Contents lists available at ScienceDirect

### Current Research in Microbial Sciences

journal homepage: www.sciencedirect.com/journal/current-research-in-microbial-sciences

# A concise review on waste biomass valorization through thermochemical conversion

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#### ARTICLE INFO

Keywords: Valorization Waste biomass Energy Biochar Bio-oil Thermochemical technologies

#### ABSTRACT

Due to an increase in industrialization and urbanization, massive amounts of solid waste biomass are speedily accumulating in our environment, which poses several adverse effects on habitat and human health thus becoming a matter of discussion in the environmental community. With reference to the circular economy, continuous efforts have been put forward for setting up an organised management approach in combination with an efficient treatment technique for increasing the profitable utilization of solid waste. This review aims to provide a systematic discussion on the recent thermochemical technologies employed for converting waste biomass generated from different sources into valuable products like biochar, bio-oil, heat, energy and syngas. The article further focuses on a few important aspects of thermochemical conversion of waste biomass to useful products like technical factors affecting thermochemical processes, applications of by-products of thermochemical conversion, and biological pretreatment of waste biomass. The review assists interesting recent and scientific trends for boosting up the systematic management and valorization of solid waste through low-cost, efficient, environment-friendly and sustainable technologies.

		min	Minute	
		MJ/kg	Megajoules per kilogram	
List of symbols/abbreviations		IHBFBSR	Indirect heated bubbling fluidized bed steam reformer	
GHG	Greenhouse gases	SNG	Synthetic natural gas	
HTL	Hydrothermal liquefaction	LHV	Lower heating value	
°C	Degree celsius	$CO_2$	Carbon dioxide	
Fig.	Figure	SBR	Steam-to-biomass ratio	
wt.	Weight	OBR	Oxygen-to-biomass ratio	
%	Percentage	Κ	Kelvin	
sec	Seconds	MPa	Megapascal	
mm	Millimetre	HTC	Hydrothermal carbonization	
m <sup>3</sup> /h	Cubic meters per hour	HTG	Hydrothermal gasification	
et al.	All others	CH <sub>4</sub>	Methane	
ZSM-5	Zeolites Socony Mobil-5	g	Grams	
CO	Carbon monoxide	w/w	Weight/weight	
mol/L	Moles per litre	K <sub>2</sub> CO <sub>3</sub>	Potassium carbonate	
kW	Kilowatt	FeSO <sub>4</sub> ·7H	<sub>2</sub> O Iron(II) sulfate heptahydrate	
GW	Gigawatt	KOH	Potassium hydroxide	
$H_2$	Hydrogen			

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https://doi.org/10.1016/j.crmicr.2024.100237

#### Available online 23 April 2024

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Ni	Nickel
Со	Cobalt
Fe	Iron
Zn	Zinc
HMF	5-hydroxymethyl furfural
BPF	Bio-based phenol formaldehyde
>	Greater than
rpm	Revolutions per minute
Py-GC/M	S Pyrolysis-gas chromatography/mass spectrometry
SDGs	Sustainable Development Goals
Btu	British thermal units
US	United States
i.e.	that is
etc.	Et cetera

#### 1. Introduction

The rapid rise in urbanisation, human population, industrialization, unsustainable consumption patterns, modern lifestyle and high living standards have resulted in the massive amount of waste generation (Ambaye et al., 2023; Bisht et al., 2022). Various activities such as domestic, industrial, and agricultural generates a large amount of waste that may or may not be biodegradable thus toxic to the society, environment and other living beings (Perera et al., 2021; Bisht et al., 2023). According to recent reports, around 1.3 – 1.9 billion tons of solid waste is produced every year globally and by 2050 this amount is expected to increase by 3.5 billion tons. However, from this huge amount of waste generated, around 70 % is directly disposed of in landfills, 19 % is recycled and only 11 % is transformed into energy leading to severe environmental and health problems (Mutz et al., 2017). The conventional waste management practices like landfilling and incineration pose several threats to society and natural habitat such as increased emission of greenhouse gases (GHG) and sudden climate change (Wang et al., 2017). Secondly, the drastic increase in human population and related activities has also increased the current energy requirements resulting in excessive consumption of traditional energy resources such as fossil fuels like natural gas, crude oil and coal (Shahbeik et al., 2022; Joshi et al., 2023). Presently, they are accountable for around 86 % of the overall global energy requirements, which holds serious environmental concerns like GHG emissions and global warming apart from financial issues and political crises (Velvizhi et al., 2023). According to statistical analyses, regulated by the US Energy Administration, by 2040 the global energy demand is anticipated to rise by more than 28 % (739 quadrillion Btu) (Elgarahy et al., 2021).

Therefore, at present several countries have been continuously working on the development of some sustainable strategies focusing on renewable energy sources for minimising the GHG emissions and substituting fossil fuels (Vrabie, 2021; Rawat et al., 2023). Moreover, United Nations Sustainable Development Goals (SDGs) 7 i.e., affordable and clean energy ensures the accessibility of sustainable, reliable, affordable and modern energy to all (Kunwar et al., 2023; Bhattacharya and Bose, 2023). In this perspective, valorization of solid waste can be seen as an environment-friendly approach that allows the generation of highly valuable products such as fuels, chemicals and similar raw materials for industrial and domestic applications (Kaza et al., 2018). In general, biomass is a renewable type of source of energy that holds the efficiency to replace petroleum-based fuels for producing bioenergy and biofuels. As compared to petroleum-based fuels, the characteristics of biofuels produced from waste biomass materials are extensively volatile both oxidatively and thermodynamically (Savi et al., 2017). Therefore, for achieving worldwide energy security and for reducing GHG emissions and environmental concerns, biofuel offers a novel opportunity (Kumar et al., 2023). Biomass can be converted into valuable products by biochemical and thermochemical techniques (Devaraja et al., 2022). Different thermochemical processes namely, combustion, gasification, pyrolysis and torrefaction involves the conversion of biomass into

