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MINI REVIEW

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Microwave-aided pyrolysis of cashew nut shell (CNS): a review of the process, products, and applications

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ABSTRACT

Microwave-aided pyrolysis (MWAP) stands as a promising and environmentally conscious approach for converting residual biomass into valuable products. The unique attributes of cashew nut shells (CNSs), often overlooked in the processing industry, have been unveiled as an attractive feedstock for MWAP, showcasing its adeptness in generating high-quality biochar, bio-oil, and syngas. This review article explores the details of MWAP of CNS, highlighting the latest scientific advancements and empirical insights into the process, products, and applications, ranging from soil amendment to bioenergy sources and liquid fuels. The study highlights CNS's potential in producing value-added materials and extends the discourse to the synthesis of activated carbon, exemplifying its versatility and practical applicability. The review concludes by urging investigations into the untapped potential of CNS products, encouraging research into their adsorption and catalytic properties, and envisioning novel applications that resonate with sustainability and environmental care principles.

KEYWORDS

Waste biomass; Thermochemical process; Valuable products; Alternative energy

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Introduction

In sustainable biomass utilization, microwave-aided pyrolysis (MWAP) has surfaced as a sophisticated and environmentally conscious technology, drawing significant attention for its adeptness in transforming residual biomass into valuable products [1]. The efficacy of this process is particularly pronounced when applied to the cashew nut shell (CNS), an often-overlooked byproduct endowed with unique attributes conducive to microwave (MW)-induced thermal degradation [2]. Waste biomass (WB), a fundamental renewable energy source, provides various outputs, encompassing electricity, heat, biofuels, and valuable chemicals [3-5]. Its transformation yields significant ecological, economic, and social advantages, marked by eco-friendly production practices that mitigate pollution, reduce reliance on petroleum-based synthesis, and repurpose otherwise released waste materials. WB circumvents the ethical challenge of competing with food crops, addressing a critical concern amid the rising global demand for food. Its sustainability, rapid generation, and carbon-neutral energy potential position WB as a cornerstone in the quest for sustainable energy solutions, emphasizing its domestic and global impact [6,7]. The cashew nut (CN), derived from the tropical evergreen cashew tree (*Anacardium occidentale*), is a notable illustration within this context. Comprising the CNS, kernel, and testa, CN exhibits distinct compositional ratios of 1-3%, 55-65%, and 35-45% of the total weight, respectively [8,9]. With global cultivation extending across regions such as the United States, European Union countries, and notably India, a key player boasting the largest production, processing, and export capacity, the CNS emerges as a consequential byproduct of the CN processing industry, generating over 450 thousand tons of waste in India alone in 2023 [10]. Pyrolysis, a thermochemical process, transforms biomass into solid fractions as biochar (BC), liquid fractions as bio-oil (BO), and gaseous fractions at certain temperatures, a phenomenon further enhanced by the application of MWs [11,12]. The innovative aspect of MW heating, characterized by direct and volumetric heating, facilitates faster and more uniform heat distribution, thereby reducing energy consumption. MWAP of CNS promises to yield high-quality BC, BO, and syngas, each bearing diverse applications ranging from soil amendment and bioenergy sources to liquid fuels and chemicals [2,13,14].

This review article explores the subtleties of MWAP of CNS, highlighting the latest scientific advancements and empirical insights into the process, products, and applications. It disentangles the compositional complexities of the solid, liquid, and gaseous products, highlighting their dependence on the pyrolysis mode and system employed. Beyond a mere analysis of the process, this review also ventures into the domain of applications, shedding light on the diverse ways in which the derived products can be utilized. It also invites us to consider a sustainable future where waste biomass, once discarded, can be transformed into a cornerstone for energy innovation and environmental guardianship.

Biomass Conversion Methods

The two primary methods of biomass conversion are thermochemical and biochemical processes. The biochemical conversion processes [15], characterized by prolonged reaction times often spanning many days, employ microbial and enzymatic agents for the biological degradation of biomass. However, this method requires careful precautions to prevent the hindrance of microbial and enzymatic activities, and pretreatment is often necessary. Despite these precautions, the applicability of biochemical conversion is restricted, with limited productivity and a focus on producing one or a few specific products [16].

