealed 2.96 MJ/kg and 38.10 USD/ton, respectively, indicating the economic viability of acid treatment [65].

The total cost of pretreatment of rice stalks using sulphuric acid (98%) at optimal conditions of 29.5% concentration, 3-h reaction time, and 120 °C temperature was reported as USD 42.2 per tone [65]. Furthermore, in another study, the energy required to treat waste from barley and bean straws was reported as 299 kJ/kg biomass with NaOH at 25 °C for 24 h and 6283 kJ/kg biomass with H_3PO_4 at 110 °C for 2 h [18]. Information on treatment costs for alkali, acid, and hydrothermal processes is scarce, necessitating comparative economic and life-cycle energy assessments.

A similar situation was also observed with hydrothermal treatment, where there are no studies on economic analysis related to treated biomass feedstock briquettes, limiting the discussion to biochar production as an indicator. Hydrothermal carbonization of off-specification composite and grape marc biomasses was conducted to understand

the costs involved in this biomass treatment process. It was reported that the production cost per ton of biochar is 157€ (Euro), and the break-even point is 200€ (Euro), while the thermal energy and power consumption per ton of hydrochar produced are 1170kWh and 160kWh, respectively. Equipment that required electrical energy included a grinder, mixer, two pumps, a decanter, an air blower, and the pelletizer in this study[150]. About 78% of the steam explosion costs are incurred at the device since high temperatures and pressures are required [142]. A summary of these indicative economic aspects is shown in Table 7. From these results, it's evident that no specific studies have focused on the economic analysis of chemically treated biomass feedstock for briquette production. It is therefore essential that future studies in this area should incorporate economic analysis to guide decision-making for real-world applications.

3.6.2 Environmental impact of briquettes from chemically treated biomass feedstocks

The environmental impact of chemical treatment is assessed through the environmental margin, which is the net effect of environmental effects associated with converting acid-treated biomass feedstock into final products such as briquettes, bioethanol, and electricity. This parameter integrates both environmental benefits and burdens across the entire product system. The assessment considers key impact categories, including global warming potential, resource depletion, and ecotoxicity within defined boundaries. It is often measured in terms of carbon dioxide equivalent [151]. The environmental margin in the production of briquettes from treated biomass feedstock is therefore significant in exploring its scalability in real-world applications. However, the literature searched does not provide information on this vital aspect of briquette production from chemically treated biomass feedstock, which limits the environmental impact assessment discussion to bioethanol and electricity production as indicators.

Generation of bioethanol from corn stover resulted in a significant environmental margin, with a reduction of 83.9 kt of CO_2 per year; therefore, low emissions were

Table 7 Summary of indicative economic aspects of acid, alkali, and hydrothermal treatment of biomass feedstock

Parameter	Acid treatment	Alkali treatment	Hydrothermal treatment	Gap
Economic	The cost parameters for the production of bioethanol from spruce wood include treatment and fermentation equipment with associated accessories, accounting for 135.1 million dollars, using dilute acid treatment in a solvent-to-solid ratio of 5:1 [148]. The total cost per varies from 2,277kUSD to 4,118kUSD, depending on the solvent-to-solid ratio of 10/1 to 30/1 for the production of bioethanol from lignocellulosic biomass with dilute sulphuric acid treatment [149]. An economic margin of 39.2 million USD was realized for a bioethanol refinery using dilute acid, performing better than steam explosion [151]	The costs for cellulose extraction include milling, manpower, feedstock, alkali chemical, and utilities, accounting for 7%, 2%, 4%, 46% and 41% respectively, indicating that the chemicals are the costly item [142]	The production cost per ton of biochar is 157€ (Euro), and the break-even point is 200€ (Euro), while the thermal energy and power consumption per ton of hydrochar produced are 1170kWh and 160kWh, respectively [150]. About 78% of the steam explosion costs are incurred at the device since high temperatures and pressures are required [142]	1. Economic analysis for the production of briquettes from biomass treated using alkali 2. Economic analysis for the production of briquettes from biomass treated using acids 3. Comparative economic analysis for briquettes from acid-treated biomass and alkali-treated biomass 4. Economic analysis of briquettes from treated hydrothermal biomass

Table 8 Summary of indicative environmental impact aspects of acid, alkali, and hydrothermal treatment of biomass feedstock

Parameter	Acid treatment	Alkali treatment	Hydrothermal treatment	Gap
Environmental impact	The environmental margin of 83.9kt of CO_2/year for a bioethanol refinery using dilute acid treatment is better compared to steam explosion, which generated up to 485.9kt of CO_2/year in emissions to the environment [151]	The environmental margin of 1.02×10^1 kg of CO_2.eq (negative global warming potential) for the treatment of wheat straws to produce lignin using NaOH at a concentration of 2% and a temperature of 105 °C [156]. Global warming potential for the production of butanol from oil palm fronds using NaOH pretreatment is 0.031 kg CO_2 Eq./MJ [157]	The impact on climate change in the production of electricity from pulp and paper bio-sludge, olive pomace, and orange peel in terms of footprint was -4.56 kgCO_2eq/kWhe, -0.63 kgCO_2eq/kWhe, and -0.25 kgCO_2eq/kWhe, respectively [152]. This indicates a reduction in environmental impact through this treatment method	1. Life cycle assessment of briquettes production from alkali-treated biomass 2. Life cycle assessment of briquette production from acid-treated biomass 3. Comparative life-cycle assessment of briquette production from acid-treated and alkali-treated biomass 4. Life cycle assessment of briquettes from hydrothermal-treated biomass

reported for dilute acid processes compared to steam explosion, which produces up to 485.9 kt of CO_2 per year, leading to higher environmental emissions [151].

Environmental impact assessment was performed using lifecycle assessment for generating electricity from hydrothermal treated pulp and paper bio sludge, olive pomace, and orange peels [152]. The system was studied using SimaProf 9.1 LCA software tool that incorporated an environmental database (Ecoinvent 3, version 3.7). The assessment was categorized into five broad compartments that include: air (climate change, ozone depletion, and photochemical oxidant formation); soil (terrestrial acidification), water (fresh eutrophication and freshwater ecotoxicity), resource depletion (water depletion and fossil depletion), and human health (human toxicity and particulate matter formation). The impact on climate change in terms of footprint was -4.56 kgCO_2eq/kWhe for pulp and paper bio-sludge, -0.63 kgCO_2eq/kWhe for olive pomace, and -0.25 kgCO_2eq/kWhe for orange peel [152]. This indicates that electricity production from hydrothermally treated paper and pulp bio-sludge has a greater environmental benefit than using treated olive pomace and orange peels. The environmental impact of bioethanol production from straws treated with steam explosion was investigated using Aspen Plus™ v10 simulation software. The impact was determined by the difference between environmental savings, which is the net carbon dioxide absorbed during straw production, and that generated during the bioethanol production process. This resulted in an environmental impact of 1.1tCO_2/h [153]. The summary results on environmental impact are presented in Table 8. These findings have shown that there is a need to incorporate environmental impact assessment in future research involving chemical treatment of biomass feedstock for briquette production.