different intermediate products such as syngas, biochar and bio-oil. Valorizing bio-wastes or biomass is possible by utilising feedstocks involving animal manure, sewage sludge, crop waste, food waste, forestry waste (woody biomass) and algae (Velvizhi et al., 2023). Contrastingly, biochemical conversion techniques involves saccharification, anaerobic digestion, transesterification, enzymatic microbial fermentation, hydrolysis etc. that are related with the production of bio-hydrogen and bio-alcohols like bio-butanol, bio-ethanol (Manikandan et al., 2023).

Therefore, the present review aims to provide an in-depth discussion on different thermochemical pathways like pyrolysis, combustion, gasification, hydrothermal liquefaction and torrefaction for converting waste biomass into value added products. The paper also summarises different technical factors affecting thermochemical processes, applications of by-products of thermochemical conversion, and biological pretreatment of waste biomass. Recent studies related to the valorization of waste biomass through thermochemical conversion processes have been discussed. The paper also assists a deep insight on the recent trends, future challenges and future perspectives for practical large-scale applications of different thermochemical techniques.

#### 2. General classification of biomass

Biomass can be referred to as a common term for all kinds of organic matter generated either indirectly or directly by photosynthesis, existing in the form of biological carriers, involving animals, plants and different microorganisms (Cai et al., 2024). In general, biomass can be categorised as primary, secondary and tertiary biomass as follows:

- *Primary biomass:* It is generated directly by the process of photosynthesis and is exactly procured from the land. The examples of primary biomass sources includes woody and herbaceous biomass, oil crops seeds, residues of agricultural crops and forest trees after harvesting such as bark, wheat straw, limbs and corn stover (Osman et al., 2019).
- *Secondary biomass:* It includes those which are produced from the processing of primary biomass like chemical processing of black liquor, biological processing of manure produced by animals and physical processing of sawdust (Osman et al., 2019).
- *Tertiary biomass:* It basically includes post-consumer by-products like packaging by-products, used vegetable oils, animal fat, and demolition and construction debris (Osman et al., 2019). The common waste biomass sources are illustrated in Fig. 1.

#### 3. Biological pretreatment of waste biomass

Since time immemorial, microorganisms are playing a vital role in the extracellular degradation of lignocellulose by the help of hydrolytic enzyme secretion which aids in the lignin depolymerization (Pérez et al., 2002). Due to the secretion of hydrolases enzyme and lignin degrading enzyme, the structure of the cell wall gets opened up and further permits the polymers hydrolysis. In the process of biological treatment the hemicelluloses and cellulose undergoes the process of hydrolysis into the monomeric sugars by utilizing the hemicellulolytic and cellulolytic microorganisms. Degradation of the lignocellulosic biomass occurs at the same time preceded by the process of fermentation resulting in the biofuel formation like ethanol, furfural and methane with the bioproducts such as acetate, lactate, organic acids (Reguera et al., 2015; Zhao et al., 2011; Faik et al., 2013). Bacteria such as (Bacillus sp, Cellulomonas sp, Streptomyces sp and Thermomonospora sp) and most of the fungi like (Aspergillus niger, Trichoderma viride, Phanerochaete chrysosporium and Trichoderma reesei etc.) are well-known for the hydrolysis of the natural biopolymers.



Fig. 1. Sources of waste biomass.

#### 3.1. Bacterial pretreatment

Most of the bacteria help in the production of several biomass enzymes capable of degradation having potential to be utilized in the biological pretreatment. Appropriate selection of the bacterial strain in the pretreatment method of lignocellulosic biomass is followed with the hydrolysis by enzymes and the fermentation process which are the fundamental steps during the production of biofuel. Lignin being distinct, hemicellulose and cellulose are moreover easy for the degradation. Thermomonospora fusca and Cellulomonas fimi being the cellulolytic bacteria have been comprehensively premeditated for the production of cellulases. Likewise, Paenibacillus campinasensis is capable for survival in inconsiderate environmental conditions and possesses a good prospect for the pretreatment of lignocellulosic biomass (Miron et al., 2001). Almost 30 of the bacterial species like (R. albus, e F. succinogenes and R. flavefaciens) own a different mechanism of hydrolysis and its adherence to cellulose (Duff et al., 1996). In addition there are several anaerobic cellulolytic bacteria like Bacteroides cellulosolvens, Clostridium thermocellum which helps in the production of high cellulose activity, which do not secrete enough of the enzymes (Dien et al., 2003). Anaerobic bacteria such as Zymomonas mobilis which is a cellulolytic bacteria could be used in the glucose, sucrose and fructose fermentation for giving high ethanol yield (Paudel et al., 2015). Gram-positive and gram-negative bacillus strains such as Firmicutes, Rahnella, and Pseudomonas produce cellulases which illustrate the highest activities in the degradation of materials composed of cellulose (Saritha et al., 2012). Few bacterial strains such as Bacillus subtilis and Azospirillum lipoferum have been widely reported for the production of bacterial laccases causing the lignin depolymerization (Bandounas et al., 2011). As compared with the fungal strains there has been a very limited study done on the bacterial strains, scientists have shown the wide-ranging interest in the bacterial lignin degradation (Palamuru et al., 2015; De Gonzalo et al., 2016) because of the lately discovered laccases (Chandra et al., 2015),  $\beta$ -etherases (Picart et al., 2015) and bacterial peroxidases (Sukumaran et al., 2005) which can be efficiently used in the delignification.