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In contrast, thermochemical conversion methods feature moderate to very low reaction times ranging from seconds to hours. These processes utilize heat and catalysts for biomass degradation. Remarkably, these processes demand no specific precautions and provide optional pretreatment, making them applicable to diverse biomasses. Thermochemical conversion is a productive and efficient process that yields a wide range of products. Unlike biochemical processes, it requires external heat but offers superior control [17].

Thermochemical conversion process

The transformation of biomass through thermochemical processes to generate beneficial products from the initial substrate can take place via six distinct conversion approaches, namely pyrolysis, combustion, gasification, liquefaction, co-firing, and carbonization [18]. Pyrolysis, a thermochemical conversion process, produces three distinct product phases via chemical reactions in an inert atmosphere. It can be categorized into three main types: fast, flash, and slow pyrolysis [19]. Table 1 illustrates these distinctions are based on factors such as reaction rate, residence period, and heating duration [20]. Fast and flash pyrolysis enhances liquid yield with moderate and high temperatures [21], while slow pyrolysis yields BC at a low heating rate [22]. Particle size distribution is crucial in pyrolysis due to the non-conductive nature of lignocellulosic biomass.

Table 1. Pyrolysis of Biomass at Different Conditions with Yield [19].

Pyrolysis Types	Temperature range (Kelvin)	Heating rate (Kelvin/second)	Residence period (Second)	Particle size (milimeter)	Yield (%)		
					BC	BO	Syn Gas
Flash	1050-1300	>1000	<0.5	<0.2	12	75	13
Fast	850-1250	10-200	0.5-10	<1	20	50	30
Slow	550-950	0.1-1	450-550	5-50	35	30	35

Microwave-aided pyrolysis (MWAP)

The MW technology application in the thermal treatment of biomass has experienced significant growth since the mid-nineties, signaling a transformative era marked by diminished energy consumption, accelerated processing times, and the introduction of innovative chemistry facilitated by the unique internal heating phenomenon intrinsic to MW energy [23]. Operating at wavelengths of 0.01m to 1m and frequencies of 0.3-300 GHz within the electromagnetic (EM) spectrum. MW irradiation has found a significant role at the 2.45 GHz frequency in various applications, including domestic MW ovens and chemical synthesis. Notably, the frequencies 915 and 2450 MHz are permitted by the Federal Communications Commission (FCC) for scientific, industrial, and medical purposes to avoid overlap or interference with cellular frequencies and telecommunications [24].

MWs, characterized as EM waves with perpendicular electric and magnetic fields, classify materials into three categories: insulators (e.g., quartz), conductors (e.g., metals), and absorbers (e.g., water, oils). MW dielectrics, absorbing MW irradiation, drive the process of dielectric heating. This intricate interplay of electromagnetic forces within the MW spectrum ensures exceptional efficiency in biomass treatment and positions MW technology as a fundamental driver for advancing sustainable and quality-centric production methodologies [25].

Conventional thermal heating, employing external sources like oil baths or heating mantles, relies on slow and inefficient heat transfer from the surface toward the center through conduction, convection, and radiation [26]. In contrast, dielectric heating transforms EM energy into thermal energy, representing an energy conversion rather than conventional heating, as shown in Figure 1. MWs penetrate materials, depositing energy throughout the volume (core volumetric heating), resulting in the material's center achieving a higher temperature than in conventional heating [27].