To balance environmental protection and operational feasibility, waste management for biomass alkali and acid treatment is essential. In rural settings, limited infrastructure, low cost, and decentralized local buffering agents, such as lime and ash, can reduce toxicity and corrosivity [154]. Constructed wetlands lined with different filler materials, such as aggregate, red bricks, and volcanic rock, and planted with vegetation can neutralize the effluent [155]. This treated effluent can also be recycled and used in the production of chemically treated briquettes. Low-cost effluent management should be

integrated into the broader design of the treated-biomass briquette enterprise in rural settings, including operator training in safe handling and monitoring, as well as alignment with national envnmental guidelines.

4 Properties for the measure of briquette quality

The quality of the briquette depends on its proximate, thermal, elemental, and mechanical properties. This section, therefore, explains and examines these properties of briquettes.

4.1 Proximate properties

Proximate properties include: moisture content, ash content, fixed carbon, volatile matter, and bulk density [158]. These properties are typically determined using thermogravimetric analyzers such as: (i) LECO, Type TGA 701 (Saint Joseph, MO, USA), following EN18134-2 (2015) and ISO 18122 (2015) standard methods for measuring moisture and ash content in solid fuels [159]; and (ii) Eltra Thermostep Thermogravimetric Analyzer that measures moisture content, ash content, volatile matter, and fixed carbon [86]. Other standard methods for proximate analysis include American Society for Testing and Materials (ASTM) D5142-09 [160], ASTM D-3172 [64] and ASTM D-3172 [69]. The impact of each of these properties on briquette quality, along with specific methods of assessment, is discussed in the following sub-sections.

4.1.1 Moisture content

Moisture content is crucial both during and after briquetting. However, having moisture levels that are too high or too low can significantly impact the physical and combustion properties; therefore, they should be maintained within an optimal range for proper briquette production and use [161]. The moisture content of biomass feedstock is typically measured using the oven drying method, where a weighed sample is dried at 105 °C until the mass remains constant, and the percentage moisture is calculated with Eq. 3 [7, 81, 162, 163]. Several standard methods are used for this determination, including the ASTM D3173 and European Committee for Standardization/Technical Specification (CEN/TS) 14,774 standards [7, 81, 162–165], ASTM E871 standard [166], European standard EN 13183–1 [49], ASTM E871 standard [161], ASTM E1756-08 [160] and ASTM standard D 3174–12 [79].

$$MC\,(\%wb) = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \tag{3}$$

where W_1 = weight of crucible (g) W_2 = weight of crucible and sample (g) W_1 = weight of crucible and sample after drying (g)

Moisture content is also determined using the British Standard European Norm (BS EN) 14,774–1 standard method with a weighed sample dried in an oven model DHG-9053A, Movel Scientific Instrument Co., Ltd, China, at 105 °C for 1 h, and is calculated using Eq. 4 [29, 62, 80].

$$MC = \frac{W_0 - W_d}{W_d} \tag{4}$$

Where MC = moisture content, W_0 = wet weight and W_d = weight after drying

Another method is using the ASTM D 2444–16 standard with the oven-dried method, where a weighed sample is dried at 105 ^{0}C to a constant mass for 24 h, and the percentage moisture content is calculated using Eq. 5 [78].

$$MC = \frac{W_1 - W_2}{W_2} \times 100 \tag{5}$$

Where W_1 = wet weight, W_2 = weight after drying and MC = moisture content

For proper briquetting, the moisture content should be below 13% [42]. This makes the densification process less challenging, as reported by Mulindwa et al. [40]. It is also reported that higher-quality briquettes, with improved durability, have been achieved at a moisture content of 5% [167]. Lower moisture content results in higher energy content because less energy is lost to evaporate moisture from the fuel, which preserves its calorific value [164]. Moisture content negatively affects combustion when not kept as low as possible [29]. This can be observed from the difficulty of the briquette burning, as reported by Duangkham et al. [36]. It is also associated with slagginess during burning and hence low calorific value, as reported by Oyelaran et al. [166]. Furthermore, increased moisture has been reported to adversely affect combustion quality, reduce energy efficiency, and generate more smoke during combustion [165]. Oyelaran et al., [165] reported that briquettes made from tannery waste, such as buffing dust, chrome shavings, fleshing, and hair, which had a moisture content of 4.38 to 6.24%, showed good combustibility characteristics. This agrees with the recommendation of Yadong Li et al. [167] on the moisture content range of 6% to 12% and an optimum of 8% for good-quality briquettes, and also with the value reported by Lubwama et al. [43] of less than 13%. Moisture content is affected by particle size, ranging between 5.57 and 8.20% for briquettes made from finer to larger particles, as reported by Abineno et al. [164]. This is likely because briquettes made from finer particles have limited pores that can be occupied by moisture, resulting from a higher compaction level, which in turn leads to low moisture content and a better calorific value. The moisture content is also affected by the mixture ratio of biomass feedstock, as evidenced by Kamdem et al. [161] in which the moisture content ranged between 4.60 ± 0.05% to 7.75 ± 0.21% for rice content from 20 to 100% in heterogeneous briquettes of rice husk and wood, compared to briquettes from pure wood at 6.88 ± 0.07% to 8.04 ± 0.17%, depending on the briquette condition. This indicates that briquettes made from a mixture of wood and rice husks have lower moisture content than those from pure wood, resulting in a higher calorific value.

Storing briquettes at high moisture levels over the long term decreases their durability, leading to shattering caused by microbial activity and weakening the bond between particles. This issue is made worse by improper storage, which introduces additional moisture due to the hygroscopic nature of biomass. This also decreases the combustion efficiency because some heat is used to remove moisture from biomass, which lowers the net heat available for actual combustion. This catastrophe can be controlled by storing briquettes at a moisture content of less than 10% in a controlled environment when packaged in airtight bags [169]. At production, it is regulated through the use of properly dried biomass feedstocks and appropriate drying of briquettes after compaction.

4.1.2 Ash content

This is inorganic matter and residue that does not burn but instead transforms into calcium oxide, magnesium oxide, silica, and other inorganic oxides [35]. The ash content is determined using ASTM D3175-20 (2018) [79], ASTM D3174 [165], ASTM E1755 [166] ASTM E-812 [161], and CEN/TS 14775 [162] standard methods. The ash content is determined using Eq. 6 [163].

$$PAC = \frac{C}{A} \times 100 \tag{6}$$

where C = weight of ash, A = weight of oven-dried sample and PAC = perntage ash content

The ash content is also determined by heating a weighed sample in a furnace model LF3/F4244, Vecstar Ltd, United Kingdom, at 800 °C for 5 h. The ash is then weighed after cooling, and the percentage ash content is calculated using Eq. (6) [29, 80]. Determining the ash content by heating a weighed solid fuel sample in an oven at 710 ± 0.005 °C for 2 h and calculating using Eq. 7 is another method [7, 170].

$$Ash = \frac{M_9 - M_7}{M_8 - M_7} \times 100 \tag{7}$$

Where Ash = Ash content (%), M_7 = mass of crucible, M_8 = mass of crucible + sample (g) and M_9 = mass of crucible + sample after heating (g)