#### 3.2. Fungal pretreatment

Fungi are very well recognized for their interactive effect on the rotten lignocellulosic residues by their own enzymes. These fungal strains are extensively distributed in nature, out of which most of them produces lignocellulolytic (Arantes et al., 2007; Shary et al., 2008), cellulolytic (Mandels and Reese, 1960; Ljungdahl et al., 2008; Arantes et al., 2007) and hemicellulolytic enzymes (Ljungdahl et al., 2008). Ascomycetes species are amongst the lignocellulolytic fungi such as (Penicillium, Aspergillus, Trichoderma reesei), basidomycetes including brown rot fungi (e.g. Fomitopsis palustris) and white rot fungi (e.g. P. chrysosporium, Schizophyllum) and few of the species amongst the anaerobic ones (e.g. Orpinomyces) (Dashtban et al., 2009; Paudel et al., 2015). Due to the impermeability and recalcitrant nature of lignin; and the crystallinity and insolubility of cellulose signifies a biggest challenge for the hydrolysis in the presence of enzymes. The reports on T. reesei have revealed the production of substantial amounts of  $\beta$ -glucosidase and xylanases with high amounts of cellulose (Tangnu et al., 1981). Like-wise soil fungus Trichoderma longibrachiatum has been widely studied and has shown promising effects in the solubilization of cellulose which is of crystalline nature due to the secretion of exoglucanases (cellobiohydrolases), endogluconases (carboxymethyl cellulose) and β-glucosidases (cellobiases). These cellulases and their substrates possess the complex interactions which function synergistically during the process of hydrolysis (Zhou et al., 2000; Pérez et al., 2002). On the other hand lignin has a much more complex pathway of delignification and acts as an obstacle in the selection of an efficient fungal strain. White rot fungi like basidomycetes play a significant role in the lignin disintegration and have been regarded as the natural lignin degrading microorganism. They help in the mineralization and depolymerization of lignin as they secrete a broad range of ligninolytic enzymes like lignin, manganese peroxidases, laccases and lignin peroxidases (Millati et al., 2011; Bandounas et al., 2011; Guillén et al., 2005). 30 different white rot fungi was isolated having capability of decomposing wood for lignin production and out of which the best delignifiers found so far were Pholiota mutabilis, P. chrysosporium, Phellinus pini-2, Phlebia brevispora-1 (Otjen et al., 1987). Nevertheless, the stand against choosing the fungal strain that can effectively degrade lignin with the recovery for cellulose at the same time exists, and no breach yet on its commercialised

appliance.

## 4. Thermochemical conversion of waste biomass to useful products

By using various thermochemical techniques, biomass can be converted to different useful products and energy sources like biochar, biooil, heat, natural gas, and thermal and electrical energy (Garba, 2020; Matsumura, 2015) as shown in Fig. 2. Basically, the process of thermochemical conversion comprises the thermal degradation of organic biomass components to generate valuable products. It is an effective alternative approach for producing bioenergy that involves controlled heating or oxidation of biomass (Perera et al., 2021). However, the choice of conversion technique is influenced by a number of factors, such as type and amount of biomass, its accessibility, affordability of manufacturing process, choices for final products, and environmental concerns (Garba, 2020; Matsumura, 2015). For instance, the biomass feedstock should be of solid state and low in moisture. Similarly, the utilization of inappropriate technology might result in low efficiency (Guran, 2020; Zhang and Zhang, 2019). Such types of thermochemical technologies generally include pyrolysis, gasification, torrefaction, hydrothermal liquefaction (HTL) and combustion (Gururani et al., 2022) as shown in Fig. 3.

#### 4.1. Pyrolysis

Pyrolysis is a process that converts biomass into energy by heating (not burning) at a high temperature and certain pressure with little or no oxygen (Fig. 4). Charcoal, which is widely used in metallurgical operations, is the most typical end product of pyrolysis. In addition, gas (methane, hydrogen, and carbon monoxide) or liquid (water, tar, and oil) are some other by-products of pyrolysis (Basu, 2018). Pyrolysis is a flexible and effective process that allows the efficient generation of heat, electricity, and chemicals from solid biomass by transforming it into a liquid that is simple to store and transport. However, for high moisture waste biomass like sludge and waste from meat processing, drying is crucial prior to pyrolysis (Wang et al., 2020a). It is a complicated method that involves both simultaneous and sequential processes while pyrolyzing biomass. When the biomass is exposed to heat in an inert atmosphere, the thermal decomposition of components occurs at 350 °C to 550  $^\circ\text{C}$  which accelerates to 700  $^\circ\text{C}$  to 800  $^\circ\text{C}$  in the absence of air. As a result of the biomass decomposition, long chains of carbon, hydrogen, and oxygen compounds break into smaller molecules during pyrolysis, and gases, condensable vapours including tars, oils, and solid charcoal are being produced. Each of these components decomposes at different rates and to a different extent, depending on the process parameters of pyrolysis (Fisher et al., 2002; Jahirul et al., 2012). The pyrolysis of wood biomass is depicted in Fig. 5.