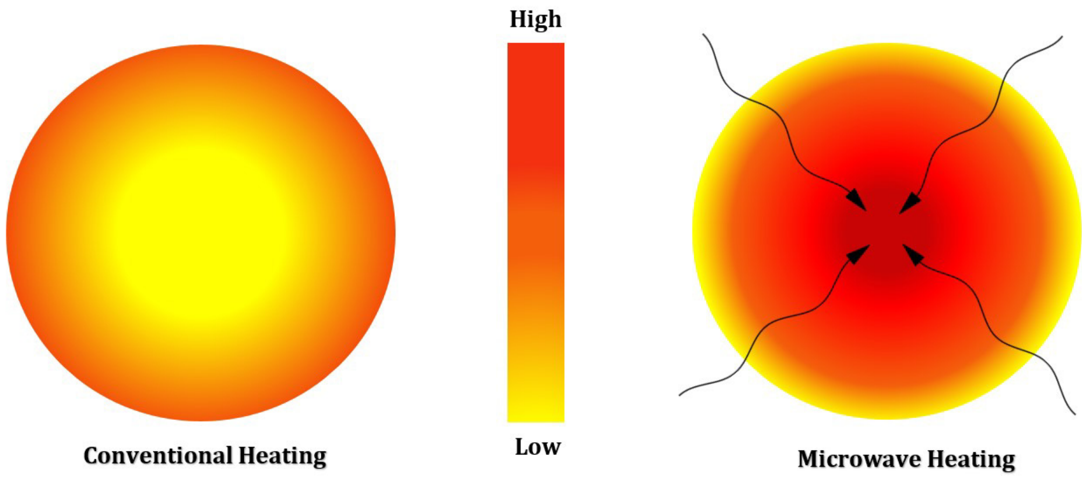

Figure 1. Difference between microwave and conventional heating [29].

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Previous literature outlines three modes of chemical reaction improvement via MW irradiation [29]:

1. Thermal effects, leveraging high reaction temperatures attainable rapidly in a MW field for polar materials.
2. Specific MW impacts unique to the MW irradiation heating mechanism.
3. Non-thermal effects, accelerating chemical transformations beyond the scope of thermal or specific MW effects.

Composition and Potential of Cashew Nut Byproducts

The processing of cashew nuts yields various byproducts, including cashew nut apple (CNA), CNS, cashew nut shell liquid (CNSL), de-oiled cashew nuts meal, rejected cashew nuts (RCNs), cashew testa (CT), effluents discharge, and residual wastes. These byproducts, rich in organic compounds and nutrients, present an opportunity for value addition through biorefinery principles, fostering environmental sustainability and offering economic benefits to the industry [30].

CT, a thin layer constituting 1-3% of the total nut weight, is an antioxidant-rich material containing hydrolyzable tannins, phenolic acids, and other bioactive compounds [31]. It has potential applications in various industries due to its chemical composition, including catechin, epicatechin, gallic acid, and p-coumaric acids. The CT shell contains proteins, crude fiber, fats, and ash. Studies have shown that CT containing cashew kernels exhibit higher concentrations of certain bioactive compounds than testa-free kernels [32].

Furthermore, CNSL, a byproduct obtained during cashew nut processing, is a valuable resource with components like cardanol, cardol, anacardic acid, and 2-methyl cardol [33]. This viscous liquid has diverse applications in pharmaceuticals, resins, coatings, adhesives, biofuel derivatives, and insecticides, making it a versatile bio-based material [34,35].

The CNSs left after CNSL extraction can produce activated carbon [36] and biomass briquettes [37]. With its increased surface area, activated carbon is suitable for various industrial applications such as dye removal, odor elimination, and catalysis [38,39]. On the other hand, biomass briquettes, composed of compressed biomass materials, can serve as an efficient and sustainable fuel source, especially in regions where conventional cooking fuels are not easily accessible. CNSs, with their high energy content, qualify as promising raw materials for biomass briquette production [37].

Moreover, MW pyrolysis of CNS has been explored to pyrolyze these byproducts further. The pyrolysis process can generate valuable products, and the MW-assisted approach enhances the efficiency of the process. The resulting products from MW pyrolysis can include BC, BO, and syngas, each with its applications.

Microwave-Aided Pyrolysis (MWAP) of Cashew Nut Shell

The following studies provide valuable insights into the formation of products from cashew nut shells (CNSs) using MWAP.

Amaliyah and Putra (2021) investigated the MWAP of CNS waste at 400°C for 60 minutes, with BO and BC yields of 45% and 35%, respectively. The study delineated key characteristics through comprehensive analyses, including proximate and ultimate assessments, SEM imaging, TGA/DTG profiles, GC-MS, and FTIR methods. The CNS exhibited a 71.25% mass loss before 750°C, with the highest decomposition rate at 261.2°C and 340.3°C. BO displayed favorable properties (density 1.036 g/ml, viscosity 19.5 cSt, flash point 138°C, HHV 21.7 MJ/kg) dominated by phenol and fatty acids. CNS-derived BC showcased increased volatile matter, fixed carbon, and a porous macropore structure [2].