It is also measured by heating a weighed sample in a crucible within an electric furnace at 700 °C for 1 h, then cooling the sample first in air and afterward in a desiccator. The ash content is calculated using Eq. (7) [37]. Heating a weighed sample in a porcelain crucible in a muffle furnace at about 815 °C for 1 h, then cooling the sample in a desiccator and calculating the percentage ash content using Eq. 8, is another method [164].

$$\%ASH = \frac{W_b - W_c}{W_{od}} \times 100 \tag{8}$$

Where W_b = weight of crucible and ash, W_c = weight of crucible and W_{od} = oven dry weight of sample

High ash content exceeding 4% negatively impacts combustion because it hinders the burning rate and ignition time. This occurs due to limited diffusion of oxygen and heat transfer to the surface of the solid fuel, leading to slagging. As a result, it causes high dust emissions, air pollution, damage to burning furnaces, boilers, and cooking stoves, poor combustion, and low thermal efficiency [39, 159, 167]. After a long run, high ash content impacts combustion efficiency and causes operational instability, leading to unplanned shutdowns of the furnaces and affecting the stove end-user acceptability of briquettes [127, 128]. Materials with high ash content include rice husk (19.2%), paddy straw (15.5%), sawdust (8.2%), forest waste (7%), and soybean husks (4.1%) [27]. However, these high ash levels can be managed through pretreatment methods such as acid treatment.

Briquettes made from tannery solid waste, including carbonized buffing dust, chrome shavings, and fleshing, showed average ash contents of 2.4157%, 2.8811%, and 2.4249%, respectively. This is favorable since it is below the recommended maximum ash content of 4%, except for carbonized hair, which has an ash content of 5.0143% [167]. Mulindwa

et al., [38] reported ash content ranged from 26.8% to 44% for briquettes made from bamboo char, maize cob char, and charcoal dust, in both homogeneous and heterogeneous forms. Brunerová et al., [158] reported that briquettes made from bamboo fiber had an ash content of 1.16 ± 0.13%, while those from sugarcane bagasse had an ash content of 8.62 ± 0.18%. Ashwath et al., [169] reported ash contents of 36.6%, 10.7%, 11.4%, 13.6%, and 10.9% for charcoal briquettes made from green waste, pine bark, pine chips, hardwood chips, and coal, respectively. The high ash content was attributed to the presence of impurities like dust and soil [159]. Ash content, for example, in heterogeneous briquettes, varies with constituent material proportion as observed in a study by Duangkham et al. (2023) [36] where ash content varied between 16.5 to 22.5% with a reduction of banana peels in the rice straw-banana peel heterogeneous briquettes. This is similar to that in a study by Oyelaran et al. [166] where the ash content of homogeneous briquettes made from maize cob, groundnut shells, and banana leaves was higher at 5.12–10.16% compared to that of heterogeneous briquettes from the same materials, which ranged from 5.51 to 9.17%. By contrast, briquettes from Tannery solid waste, bamboo fiber, and *Lantana camara* consistently showed ash content of less than 4% [172].

Slagging behavior is governed by alkali oxides such as potassium oxide (K_2O) and sodium oxide (Na_2O), alkaline earth oxides such as calcium oxide (CaO) and magnesium oxide (MgO), and silica (SiO_2), in addition to total ash content. Slagging increases with a higher K_2O-to-SiO_2 ratio. Higher CaO and MgO stabilize the silicates, thereby mitigating these effects [173]. Ash fusion temperatures for biomass briquettes are strongly correlated to these compositional ratios, showing that fuels rich in alkali metals exhibit lower deformation temperatures ranging from 900 to 1000 °C compared to > 1200 °C for those rich in CaO and SiO_2 [174]. Therefore, during briquette quality evaluation, ash chemistry and fusion behavior should be considered, as slagging risks are not determined solely by ash content.

4.1.3 Volatile matter

Volatile matter, which is a mixture of short- and long-chain hydrocarbons, consists of both combustible and non-combustible gases released during the burning of briquettes and other solid fuels [39]. In addition, it consists of elements such as hydrogen, oxygen, and carbon.

The volatile matter is determined using ASTM D3174-12 [79], ASTM D3175 [165], ASTM E872 [166], and ASTM D-1102 [161], CEN/TS 15148 [162], standard methods. The percentage of volatile matter (PMV) is calculated using Eq. 9 [163]

$$PVM = \frac{A - B}{A} \tag{9}$$

Where A = weight of oven dried sample. B = weight of sample after 10 minutes in a furnace.

The volatile matter content is determined by drying the sample to constant mass in an oven, then heating it in a furnace model LF3/F4244, Vecstar Ltd, United Kingdom, at 900 °C for 7 min. The percentage of volatile matter is calculated using Eq. 9 [29, 80]. The Meynell method is also used to determine volatile matter by pretreating a sample used in moisture content measurement at 250 °C in a furnace for 2 h, then heating it at 470 °C

for another 2 h. Just before it turns black, the volatile matter is determined using Eq. 10 [164].

$$\%Volate = \frac{W_{rd} - W_{ds}}{W_{st}} \times 100 \tag{10}$$

Where W_{rd} = weight due to removal of volatile matter. W_{ds} = dry sample after heating and W_{st} = weight of sample taken

The volatile matter can also be determined by placing a sample in a closed crucible until a constant mass is obtained, heating it in an oven at a temperature of 950 ± 20 °C for 7 min, and then cooling it in a desiccator and calculating it using Eq. 11 [7, 37]

$$VM = \frac{M_5 - M_6}{M_5 - M_4} \times 100 \tag{11}$$

Where VM = percentage volatile matter (g), M_4 = mass of crucible, M_5 = mass of crucible+sample (g) and M_6 = mass of crucible + sample after heating (g).

High volatile matter content indicates the readiness of heterogeneous briquette fuel to ignite with high proportionate flames during combustion, resulting in high efficiency [29, 35]. While low volatile matter can complicate fuel ignition, it also signifies lower emissions, highlighting the need for an optimal value to improve fuel combustion efficiency. In a study by Oyelaran et al. [166] on tannery, the average volatile matter of solid waste, including buffing dust, chrome shavings, hair, and flesh, was 1.16135%, 1.7312%, 4.5556%, and 2.1117%, respectively. Abineno et al., [163] reported higher levels of volatile matter of 70.32% for particle size 60 mesh and 73.47% for 20 mesh particles. Similarly, higher values of volatile matter of 14.83% were realized by Haba Bunga et al. [165], though less than those for a study by Abineno et al. [164]. Volatile matter ranged between 37.0% to 84.6% in a study by Mierzwa-Hersztek et al. [174], for which its maximum is higher than all those from studies by Oyelaran et al. [166], Abineno et al. [164], and Haba Bunga et al. [165]. Volatile matter varies for different materials, as evidenced by Lubwama et al. [87], who reported higher volatile matter in coffee husks compared to rice husks. The high level of volatile matter indicates that more energy is needed to burn it off before releasing heat. The volatile matter comes from organic compounds released during combustion. The release of these compounds depends on particle size. Smaller particle-size fuels release lower volatiles as compared to larger particle fuels, as revealed by Abineno et al. [164]. This is because smaller particle fuels have a uniform distribution of heat. High volatile matter requires a high air pressure for complete combustion; otherwise, incomplete combustion occurs, leading to dark smoke, heat loss, pollution, and soot deposits on boiler surfaces [175]. On the other hand, highly volatile matter causes the fuel to burn quickly and ignite easily during combustion; therefore, an acceptable level of volatile matter is less than 40% [35]. The volatile matter increases when biomass is treated with HCl, ammonium acetate, and water, indicating potassium removal [114]. A reduction in volatile matter from 70.2% to between 61.2% and 69.2% is observed in the treatment of spruce biomass with water, NaOH, and H2SO4 [123].