Moreover, pyrolysis is further categorised into different types, such as catalytic hydropyrolysis, slow pyrolysis, fast pyrolysis, catalytic pyrolysis and flash pyrolysis (Bhatnagar et al., 2021). Typically, slow pyrolysis takes place at atmospheric pressure that involves the generation of heat from an external energy source, most often from the incomplete combustion of the biomass feedstock or from the combustion of the produced gases. Under such conditions, the biochar yield is usually very low (Laird et al., 2009). Secondly, fast pyrolysis has been considered as the most efficient conversion process for the production of bio-oil, liquid fuel, and gases as shown in Fig. 6. This process is generally carried out in an inert atmosphere at a medium temperature. However, the process efficiency and quality of the resulting product is influenced by certain operating conditions like temperature, catalysts, pressure, additives, and type of reactor (Inayat et al., 2022). Thirdly, flash pyrolysis is an advanced technique that may produce high-grade biomass energy from low-grade biomass energy (Yu et al., 2007). The bio-oil yield produced through flash pyrolysis of biomass ranges from 70 to 85 wt.%. It is made up of a very complex combination of oxygenated compounds whose composition is influenced by both the kind of biomass employed and the operating circumstances (Amutio et al., 2013). This process is characterised by a very short residence time, which is generally less than 0.5 s, and high heating rates (103-104 °C/s) (Kan et al., 2016).

For instance, thermal pyrolysis of the bio weed (Ficus religiosa) was reported by Rao et al. (2022). The wood and bark of Ficus religiosa have been selected as the feedstock due to their high volatile content. The optimum conditions for obtaining maximum yield of bio-oil were found to be of 1.0 mm particle size, a 2.0  $\text{m}^3$ /h sweep gas flow rate, and a 450 °C temperature. The chromatographic analysis of bio-oil revealed that the bio-oil contains different chemical components, such as alcohols, phenols, alkenes, saturated fatty acids, and esters. Zhang et al. (2012) investigated the catalytic fast pyrolysis process of pine wood, alcohols and their mixtures by using Zeolites Socony Mobil-5 (ZSM-5) catalyst. At 600 °C, it was found that petrochemicals had a total carbon yield of 23.7 %. From 16.2 % and 0.3 % at 400  $^\circ C$  to 44.1 % and 6.9 % at 650  $^\circ C$  , respectively, the carbon monoxide (CO) and methane outputs increase with temperature. The pyrolysis of algal biomass derived from high-rate algae ponds treating sewage was reported by Vargas e Silva and Monteggia (2015). In order to produce the biofuel, pyrolysis was used in a quartz glass reactor that was put into a furnace and heated outside. The investigations carried out demonstrated the impact of temperature on the product yield during pyrolysis, with a maximum rate of production of the liquid phase (bio-oil and water) of 44 % at 500 °C, 45 % for char, and around 11 % for gas. The pyrolysis reaction of naturally occurring microalgae obtained from Taihu Lake was studied by Liu et al. (2021). Experiments on pyrolysis were conducted at 500 °C for around two hours. In order to determine the impact of the ash on the pyrolysis behaviour, the products were studied using a variety of methods. The findings demonstrated that the ash prevented microalgae from transforming them thermally. The highest ash removal was achieved with 2 mol/L hydrochloric acid, and the liquid yield increased from 34.4 % to 40.5 %. A microalgae biorefinery process that uses pyrolysis with the HZSM-5 catalyst to transform entire microalgae into aromatic hydrocarbons was reported by Wang and Brown (2013). This process yields



Fig. 2. Useful products of biomass conversion.



Fig. 3. Different routes of thermochemical conversion of biomass.



Fig. 5. Important pathways for wood pyrolysis.



Fig. 6. Important by-products of fast pyrolysis.

useful petrochemicals and ammonia, which may be recycled as fertilizer for the growth of microalgae.

#### 4.2. Combustion

An exothermic chain of reactions makes up the combustion process. Chemical bonds often serve to store energy, which is released when the bonds disintegrate. This energy is employed to develop the necessary steam for turbines that ultimately produce electricity and heat in most of the industries and power plants. Burning organic materials is the definition of combustion in the context of alternative fuels like biomass. The most popular fuel for burning during the biomass combustion is wood (Abuelnuor et al., 2014). The size range of biomass combustion systems ranges from a few kilowatt (kW) to more than 100 gigawatt (GW). Heat from biomass can be generated with a high degree of efficiency and at a cost that is really affordable. Applications involving enormous scales are noteworthy in terms of the specific cost and efficiency of steam plants (Nussbaumer, 2003). Typically, biomass combustion models are divided into two groups: macroscopic and microscopic. For macroscopic analysis, particularly the macroscopic properties of biomass such as moisture content, heating value, density, particle size, and ash fusion temperature are provided. Thermal, chemical kinetics and mineral data are some of the properties that can be examined under a microscopic analysis (Demirbas, 2004). The three basic combustion operations may be thought of as the interactions between fuel, energy, and environmental factors. In the boiler, the combustion of biomass fuel produces flammable vapours that volatilize and blaze like flames. The remaining material, which is still a carbon char, will then ignite in the presence of additional air. The heat generated during combustion may be used as a source for further conversion processes for generating electrical energy, which again depends on various other parameters (Sivabalan et al., 2021).