In this recent study by Waitongkham et al. (2023), MW heating was employed to investigate BO production from CNSs through pyrolysis experimentally by using two magnetrons of 1,600 W with maintained electric field strength of 185.38 V/m at 2.45 GHz MW frequency. Pyrolysis was conducted at temperatures of 400°C, 500°C, and 600°C, alongside varying biomass-to-activated carbon (AC) ratios (70:30, 80:20, and 90:10). The highest bio-oil yield, an impressive 20.0%, was recorded at 600°C with a 90:10 CNS to AC ratio. Gas chromatograph-mass spectrometer (GC-MS) data revealed a rich composition of BO components, dominated by phenolic derivatives, reaching 23.56% at 500°C. Notably, the phenolic content, assessed with Folin-Ciocalteu reagent, ranged from 146.83 to 164.83 mg·GAE·g/DW for CNS at a 90:10 ratio. The research emphasized the influence of temperature and biomass-to-AC ratio on BO yields, with liquid yields escalating from 6.0% to 18.7% over the 400°C to 600°C temperature range. GC-MS identified acids, esters, ketones, furans, pyrans, guaiacol, syringol, and phenols as key BO components [40].

The synthesis of Cashew Nut Shell Carbon (CNSC) involved pyrolysis within the temperature range of 395-600°C at a flow rate of 10 ± 5°C min^{-1}, producing 24.67% carbon. Variations in MW heating power (400 W, 500 W, 600 W) led to differing moisture and ash content, meeting SNI 06-3730-1995 standards. Lower ash content enhances adsorbent quality by preventing pore blockage. FTIR characterization revealed distinct features: at 400 W, hydroxyl group vibrations, C≡C bonds, and aromatic C=C ring bonds; at 500 W, intensified C≡C bond, absence of OH group, and aromatic compounds; at 600 W, hydroxyl group reappearance, aromatic C=C, C≡C bonds, and enhanced carbon content. These spectral patterns indicate improved aromaticity and carbon purity with increasing MW power [41].

In a study conducted by Fombu et al. (2023), cashew nut shells (CNSs) were subjected to pyrolysis in a fixed-bed reactor at a temperature of 700°C with a heating rate of 100°C/min over a 45-minute duration under a N_2 atmosphere. The resulting product comprised 61.3% cashew nut shell liquid (CNSL). The proximity analysis of CNS showed moisture content, volatile matter, fixed carbon, and ash content of 8.98%, 88.83%, 0.12%, and 2.07%, respectively, and the elemental analysis indicated C, H, N, S, and O content of 64.64%, 7.39%, 0.510%, 0.36%, and 25.39%, respectively, with a calorific value of 29,775.48 kJ/kg. The CNSL proximate analysis showed moisture, volatile matter, fixed carbon, and ash content of 6.68%, 93.24%, 0.02%, and 0.06%, respectively, and the elemental composition of CNSL included C, H, N, S, and O of 66.23%, 10.72%, 0.148%, 0.30%, and 22.84%, respectively, with a calorific value of 30,735.78 kJ/kg. Differential thermal analysis (DTA) results indicated CNS's high melting point (405.5°C), with vapor evolution noted around 350°C. CNSL, as characterized by FT-IR and GC-MS analyses, demonstrated the presence of aromatic and aliphatic

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hydrocarbons. The liquid's properties (density 0.900 g/ml, viscosity 52 cp, and pH 4.3) suggested potential challenges for direct use as diesel fuel, necessitating further treatments [42].