4.1.4 Fixed carbon

Fixed carbon is the amount of solid fuel available for char combustion after volatile matter is driven off into the atmosphere [167]. It gives the char, which is a combustible

material remaining after volatile matter and moisture are removed, and is therefore a primary source of heat during combustion [39, 170]. It also gives a rough estimate of the heating value of the fuel [175].

The fixed carbon is determined using the relation of moisture content, ash content, and volatile matter as shown in Eq. 12 [29, 80, 162–165].

$$FC = 100 - (MC + AC + VM) \tag{12}$$

Where FC = percnatage fixed carbon, MC = percentage moisture content, AC = percentage Ash content and VM = percentage volatile matter.

Fixed carbon is also determined using Eq. 13, which relates volatile matter and ash content [37].

$$Percentage\ FC = 100 - (\%eVM + \%e\ ash\ content \tag{13}$$

It is also determined using the ASTM D3172-13 (2021) standard method [79].

The fixed carbon is reported by Mulindwa et al. [40] to range between 30.4 and 50.6% for briquettes made from bamboo and agricultural residues, while Oyelaran et al. [166] reported a range of 89.93% and 95.45% for briquettes from tannery solid waste. Duangkham et al., [33] reported a fixed carbon of approximately 46.9% and 41.1% for briquettes from charred rice straws and banana peels, respectively. Ramkumar et al., [171] reported a fixed carbon of 18.6% for Lantana camara briquettes. High fixed carbon levels indicate the briquette's high heating value [29]. It also indicates a decrease in the residence stage until combustion is completed. Fixed carbon has a positive coefficient compared to all other physical properties of solid fuels. The fixed carbon can be improved by carbonization, as reported by Lubwama et al. [87] where carbonized rice husks and coffee husks had a higher fixed carbon compared to their uncarbonized counterparts. This is because of the volatilization process that occurs during carbonization [86]. Treating biomass with HCl, ammonium acetate, and water has shown a decrease in fixed carbon content [114].

4.2 Thermal properties

This involves critical analysis and discussion of properties such as calorific value, burnout time, ignition time, and combustion rate that determine briquette quality, as detailed below sub-sections.

4.2.1 Calorific value

Calorific value is the best indicator of a fuel's chemical quality and determines the amount of energy released during combustion [39]. As a key parameter for energy quality, it is influenced by the material quality, moisture content, and ash content of the briquettes [158].

The calorific value of briquettes is determined using ASTM D2015-96 for the net calorific value [161], ASTM D5865-19(2013) [79] and ASTM D5865-10 [160, 176] standard methods. Other methods for determining calorific value include using the IKAC 2000 basic bomb calorimeter according to the ASTM D5865-13 standard method [78], GDY-1A bomb calorimeter using the American Society for Testing and Materials standard method [177], PARR INSTRUMENT COMPANY automatic bomb calorimeter made in USA N^0: 101A C20 032614 M4013, using method provided in European Norm

International Organization for Standardization (EN ISO) 21,654, 2021 [7], IKA C200 bomb calorimeter [39, 178], oxygen bomb calorimeter IKA C 2000 [86], LECO UK AC 500 bomb calorimeter [14], bomb calorimeter [179], LECO AC 350 Bomb calorimeter using standard protocols [69], Isoperibol calorimeter C 6000 Isoperibol, IKA, using Polska Norma-European Norm (PN-EN) 14,918:2010 standard method [175] and Isoperibol calorimeter LECO, Type AC 600, Saint Joseph, USA, using standard methods of European Norm (EN) 14,918 (2010) and International Organization for Standardization (ISO) 1928 (2010) [159], LECO AC 350 bomb calorimeter using standard procedure [64], Gallen Kamp ballistic bomb calorimeter using ASTM E711-87 standard method [170], and IKA C2000/Kv600 bomb calorimeter using ASTM D5865-04 (2004) standard [37].

Calorific value can also be determined by expressions developed by Nhuch-hen and Afzel [29]; Wahid, Nhuchhen, and Kieseler [166] as shown in Eqs. 14, 15, 16, and 17.

Nhuch-hen and Afzel

$$HHV\,(MJ/kg) = 0.1846Vm + 0.0352Fc \tag{14}$$

Where HHV = higher heat value, Vm = volatile matte and Fc = fixed carbon

Wahid model equation

$$HHV = 15.85 + 1.93\frac{FC}{VM} + 0.04\frac{VM}{ASH} + 0.14\frac{ASH}{FC} + 0.02t + 0.01T \tag{15}$$

HHV = high heat value, FC = fixed carbon, VM = volatile matter and ASH = ash content

Nhuchhen model equation

$$HHV = 0.1846 \times VM + 0.35 \times FC \tag{16}$$

Where HHV = high heat value, VM = volatile matter and FC = fixed carbon

Kieseler model equation

$$HHV = 0.4108 \times FC + 0.19 \times VM \tag{17}$$

Where HHV = high heat value, FC = fixed carbon and VM = volatile matte

The calorific value is also determined using an adiabatic calorimeter, where a weighed sample is completely combusted, and the difference between maximum and minimum temperature is used to compute the gross calorific value, as shown in Eq. 18 [163].

$$Q = \frac{(C_{water} + C_{cal})\,(T_2 - T_1)}{W_f} \tag{18}$$

Where Q = calorific value of sample (kJ/kg). W_f = weight of the biomass sample kg. C_{cal} = heat capcity of bomb calorimeter (kJ/kg^{0}C)

$T_2 - T_1$ = rise in temperature

$C_{water} = heatcapacityofwaterkJ/kJ^0C$

Other expressions for the determination of calorific value are in Eq. 19 [42], and Eq. 20 [81].

$$HHV\left(\frac{MJ}{kg}\right) = 17300 - 117.51AC + 165.55FC - 232.69MC \tag{19}$$

where HHV = high calorific value, AC = ash content, FC = fixed carbon, MC = moisture content.

$$Calorificvalue\,(\%) = 2.326\,(147.6FC + 144VM) \tag{20}$$

Where FC = Percentage fixed carbon (%) and VM = Percentage volatile matter (%).