#### 4.3. Gasification

The flexibility of the gases generated by biomass gasification is the primary factor driving attention to it (Rajvanshi, 1986). Variable low-energy-density fuels can be converted into combustible gases with the use of this process. A solid fuel burns through heat and oxidative breakdown with the help of air or oxygen (Fig. 7). To improve the efficiency of conversion, though, other gasification agents can be used (Kan and Strezov, 2014). In general, in the biomass gasification process, interactions between char and gasifying agents are frequently used as the regulatory phase due to their relatively slow reaction rates. There is a



#### GASIFICATION

Fig. 7. Overall gasification process.

significant impact on the char's reactivity with volatile components including tarry components, steam, hydrocarbons, and other light gas species (Zhang et al., 2020). The basic outline of the combustion process is presented below:

Generally, three types of gasifiers are used in the gasification of biomass, including fixed-bed, fluidized-bed, and entrained-flow gasifiers (Sikarwar et al., 2016). The fixed bed gasifiers are further divided into updraft and downdraft fixed bed gasifiers (Fig. 8). In an updraft gasifier, the biomass is fed from the top and flows downward, and gasifying agents are introduced into the grate from the bottom, causing the resultant gas to rise upward. In this instance, combustion occurs at the gasifier's hottest area, the bed's bottom, while the resultant gas exits the top at a lower temperature. The resulting gas contains tar in large quantities due to the lower exit temperature. Both the feed and the product gas fall into a downdraft gasifier, and the product leaves from the bottom at higher temperature. Most of the tar is burnt in this instance due to the passage of gas from a high-temperature zone (Kumar et al., 2009). In fluidized-bed gasifiers, the biomass particles are suspended in an oxygen rich environment. The resulting bed behaves like fluid. Back-mixing is a process used by such gasifiers to effectively combine biomass with coal that has previously undergone gasification. Biomass particles enter through the reactor side, and the oxidant and steam enter from the bottom with adequate velocity. These gasifiers are usually operated at moderately high temperatures for getting a high carbon conversion rate and for decomposing the products accumulated at the side (Ram and Mondal 2022). One of the simplest types of gasification is cross-draft gasification, which uses a reactor much like an updraft gasifier in which the fuel enters from the top and undergoes a gradual thermochemical reaction as it descends into the reactor (Fig. 9) (Saravanakumar et al., 2010).

Raheem et al. (2018) studied the catalytic gasification of algal biomass under different reaction conditions such as the dose of catalyst, temperature, and reaction time. The influence of operational factors on response variables was investigated using central composite design and optimisation techniques. The results showed that the two most important reaction parameters influencing the formation of hydrogen (H<sub>2</sub>) and thus, lowering the amount of tar formed during the gasification process were temperature and catalyst loading. The maximum hydrogen fraction was found to be 48.9 % at a reaction time of 28.8 min, catalyst dose of 16.4 wt%, and 851 °C, respectively. Ebadi and Hisoriev (2019) reported that the operating conditions, hydrodynamic characteristics of the gasifier, and kind of feedstock all play a role in the quality of the generated syngas. They investigated the modelling of syngas production via circulating fluidized bed gasification of algal biomass using different gasifying agents and particularly at different particle sizes. The experimental results revealed that the gasification of biomass using pure oxygen as the gasifying agent poses a remarkable impact on increasing the calorific value of the generated gas.

Montiel-Bohórquez and Pérez (2022) studied the influence of ash-rich biomass combined with woody biomass on the thermodynamic efficiency of a bioenergy power plant. The study was based on a downdraft gasifier linked to an engine-generator. Aspen Plus and the Engineering Equation Solver have been used to simulate the biopower plant. By correlating their chemical characterization with the output of the power plant, the constructed model was utilized to evaluate the garden waste energy valorisation strategies. Shone and Jothi (2016) reported that the dried leaves may be implemented as a source of energy even though they are frequently used in rural areas for satisfying the daily energy demands. Leaf material from Tectona grandis (teak) and Hevea brasiliensis (rubber) trees are used to fulfil the objectives of this investigation. As per the results, the leafy biomass produced by teak and rubber leaves has the calorific values of 17.5 and 17.8 MJ/kg, respectively. An indirect heated bubbling fluidized bed steam reformer (IHBFBSR) with a 50 kW capacity and its activation trials were reported by Tsekos et al. (2021). Experiments have been conducted using two woody biomass feedstocks and two bed material of particle sizes. The IHBFBSR's cold gas efficiency and product gas composition and quality were in a fair amount with conformity compared with those of comparable systems. It was established that the IHBFBSR technology represents a potential advancement in the biomass gasification industry.

The approach for a waste biomass for the synthetic natural gas (SNG) conversion process that includes a catalytic hydrothermal gasification



Fig. 8. Updraft and downdraft gasifiers.



Fig. 9. Fluidized bed and cross draft gasifiers.

process was proposed by Luterbacher et al. (2009). According to process modelling, 62 % of the lower heating value (LHV) of manure and 71 % of that of wood are both transformed to SNG. The renewable SNG produced contains roughly 10 % of the fossil energy used during all operations. Haydary et al. (2021) reported the potential utilisation of lignocellulosic waste biomass as a renewable energy source. The waste material has been used to generate H<sub>2</sub>, CO, and CO<sub>2</sub> (carbon dioxide). These gases were then used in the synthesis of methanol. The maximum methanol production was achieved when both oxygen and steam were used as gasifying agents. Both the steam-to-biomass ratio (SBR) and the oxygen-to-biomass ratio (OBR) were found in the optimal range at 0.89.