The studies by Fombu et al. (2023) and Amaliyah and Putra (2021) both investigated the pyrolysis of CNS to generate CNSL, a predominant product in both methods, constituting up to 61.3% and 45% yield for conventional and MWAP, respectively. Shared characteristics include increased carbon content, reduced ash content, favorable calorific values, and the presence of aliphatic and aromatic hydrocarbons in the resulting CNSL. However, distinctions arise, as conventional pyrolysis yields a higher BC content (0.12%) than MAP (0.02%). At the same time, the latter produces CNSL with a higher density (1.036 g/ml) than the former (0.900 g/ml). Microwave-assisted pyrolysis's advantage lies in its lower operating temperature (400°C vs 700°C), promising energy efficiency, and reduced environmental impact, though further optimization and characterization are essential for fully realizing its potential [2,42].

Applications of Microwave-Aided Pyrolysis Products

The research by Mashuni et al. (2022) demonstrated the versatile applications of MWAP products, specifically focusing on preparing activated carbon (AC) from CNSs. The study utilized MW heating at 500 W to yield cashew nut shell activated carbon (CNSAC) with enhanced properties, including aromatic groups and increased carbon content. In wastewater treatment, CNSAC showed promising results as an adsorbent. Adsorption experiments using methylene blue (MB) as an experimental dye revealed an optimal adsorption rate of 3.356 mg/g at pH 9 and with a 90-min. Contact time operating under a 500 W microwave input power. The Freundlich isotherm model accurately described the adsorption process, indicating physical adsorption with an adsorption rate of 8.719 mg/g and an energy of 1.717 KJ/mol. The study systematically explored the impact of multiple factors, such as MW power, pH, contact duration, and MB concentration, on the adsorption efficiency, highlighting the importance of optimizing these conditions for effective adsorption [41]. These findings align with the broader discussion on utilizing pyrolysis products from CNSs, reinforcing the potential of MWAP in producing value-added materials with practical applications. The integration of such research outcomes contributes to the comprehensive understanding of the applications of MW pyrolysis products, showcasing their relevance in areas such as environmental remediation and sustainable material production.

Additionally, the study by Waitongkham et al. (2023) studied the MWAP of CNSs and Cassia fistula pods for BO production. The outcomes indicated that the BOs contained phenol derivatives with high phenolic content. The characterization of BOs provides insights into their potential applications, and this information can be integrated into the broader discussion on the microwave pyrolysis of CNSs, enriching the understanding of the diverse products obtained through this process [40].

Limitations and Future Prospects

Despite the promising results of these studies, there are still some limitations to using MWAP for CNS pyrolysis, such as the relatively high energy consumption of MW heating compared to conventional heating, the requirement of specific optimization in the pyrolysis process parameters for CNS pyrolysis compared to other lignocellulosic biomass, and the scarcity of efficient and scalable MWAP reactors [24,43,44]. Future research should focus on the following areas [45,46].

- Developing more energy-efficient MW heating technologies for MWAP.
- Optimizing the pyrolysis process parameters for an efficient product yield of CNS.
- Developing efficient and scalable MWAP reactors.
- Investigating the adsorption and catalytic characteristics of BC generated by CNS pyrolysis.
- Developing new applications for BC and BO generated by CNS pyrolysis.

Conclusions

In conclusion, the review illuminates the transformative landscape of MWAP as applied to CNS, emphasizing its pivotal role in sustainable biomass utilization. The unique attributes of CNS, often overlooked in the CN processing industry, have been unveiled as a promising feedstock for MAP, showcasing its adeptness in generating high-quality BC, BO, and syngas. This comprehensive exploration examines the intricacies of CNS pyrolysis, revealing the diverse spectrum of resulting products and their applications, ranging from soil amendment to bioenergy sources and liquid fuels. The contrast between conventional and MWAP methods underscores the efficiency of MWAP, characterized by lower operating temperatures, reduced environmental impact, and enhanced energy conversion. Scientific insights from recent studies highlight CNS pyrolysis dynamics, revealing details in BC and BO properties. The studies underscore CNS's potential in producing value-added materials and extend the discourse to the synthesis of activated carbon, exemplifying the versatility and practical applicability of MWAP products. The review concludes by urging investigations into the untapped potential of CNS pyrolysis products, encouraging research into their adsorption and catalytic properties, and envisioning novel applications that resonate with sustainability and environmental care principles. In essence, the MWAP of CNSs emerges as a scientific exploration and a guiding light directing the path toward innovative, eco-conscious solutions in biomass utilization.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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