It is also determined by measuring the higher calorific value using a bomb calorimeter, following the NBR 8633 standard method, and employing Eq. 21 to calculate the lower calorific value and Eq. 22 to find the useful heating value [180].

$$PCI = PCS - 600 \times \left(\frac{(9 \times 6)}{100}\right) \tag{21}$$

Where PCI = lower heating value (kCal kg^{-1})

PCS = higher heating value (kCal kg^{-1})

$$PCU = \left(\frac{(PCl - 6 \times U)}{(100 + U)}\right) \times 100 \tag{22}$$

Where PCl = lower heating value, PCU = useful heating value and U = dry basis moisture content

Mulindwa et al., [40] reported a calorific value range of 16.027 MJ/kg to 21.26 MJ/kg for briquettes made from carbonized maize cob, bamboo poles, and charcoal, both in homogeneous and heterogeneous states. Kamdem et al. [161] reported calorific values for rice husk and wood shavings, ranging from 12.1 to 15.6 MJ/kg. The net and gross calorific value reported by Brunerová et al. [159] is 16.92 MJ/kg and 18.15 ± 0.03 MJ/kg, respectively, for Bamboo fiber and 17.23 MJ/kg and 18.47 ± 0.50 MJ/kg, respectively, for sugarcane bagasse. The calorific value in a study by Mierzwa-Hersztek et al. [174] was reported as 23.43 MJ/kg and 26.59 MJ/kg for charred sawdust and miscanthus straw. Further, the high calorific value reported in a study by Duangkham et al. [36] was between 20.98 MJ/kg and 21.26 MJ/kg for a blend of rice straws and banana peels. Lubwama et al., [89] reported the highest calorific value of 23 MJ/kg for briquettes from coffee husks with cassava binder. The calorific value shows the fuel's chemical quality, reflecting the energy released during combustion. Briquettes should exhibit a net calorific value of at least 14.50 MJ/kg for nonwoody biomass briquettes and at least 15.00 MJ/kg for woody biomass briquettes [159]. A positive effect of the treatment method of water, NaOH, and H_2SO_4 on the higher heat value has been reported for spruce biomass [123].

4.2.2 Ignition time

This is the time required to reach a steady, glowing fire [167]. It determines how long a briquette takes to ignite [181]. Ignition time indicates the safety of briquettes during storage. It depends on volatile matter and particle size [167]. It is determined by placing a Bunsen burner on a platform 4 cm below until the bottom surface of the briquette is ignited and enters the steady burn phase, using a blue flame, and the ignition time is recorded with a stopwatch [170]. This is done following the ASTM-E1321-13 (2013) standard test method for determining material ignition and flame properties [37, 81].

Briquettes with high volatile matter have a low ignition time; therefore, the risk of fire outbreaks is higher during storage. Oyelaran et al., [166] for both homogeneous and heterogeneous briquettes, the reported ignition times ranged from 67.23 to 88.54 min

and 64.43 to 87.14 min respectively. An ignition time reported by Navalta et al. [182] ranges from 0.17 to 1.83 min for briquettes from a blend of sugarcane bagasse and rice bran. Similar to Palanisamy et al. [183], an ignition time of 3.3 s is reported for briquettes made from Gloriosa superba waste and turmeric leaves with a starch binder. Similarly, Achebe et al. (2018) reported an ignition time for briquettes made from a blend of sawdust from Gmelina, mahogany, and oak, with rice husk, using clay and starch binder, which ranged between 0.117 min and 0.368 min. Ignition time reported by Akpenpuun et al. [38] ranged from 18 to 49 s for briquettes from rice husk, sawdust, and paper combination, and 45 s to 79 s for briquettes from groundnut shells, sawdust, and paper combination. Aliyu et al., [82] reported an ignition time of 3.58 ± 0.11 min to 5.35 ± 0.75 min for briquettes made from orange peels and corn cobs, both in Homogeneous and heterogeneous states. The low ignition in heterogeneous briquettes could be due to high porosity in the inter and intra particles, which enables easy percolation of oxygen and outflow of combustion due to weak bonding of the briquettes. Ignition time is also dependent on the quantity of fuel, as smaller quantities take less time to ignite [181]. Briquette ignitability is affected by the level of volatile matter [183].

4.2.3 Combustion rate

This is the amount of fuel that undergoes combustion per unit of time [167]. It is a critical parameter in determining the quality of a fuel [170]. The combustion rate, also known as the burning rate, is determined by weighing a briquette sample before and after burning or combustion, and recording the time it takes to burn. Then, the combustion rate or burning rate is determined using Eq. 23 [184]

$$FBR = \frac{M_F}{T} \tag{23}$$

Where FBR = fuel burning rate, M_F = mass of fuel burnt (kg) and T = time taken to burn fuel (hr)

The burning rate can also be determined using the expression in Eq. 24, which is in terms of initial briquette mass m_i, the mass of ash and remaining briquette after combustion m_f, and the total combustion time t_t [42, 161].

$$BR = \frac{m_i - m_f}{t_t} \tag{24}$$

Where BR = burning rate

The combustion rate can also be determined by burning a weighed sample on a wire gauze placed above the burner, with the entire setup on a weighing scale to record weights every 10 s throughout the combustion process. The combustion rate is then calculated using Eq. 25. [185]

$$Combustion\ rate(g/\min) = \frac{M_d}{T_d} \tag{25}$$

Where M_d = Mass of burned briquettes (g) and T_d = Total time taken (min)

A high combustion rate requires more fuel to cook a given amount of product because it burns off quickly. In a study by Oyelaran et al. [166], the combustion rate ranged between 0.163 and 0.225gm^{-1} for briquettes from groundnut shells, corn cob,

and banana leaves in homogeneous and heterogeneous states. In a study by Ajagbe et al. [185], a combustion rate range of 0.39 kg/h (6.5 g/min) to 0.85 kg/h (14.2 g/min) for briquettes made from carbonized cassava peels and sawdust, both in the Homogeneous and heterogeneous state, was reported. In another study by Navalta et al. [182], a combustion rate range of 1.21 g/min to 1.80 g/min was reported for briquettes made from a combination of sugarcane bagasse and rice bran. Further, a study by Achebe et al. [96] reported a combustion rate range of 0.04 kg/min (40 g/min) to 0.232 kg/min (232 g/min) for briquettes from sawdust of gmelina, mahogany, and oak combined with rice husk using starch as a binder. In addition, a study by Kpelou et al. [187] reported a lower combustion rate ranging between 2.9 to 7.71 g/min for briquettes made from carbonized corn cobs, tender coconut husks, and palm kernel shells in a Homogeneous state.

4.3 Elemental composition

Elemental composition influences the energy content and emissions released by briquettes, along with other solid fuels. Elements responsible for this include nitrogen (N), hydrogen (H), carbon (C), oxygen (O), and sulphur (S). These elements differ depending on the feedstock materials used in briquette production. The elemental composition is determined by ultimate analysis using the ASTM D5373-10 standard method for determining elements of nitrogen, carbon, and hydrogen [160, 176]. The elements are also determined by the elemental analysis method for nitrogen, sulphur, and carbon, and the trace elements are determined using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique [179]. A CHNS analyzer Vario EL Cube, Elementar, is also used to determine the composition of carbon (C_d), hydrogen (H_d), nitrogen (N_2), and sulphur (S_d) using standardized methods, while oxygen (O_d) and trace elements can be determined using German Institute for Standardization (DIN) 51,733:2008-2012 standard as in Eq. 26 and Polska Norma-European Norm-International Organization for Standardization (PN-EN ISO) 16,968:2015–2007 standard method, respectively [175].