#### 4.4. Hydrothermal liquefaction (HTL)

Biomass is thermochemically converted into liquid fuels by HTL after it has been sufficiently processed in a hot, water pressure environment to liquefy the solid structure primarily into liquid components. A temperature of 523 to 647 K and working pressures between 4 and 22 MPa are typical hydrothermal processing conditions (Elliott et al., 2015). This technology allows the direct conversion of wet biomass feedstock into liquid fuels with any energy-demanding drying process (Kumar et al., 2022a). Moreover, the resulting oil is equipped with a high calorific value. In this process, water acts as a solvent and has many advantages, such as low viscosity and a low dielectric constant, better solubility of biomass, and support for acid-base reactions. The oxygen in biomass is partly removed via decarboxylation and dehydration reactions. These reactions produce carbon dioxide, carbon monoxide and water. With hydrothermal processing technology; biomass goes through a series of chemical processes to create biofuels. These processes are hydrolysis, pyrolysis, depolymerization, reforming, condensation, and gasification. Fig. 10 illustrates the classification of hydrothermal technology categorised into three areas based on the major products: hydrothermal carbonization (HTC), HTL, and hydrothermal gasification (HTG) (Shah et al., 2022).

Raw feedstock is subjected to high-pressure water during the HTC of biomass (Fig. 11). Gaseous and water-soluble compounds, as well as water itself and a solid char, are generated by a variety of hydrolysis, dehydration, and decarboxylation reactions (Yang et al., 2020; Hoekman et al., 2011). This process is an approach for converting waste from many sources, including sewage, lignocellulosic biomass, sludge, algae, and others. The waste is made more hydrophobic and dewatered by this process, which also enhances the solid products' fuel-producing capabilities. In hydrochar produced from material with high ash content, it was revealed that the HTC process enhanced the ash yield (Czerwińska et al., 2022). The advantages of HTC are that biomass may be converted to carbonaceous solids without using an energy-intensive drying process. Compared to the starting material, the energy-dense hydrochar has a higher energy-to-weight ratio. Toxic substances and residual micropollutants are also broken down during the HTC phase (Yoganandham et al., 2020). Numerous properties of water are substantially altered as the reaction state approaches the critical point of water, which can result in rapid, homogeneous, and effective reactions (Zhang and Chen, 2018).



Fig. 10. Classification of hydrothermal technology.



Fig. 11. Hydrothermal carbonization of biomass.



Fig. 12. Hydrothermal liquefaction of biomass.

Both wet and dry biomass may be processed satisfactorily using HTL (Fig. 12). The biomass is subjected to processes such as hydrolysis, dehydration, or decarboxylation. The biocrude oil obtained via this process is an energy-dense intermediate that may be transformed into a variety of liquid fuels. This major product is the renewable counterpart

of oil. HTL produces biocrude oil from organic matter in the presence of water under hydrothermal treatment, at temperatures ranging from 250 to 450 °C and pressures between 100 and 300 bar. Moreover, other byproducts are also produced, such as soluble organic compounds or gases (CO<sub>2</sub>, CO, H<sub>2</sub>, or CH<sub>4</sub>) (Grande et al., 2021). A continuous HTL



Fig. 13. Hydrothermal gasification of biomass.

process design is superior to batch systems for large-scale commercial production. Rather than this, continuous HTL has a lot of benefits, such as cost and waste reduction, chemical and process operability, safety, etc. The large-scale commercial conversion of different wet biomasses into energetic fuels and valuable chemicals offers a lot of potential for continuous HTL. In a continuous HTL process, water molecules break down the bigger biomass molecules into smaller fragments (Sahu et al., 2020).

Hydrothermal biomass gasification (Fig. 13) involves a thermochemical process to convert wet biomass with natural water content to hydrogen. Water present in the biomass acts as a reactant and reaction medium (Kruse et al., 2010). Hydrothermal methods have great potential for effectively monetizing wet biomass feedstocks or trash. The feedstock's composition has a significant impact on how well they work, and techniques for analysing such complicated mixtures as well as the generated effluents are constantly being improved (Baudouin et al., 2021). As the reaction medium, hot, compressed water has excellent properties. Water demonstrates the properties of a non-polar solvent at this point since its dielectric constant decreases significantly. In water, most organic compounds and all gases completely dissolve, causing a homogenous response that lowers the mass transfer barrier between phases (Kean et al., 2013). Several operating temperatures and pressures can be used for HTG. In initial studies, supercritical water was first found to be a significant working medium, with the supercritical state serving as the primary variable (Elliott, 2008). Comparing this approach to traditional gasification technology reveals significant advantages. Wet biomass may be used immediately without requiring an energy-intensive drying process. Likewise, the density and dielectric constant of supercritical water are also low (Zhang and Zhang, 2019; Salimi et al., 2016).

Leow et al. (2015) reported the HTL of algal biomass into biocrude oil at high pressures and temperatures. The yield of HTL biocrude and the dispersion of carbon increased in direct proportion to the fatty acid concentration. A major obstacle to HTL biofuel generated from microalgae was eliminated by the combination of the fatty acid model and an upstream cultivation model. Frank et al. (2013) reported that lipid extraction does not yield as much oil from algae as HTL. When yields exceeded 0.4 g HTL oil/g of algae, insufficient carbon was left for the production of biogas, which resulted in an increase in GHG emissions. Cao et al. (2016) investigated the feasibility of using certain green landscaping waste as a feedstock for HTL to generate bio-oil. The yields and higher heating values of the bio-oils and biochar produced from leaves clearly distinguished them from those produced from branches.

Saengsuriwong et al. (2023) studied the production of biocrude oil using HTL of high moisture content waste from the tobacco processing industry. A maximum production of liquid biocrude oil was achieved through investigating and optimising the impacts of operating conditions. Temperatures between 280 and 340 °C and residence periods between 15 and 45 min were taken into account for HTL operating conditions, with a fixed biomass to deionized water ratio of 1:3. At 310 °C and 15 min, the liquid biocrude oil yield exceeded a maximum of more than 52% w/w. The hydrothermal liquefaction of woody biomass (birchwood sawdust) in the presence of the catalysts colemanite, hydrotalcite, potassium carbonate (K2CO3), and iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was studied by Nazari et al. (2015). The best performance was demonstrated by the catalysts K<sub>2</sub>CO<sub>3</sub>, potassium hydroxide (KOH), and colemanite in terms of oil production and solid residue yield. Utilising KOH, the production of biocrude oil was enhanced to about 40 wt.%, which is more than double the yield of the uncatalyzed operation.

Tai et al. (2021) studied the HTL of oak wood to produce high-quality biocrude. They studied how the use of nickel (Ni) and cobalt (Co) as hydrodeoxygenation catalysts and iron (Fe), zinc (Zn), and other metals as hydrogen generators affects the quality of biocrude. Active hydrogen is formed when Fe and Zn are oxidised by supercritical water. This hydrogen is then employed to stabilise biomass fragments during the

process and to fuel hydrodeoxygenation processes when Ni and Co are present. The findings indicate that the use of hydrogen generators has a considerable impact on biocrude yields. Shimizu and coworkers (Shimizu et al., 2021) investigated the HTL of conifer wood chips between 180 and 425 °C. These investigations enable the effective extraction of 5-hydroxymethyl furfural (HMF) and other important chemical compounds from lignocellulosic biomass, including glycolic acid and acetic acid. Acetic acid, glycolic acid, and HMF may all be produced at their best temperatures at 300 °C, 250 °C, and 180 °C, respectively. The breakdown process characterising HTL treatment of wood chips may be clarified based on the findings of the tests done in this study. Chen et al. (2018) studied the HTL of mulberry bark using subcritical water and an ethanol-water medium. The salt K<sub>2</sub>CO<sub>3</sub> was provided as the catalyst. The obtained results revealed that the maximum liquefaction efficiency was found to be 97.7 wt% in an ethanol-water medium with a yield of bio-oil of 30.32 wt%.

Li et al. (2016) studied the HTL of outer and inner white birch bark to form oils in an ethanol-water medium and the formation of BPF (biobased phenol formaldehyde). The developed BPF foams had good elastic modulus, compressive strength, and thermal conductivity. As compared to outer bark, inner bark was found to be more suitable for the formation of BPF foams. Feng et al. (2014) reported the HTL of the barks of white pine, white spruce, and white birch in ethanol-water co-solvents. The experimental findings showed that the liquefaction efficiency varied with bark species as well as ash content/composition. The conversion rate of the bark proceeded in the following order: white spruce bark > birch bark > white pine bark. The ash content order was white birch bark > white pine bark > white spruce.

#### 4.5. Torrefaction

Torrefaction is a thermal method involving the treatment of biomass to yield a charred product that can be used as fuel or organic manure. When used as fuel, torrefied materials are commonly referred to as bio coal. Contrastingly, the word biochar is most commonly used when the torrefied product is used as a soil amendment (Barskov et al., 2019). Torrefaction is a type of thermal pre-treatment that helps in lowering the heterogeneity of biomass in terms of its physical characteristics and chemical composition. It raises its energy content, decreases biological degradation, and lowers the moisture content (Tumuluru et al., 2021). The torrefaction process is generally carried out at a relatively low temperature (225 to 300 °C). The lignin and hemicelluloses found in wood are partially broken-down during torrefaction. Torrefaction enhances calorific value, and when the product is pelletized, the density might be even higher than with conventional pellets (Caillat and Vakkilainen, 2013). Utilising the energy released in the volatiles is essential to the economic sustainability of a biomass torrefaction operation. Additional support fuel is required for handling large amounts of moisture, thus aiding in the production of energy needed for the drying process. The time length of the biomass is subjected to torrefaction as well as the temperature at which it occurs determines the degree of torrefaction (Basu, 2018). Densification can increase the weak mechanical strength of biochar, which might prevent the significant loss in the mass during the handling and transportation. The latest evidence has addressed a variety of prospective applications where the use of biochar is restricted by its poor mechanical properties due to densification of the material (Riva et al., 2021). The torrefaction process for biomass conversion is presented in Fig. 14.

Alizadeh et al. (2022) studied the waste product (wood sawdust) of the torrefaction process. In a fixed bed reactor, sawdust was torrefied inside at the temperatures of 230 °C, 260 °C, for increasing the mechanical strength of the pellets, resulting in the 50 % boost in the tensile strength. Granados et al. (2017) developed a two-stage, inclined, continuous rotary torrefier for optimising biomass torrefaction processes. The change in heating value for the torrefaction process at 300 °C, 1° of tilt angle at a speed of 5 rpm (revolutions per minute) was 40 %,



Fig. 14. Torrefaction of biomass.

whereas the energy and mass yield were 48 % and 34 %, respectively. Wang et al. (2020b) investigated the torrefaction-based production of pellets from spruce stem wood, bark, and forest waste. Raw pellets had a significantly better capacity to be grounded after being torrefied. Less than half as much energy is needed to process torrefied pellets as it is to grind untreated pellets. Torrefaction severity increased, which enhanced the pellets' hydrophobicity. These pellets have a high resistance to water absorption and help in preserving their integrity followed by immersion testing. Phuang et al. (2021) studied the wet torrefaction of lignocellulosic biomass under different operating conditions, such as water-to-biomass ratio, and at different reaction temperatures. In comparison to the water-to-biomass ratio, temperature was known to exert a high influence on the fuel characteristics of biomass. Wet-torrefied biomass was known to possess improved properties over the raw biomass, including high heating values, less ash, and low moisture content.