$$O_d = 1 - C_d - N_d - H_d - S_d \tag{26}$$

The elemental composition is determined by LECO, Type CHN628 + S, Saint Joseph, MO, USA, equipment following the EN ISO 16948 (2016) standard method [159]; and CHNSO elemental analyzer model LECO, CHN628, Saint Joseph, MO USA [79]. It is also determined using Eqs. 27, 28, and 29 for elements of carbon (C), hydrogen (H), and oxygen (O), respectively [29, 64, 69].

$$C = 0.637FC + 0.455VM \tag{27}$$

$$H = 0.052FC + 0.062VM \tag{28}$$

$$O = 0.304FC + 0.476VM \tag{29}$$

Where FC = fixed carbon (%) and VM = volatile matter (%)

Another method is Leibig-Pregl, which determines the carbon and hydrogen content by placing a weighed sample in a quartz test tube and burning it off through absorbent magnesium for water absorption and sodium hydroxide for carbon dioxide absorption. The sample weights are taken afterward, and the percentage of carbon and hydrogen is calculated using Eqs. 30 and 31, respectively [170].

$$\%C = \frac{a(0.2727)}{weight\ of\ sample} \times 100\% \tag{30}$$

$$\%H = \frac{b(0.2727)}{weight\ of\ sample} \times 100\% \tag{31}$$

Where a = quantity of carbon dioxide and b = quantity of water

Nitrogen is determined by the Dumas-Pregl method, in which a weighed sample of briquette is mixed with copper oxide powder in an ignition system through which carbon dioxide is passed to burn at a temperature range of 700–750 °C. Later, burning occurs in an atmosphere of carbon dioxide, where, after ignition, the combustion product is displaced with carbon dioxide into a nitrogen flow meter, and the percentage of nitrogen (%N) is calculated using the Eq. 32 [170].

$$\%N = \frac{V(1.097)}{weight\ of\ sample} \times 100\% \tag{32}$$

where V = volume of nitrogen in the nitrogen flow meter. 1.097 = mass of 1ml of nitrogen at the test tube.

Sulphur is determined by holding a weighed sample wrapped in filter paper, secured by a platinum wire to the stopper of a flask filled with oxygen. It was then ignited, and the resulting product was oxidized using a mixture of water and hydrogen peroxide. Finally, it was titrated with Barium percolate in the presence of Toron, indicated with a pH of 4.5, and the percentage sulphur (%S) was calculated using Eq. 33 [170]

$$\%S = \frac{(T \times V)}{weight\ of\ sample} \times 100\% \tag{33}$$

Where T = titre of Barium percolate solution

Sulphur is also determined through the ignition of a sample and two portions of calcium oxide and magnesium oxide, with the other sample in anhydrous sodium carbonate. The sulphur is then dissolved in water, and a precipitate of barium sulphate is formed, which is then filtered. The ash content is then weighed. The percentage sulphur content is then calculated using Eq. 34 [81].

$$Sulphur\ content\ (\%) = \frac{A - B}{C} \times 13.74 \tag{34}$$

where A = mass of barium sulphate from sample (g). B = mass of barium sulphate from blank (g), and C = mass of the sample used (g).

In addition, the elemental composition is determined by calculating the percentages of carbon, hydrogen, nitrogen, and oxygen using Eqs. 35, 36, 37, and 38 respectively [81, 187].

$$carbon\ content\ (\%) = 0.97FC + 0.7\,(VM - 0.1A) - M(0.6 - 0.01M) \tag{35}$$

$$Hydrogen\ content\ (\%) = 0.036FC + 0.086\,(VM - 0.1A) - 0.0035M^2\,(1 - 0.02M) \tag{36}$$

$$Nitrogen\ content\ (\%) = 2.10 - 0.020VM \tag{37}$$

$$Oxygen\ content\ (\%) = 100 - (C + H + N + A) \tag{38}$$

where FC = percentage fixed carbon content (%), VM = percentage volatile matter, M = percentage moisture content (%), A = percentage ash content (%), C = carbon content, H = hydrgent content (%) and N = Nitrogen content (%).

Ajimotokan et al., [30] reported that the elemental composition of carbon, oxygen, and hydrogen ranged from 41.6 to 50.1 wt%, 5.1 to 5.6 wt%, and 34.4 to 41.5 wt%, respectively, for briquettes made from pine sawdust and charcoal dust. Oyelaran et al., [166] reported the elemental composition of carbon and hydrogen, ranging from 44.28 to 48.23% and 3.44% to 7.13%, respectively, for briquettes made from maize cob, groundnut shells, and banana leaves, both in homogeneous and heterogeneous form. While Aliyu et al. [82] reported values of carbon ranging between 83.67 and 86.29%, hydrogen ranging between 3.39% and 6.29%, and oxygen ranging between 5.28 to 10.29% for briquettes made from orange peels and corn cobs, both in homogeneous and heterogeneous forms. It also reported nitrogen and sulphur compositions ranging between 2.02 to 2.02% and 0.11 to 0.28%. For Ajagbe et al. [79] elemental composition of carbon ranged between 55.25 to 57.07%, hydrogen ranged between 3.77 to 4.26%, oxygen ranged between 38.29% to 40.32%, nitrogen and Sulphur ranged between 0.10 to 0.55% and 0.01 to 0.07% respectively for briquettes made from carbonized cassava peels and Gmelina sawdust both in Homogeneous and Heterogeneous form. Elements of carbon and hydrogen have a positive impact on calorific value, while oxygen impacts it negatively; and nitrogen and sulphur release toxic gases of NOx and $SO_{2,}$ respectively, which cause diverse effects on living organisms, including humans [167, 188]. Interestingly, some standards have been set, like for nitrogen, the German national standard for fuel pellets, Germany DIN51731/DIN Plus, sets it at less than or equal to 0.3%, while the Austrian national standard for pellets and briquettes, Austria ONORM M7125, is at less than or equal to 0.6% [167]. Meanwhile, sulphur is less than or equal to 0.8% by the German and Austrian national standards for pellets and briquettes. These NOx and SOx are a result of nitrogen and sulphur and, therefore, should be kept as low as possible according to the minimum standards set above [81]. Washing biomass with HCl has little effect on hydrogen and carbon contents but greatly reduces the nitrogen levels in the fuel [114]. An increase in the elemental composition of carbon from 50.2 to 51.3% and 66.1% was reported in the treatment of spruce biomass with water, NaOH, and H_2SO_4 [123].

4.4 Mechanical properties

Mechanical properties are crucial in the use of solid fuels, including briquettes. These determine how well briquettes resist crushing under stresses during use and transportation. It is reported that these properties improve when biomass undergoes treatments such as hydrothermal processing [130]. This section discusses the mechanical properties of drop strength, compressive strength, and bulk density, and their determination of briquette quality.

4.4.1 Drop resistance

The ability of a briquette to resist drops and collisions during transportation and use is essential for its industrial development. Drop resistance is measured by determining the percentage chance of breakage when dropping a weighed sample from a height of 150 cm, weighing the broken solid particles, and calculating the result using Eq. 39 [39].

$$Percentage\ possibility\ of\ breakage\ = \frac{M_1 - M_2}{M_1} \times 100\% \tag{39}$$

Where M_1 = Initial weight of sample and M_2 = weight of remaining solid

Uganda National Bureau of Standards (UNBS) US 765 -2:2019 has established a standard for the drop resistance level, ranging from 2.5 to 10%. Researchers such as Mulindwa et al. [40] have reported improved drop resistance of briquettes higher than the standard. This improvement was attributed to the small particle size of biomass, which enables mechanical interlocking of relatively short fibers. Lubwama et al., [41] reported a decrease in strength ranging from 84.2 to 100% for briquettes made from a mixture of groundnut shells and coffee husks with cassava starch as a binder. Lubwama et al., [88] reported a decrease of over 94% in strength for briquettes made from rice and coffee husks using cassava starch binder. Good drop resistance results in briquettes that are easier to handle, stack, transport, and store [42]. The use of binders greatly contributes to this good drop resistance; cassava starch can form intermolecular hydrogen bonds between its amylose and amylopectin components, thereby creating strong bonds [86]. Incredibly, drop resistance also indicates the strength of the C–C bond in solid fuel heterogeneous briquettes, thereby reflecting the calorific value.

4.4.2 Compressive strength

This is the ability of a briquette to withstand destructive forces during handling, transportation, and storage; it also helps to determine the force a briquette structure can withstand before breaking [39]. The compressive strength can be determined using a rotary drum with a diameter of 598 mm rotating at 21 rpm, following the ISO 17831–2:2015 standard methods [179]It can also be determined with the ELE Tritest 50 compression machine according to D 3173–878 specifications [64, 69]. Other methods involve using an Instron Universal Testing Machine, model 3369, according to ASTM D1037-93 (1995) [62], Universal testing machine INSTRON 3382 following ASTM D2166-85 [78], Computerized Testometric Universal Machine, UK [39], the ASTM E9 standard method [165] and the ASTM E9-89 standard method, considering aspects of the Spanish Standard European Norm (UNE EN)12,504–1[49]. The compressive strength can also be measured with the Universal Testing machine that has digital control and display, and it is calculated using Eq. 40 [184].

$$Compressive\ strength\ = \frac{Maximum\ force\ applied}{Surface\ area\ of\ briquette} \tag{40}$$

It can also be determined using a universal testing machine by applying a force to the briquette until a fracture occurs, then calculating it with Eq. 41 [189].

$$CS = \frac{F(stress)}{A(strain)} \tag{41}$$

Where CS = compressive strength

The compressive strength can be further determined using a compression test fixture, with a load applied at a constant rate of 0.305 mm/min until the briquettes crack. It is calculated using Eq. 42 [163]

$$Compressive\ strength\ in\ cleft = \frac{3 \times The\ load\ fracture\ point\ (N)}{(l_1\ (mm) + l_2\ (mm) + l_3\ (mm))} \tag{42}$$

Where l_1, l_2, and l_3 are length of briquettes at point 1, 2 and 3 respectively.

Further compressive strength can be measured using a Hydraulic Universal Testing Machine Model WEW-600, Class 1, in which the briquette is loaded at a rate of 50 mm/min until a crack forms, and it is calculated using Eq. 43 [182].

$$CS = \frac{F\left(\frac{101.97kg_f}{1kN}\right)}{A} \tag{43}$$

Where CS(kg_f/mm^2) = compressive strength of briquette, F(kN) = force applied on the sample at which it starts to break and A(mm^2) = surface area of briquette.

Higher drop strength extends cooking time and thus improves cooking efficiency. However, strength depends on compaction parameters such as pressure, temperature, and feedstock moisture content. As evidenced in a study by Wilczyński et al. [190], the highest strength of the briquettes was achieved at a compressive pressure of 150 MPa, a temperature of 150 °C, and a moisture content of 10%. Okot et al., [190] reported that compressive strength increases with increasing compacting temperature (20–800 °C) and pressure (150–250 MPa). Kujawiak et al., [178] reported a mechanical strength ranging from 14.47 to 81.2% for briquettes made from a blend of sewage sludge and organic materials such as bark, sawdust, woodchips, walnut shells, and straws. Abineno et al., [163] reported a compression strength ranging from 2.16 to 2.81 MPa for briquettes made from Kasembi (*Schleichera oleosa*). Navalta et al., [181] reported a higher briquette compressive strength ranging from 5.12 kgf/mm^2 (50.21 MPa) to 10.02 kgf/mm^2 (98.26 MPa) for briquettes made from sugarcane bagasse and rice bran in the homogeneous form at a compression pressure of 8 MPa. One possible reason for this is the high compression pressure used during briquetting, which causes particles to interlock because of natural binders released. These binders include lipids, lignin, starch, and protein that are expelled from the original matrix and are distributed to fill the compressed biomass, forming a new matrix and increasing the briquettes' compressive strength [165]. It is also caused by an increase in compression temperature, which melts the lignin, causing it to exhibit thermosetting properties in biomass and binding cellulose and hemicellulose within the cell walls, thereby improving the compression strength of briquettes [190].

4.4.3 Bulk density

This shows the compactness of the briquette and is directly proportional to its strength [35]. The bulk density is measured according to ASTM D7481-09 (2009) standard method and calculated using Eq. 44 [37].

$$Bulkdensity = \frac{Initial\ mass\ of\ material\ ,g}{volume\ of\ cylinder\ cm^3} \tag{44}$$

It is also determined by measuring the mass, height, and diameter of the briquette, and calculating it using Eq. 45 [189].

$$Bulk\ density\ \left(kgm^{-3}\right) = \frac{weight\ of\ briquette\ (kg)}{volume\ of\ briquette\ (m^3)} \tag{45}$$

The bulk density of the briquette is affected by the particle size and moisture content of the biomass feedstock. The particles can be either fine or coarse. Fine particle-size raw materials produce briquettes with higher density compared to coarse ones; however, they require more compaction pressure when the binder is not used in the briquetting process [31]. Moisture also affects briquette density because it hinders the compression of raw material as it evaporates, leaving voids in the briquette due to temperature rise during the process. Bulk density is reported to improve with carbonization and mixing of the material. Lubwama et al., [42] reported that carbonized briquettes of higher density, ranging between 476kgm^{-3} and 578kgm^{-3} were developed for heterogeneous briquettes made from groundnut shells and coffee husks with cassava starch. This is due to the combined weighted effect of different raw materials. Carbonization also increases bulk density because it exposes radicals in the raw materials to bond freely. Depolymerization and devolatilization happen when the lignin in biomass softens, enabling it for densification [42]. High density results in a high calorific value due to increased compactness and fixed carbon. Density also directly affects the energy-to-volume ratio of briquettes, influencing their management, transportation, and ignition [35]. Duangkham et al., [33] reported that bulk density increases and ranges from 659 to 831.63 kg/m^3 in briquette blends of rice straws and banana peels. This is so because rice straws and banana peels have a high level of nitrogen, which is a nitrogen atom residue in the lignin ($C_{18}H_{13}N_3Na_2O_8S_2$), which is a natural binder [192].

5 Challenges of chemical treatment of briquettes

Using biomass for energy through briquettes and other methods offers an affordable solution to low energy access and an environmentally friendly way to dispose of waste. This is because it does not contribute to carbon dioxide (CO_2) buildup in the atmosphere, as it originates from biogenic sources [193]. However, briquettes made from forest wastes and agro residues have physicochemical properties that make their use for energy conversion more difficult. These properties include high moisture content, harmful emissions during use, low calorific value, and high ash content. Most briquettes made from waste materials such as corn cobs, groundnut shells, banana leaves and peels, sugar cane skin, and rice husks have ash contents between 5.12% and 22.5%, exceeding the recommended level of less than 4% (< 4%), leading to lower calorific value and reduced thermal efficiency due to increased slagging potential [14]. This is due to the presence of alkaline earth metals, which lowers fusion temperature. The use of chemical treatment reduces the ash levels; however, high concentrations, such as those found in sulphuric treatment, can cause more damage to the physicochemical structure of the feedstock biomass. Further, there are high costs associated with chemical treatment in terms of acquisition, handling, and disposal [25]. Chemical treatment can also cause the production of inhibitors such as furfural and hydroxymethylfurfural for acid treatment and phenolic compounds and lignin-derived inhibitors for alkali treatment, leading to retardation of treatment processes [120, 143]. The disposal of effluent from chemical reagents, including acids and alkalis, causes environmental pollution when not properly neutralized, particularly in large-scale processing [99, 142]. Using acids at high

concentrations for chemical treatment causes equipment corrosion, making it economically unfeasible [112].

6 Limitations to this review

While extensive effort was made to ensure comprehensive coverage and methodological rigor, some limitations are acknowledged in this study and are presented as follows:

(i) The reviewed studies had variability in experimental design, reporting matrices, and feedstock types, thus limiting comparative analysis and synthesis
(ii) Insufficient peer-reviewed data since most of the studies were on acid and alkali treatment for enzyme activity, bioethanol production, and sugar, whereas the focus of this study was acid, alkali, and hydrothermal treatment for briquette production.
(iii) Most of the studies lacked integration of environmental impact assessment, as well as cost–benefit analysis, which are crucial for real-world technology application. This limited the data on environmental impact assessment and the costs involved in biomass treatment.
(iv) Limited information on the effect of alkali, acid, and hydrothermal treatment on briquette combustion-related characteristics. Most of the studies were limited to the impact on biomass feedstock, and little attention was given to post-material treatment
(v) In the articles reviewed, there was no study on the effect of chemical treatment on heterogeneous materials, yet the interaction of different materials during chemical treatment varies. This limited analysis and synthesis of data on heterogeneous materials and treatments using alkali, acid, and hydrothermal.

7 Future research directions for the quality and sustainability of chemically treated biomass briquette production

Despite significant progress in biomass feedstock treatment and briquetting, several critical research gaps hinder the practical application and scalability of the technology. The results of this review suggest that future research should focus on three broad areas:

(a) *Expansion of biomass feedstock base:* Investigate chemical treatment of heterogeneous biomass feedstock. This aims to enhance the quality, sustainability, and adaptability of blended briquettes. In this, a mixture of two or more biomass feedstock materials is treated with the chemical together in the same reactor at the same time at a specified temperature, reaction time and concentration. However, care should be taken to avoid over-degradation of cell-wall structure for certain biomass feedstock in the blend since chemical treatment hydrolyzes biomass feedstock at different rates. Therefore, optimization studies are encouraged to overcome the over-degradation of the cell wall structure.
(b) *Parameter optimization for chemical treatment of heterogeneous feedstock materials:* Optimize chemical treatments for heterogeneous feedstock materials with concrete practices. The optimization process should include production and analysis of the quality of the blended briquette from the treated heterogeneous feedstock materials. Suggested chemical treatment practices are: (i) Sulphuric acid or hydrochloric acid at a concentration of less than 5%, temperature less than 121 °C, and retention time of 30 min; (ii) Sodium hydroxide at several concentrations of at least 1% but less than 5%, temperature ≥ 25 °C, and retention time of more than one hour; (iii) Single and

mixed feedstock hybrid treatment involving a combination of NaOH and H2SO4 or HCl under the conditions in (i) and (ii). The key performance indicators for evaluating the success of new chemical treatments in briquette production are net calorific value (more than 14.5 MJ/kg), ash content (less than 4%), and moisture content (less than 13%). These parameters should be measured using standard procedures as described in section four of this paper. In addition to briquette quality parameters, other key performance indicators include environmental impact margin and socio-economic aspects. Challenges during the chemical treatment of heterogeneous biomass feedstocks primarily involve inhibitor formation, equipment corrosion, and effluent management. Inhibitor formation and equipment corrosion can be addressed through techniques such as: (i) using low concentrations of acids, (ii) maintaining low treatment residence times, and (iii) conducting treatments at temperatures below 121 °C. Non-chemical methods, such as anion membrane separation, are suitable for treating effluents and have industrial applications.

(c) *Scalability of chemical treatment and briquette production innovations:* For real-world application, integrate environmental impact factors through life cycle assessment, techno-economic analysis, and case studies during research on chemical treatment of heterogeneous biomass feedstocks and the resulting briquettes and their production technologies. The life cycle assessment should cover chemical treatment practices, effluent disposal, and production technologies.

8 Conclusion

Applying effective chemical treatment to biomass feedstock in briquette production offers promising solutions for improving briquette quality, addressing environmental issues related to biomass disposal, and ensuring sustainable access to bioenergy. Despite the study's limitations and challenges in chemical treatment, the review highlights the essential role of chemical pretreatment of homogeneous biomass feedstock in enhancing briquette properties. The main conclusions from this study are as follows:

1. Sodium hydroxide is the most alkaline chemical used in the treatment of biomass feedstock, with percentage improvements in calorific values of 11.5%, 12.9%, and 16.2% for wastes of Celosia argentea, cabbage, and banana leaves, respectively.
2. Sulphuric acid is the most commonly used acid, with a percentage improvement in calorific value of 31.83% for watermelon peels and 22.64% for rice stalks. This is followed by hydrochloric acid, which shows a percentage ash reduction of 96.26% for soybean stalks and 48.74% for maize stalks.
3. The findings show that chemical treatment of biomass feedstocks can improve briquette quality and energy performance, enabling them to meet international fuel standards. This has direct implications for national bioenergy policies and clean cooking initiatives, as these briquettes reduce reliance on traditional wood fuels and promote the use of locally available biomass feedstock. This review offers evidence to guide policymakers in supporting cleaner, more sustainable cooking solutions that align with energy access and climate goals.
4. Studies on chemical treatment have mainly focused on homogeneous biomass feedstocks, which offers a chance to explore heterogeneous biomass feedstocks.

5. Limited studies on environmental and economic aspects of chemical treatment of biomass feedstock pose significant challenges for the acceptance and scalability of emerging innovations within communities.
6. Future studies in chemical treatment for advancing bioenergy should focus on heterogeneous biomass feedstock, parameter optimization, scalability of innovations to societies, environmental impact assessment, techno-economic analysis of the chemical treatment methods for real-world application, and policy development that guides effective, sustainable, and profitable use of biomass feedstock for energy.

Author contributions
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I confirm that the review is original and correctly cites sources. No ethical approvals were required since there was no direct human or animal interaction.

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