Torrefaction of banana leaf waste was investigated by Alves et al. (2022). Torrefaction pre-treatment led to the drop in the weight of the raw biomass by 60 %, but the solid biofuel which was produced retained up to 77 % of the original biomass energy. In terms of combustion, ignition, and flammability indices, torrefaction was known to improve the performance of biomass combustion. The effects of torrefaction pre-treatment on the pyrolysis of Chlorella vulgaris biomass were studied by Gan et al. (2020). The emission of carbon monoxide in the pyrolysis gas was successfully eliminated by the wet torrefaction. The pre-treated algal biomass with dilute sulphuric acid during pyrolysis produced the largest amount of C-H. The pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis revealed the presence of fatty acids (48.22 %) which mainly reported the majority of the bio-oil produced from the algal biomass which had been processed with diluted sulfuric acid during wet torrefaction. In a fixed-bed tubular reactor, Phusunti et al. (2018) examined the torrefaction of Chlorella vulgaris at various temperatures, different time intervals, and at different atmospheric pressure. These findings indicate that in contrast to the torrefaction time and atmosphere, torrefaction temperature exerts a greater impact on mass yield and modifications in the characteristics of the algal biomass.

#### 5. Technical factors affecting thermochemical processes

Though thermochemical techniques such as pyrolysis, HTL, gasification etc. possess significant advantages but still there are several issues or factor like tar formation, catalyst deactivation, high moisture content, high Sulphur and nitrogen content, production separation and many more factor crucially effect thermochemical conversion process (Gururani et al., 2022). Tar production during pyrolysis or gasification can lead to blockage in lines and filters which leads to operational obstruction (Han and Kim, 2008). Similarly, the catalyst may get inactivated during pyrolysis and gasification due to production of fly ash which can block pores of the catalyst (Sadooghi and Rauch, 2013). Moreover, moisture content of biomass can also alter the characteristics of gas produced by gasification. High moisture content also leads to high energy consumption (Ferrasse et al., 2003). A moisture content of 30% or lower is recommended to reduce energy loss during gasification as a result of vaporisation and heating of water (Seggiani et al., 2012). On the other hand, high nitrogen and Sulphur content of biomass can lead to production of hydrogen sulphide, hydrogen cyanide and ammonia which act as secondary environment pollutants (Syed-Hassan et al., 2017).

Similarly, catalyst recovery is one of the crucial factors that affect HTL efficiency. Generally, catalysts are used during the HTL process to maximize bio-oil yield but their recovery from end product becomes quite challenging needing several expensive and energy driven techniques (Kumar et al., 2018). Furthermore, the reactor system used to carry out the HTL process is also one of the crucial factors affecting the process. During HTL corrosion can take place in reactor systems which require more resistant material for constructing reactors (Gururani et al., 2022). Operating conditions such as high temperature and pressure during HTL demands material from the reactor system which can sustain this challenging condition which can lead to increased capital cost (Gururani et al., 2022). In addition, separation after the HTL process utilises organic solvent for separating bio-oil from solid residues and liquid phase. Addition of organic solvent can increase the overall cost of the HTL process (Hu et al., 2021).

#### 6. By-products of thermochemical conversion

Thermochemical conversion processes involve the conversion of carbonaceous feedstocks into liquid or gaseous byproducts with the intention of producing more fuels, chemicals, power, or heat. There are several other thermochemical conversion techniques for biomass. Each offers a unique range of products and uses equipment setups which function in multiple modes. A number of factors, such as contact time, feed pre-treatment, catalysts, heating rate, moisture content of feed, type of feed, pressure, particle size of feed, reagents, and residence time, can affect the product quality in all the thermochemical processes (Mussatto et al., 2022; Bridgwater, 1994). Table 1 presents some common and important products of the thermo-chemical conversion of biomass.

#### Table. 1

Some important products via thermo-chemical conversion of biomass.

S. No.	Primary products	Applications	References
1.	Biochar	<ul> <li>Bio-char is used as a beneficial soil amendment.</li> <li>Water purification,</li> <li>Building materials,</li> <li>Composting,</li> <li>Carbon sequestration,</li> <li>Activated carbon, catalysts for anaerobic digestion</li> <li>Usage in agriculture and horticulture.</li> </ul>	(Brewer and Brown, 2012; Armah et al., 2022)
2.	Bio-oil	The bio-oil is derived from different biomass resources and consists of alcohols, acids, aldehydes, and lignin-derived compounds. When compared to diesel and petrol, bio-oil generates far lower levels of nitrous oxide and sulphur dioxide, earning it the label "clean fuel." To improve bio-oil for use as a liquid fuel for transportation and other uses, a variety of approaches have been employed.	(Guruviah et al., 2019)
3.	Syngas	Syngas is mostly used for producing methanol and diesel fuel. A great deal of waste gas with these properties is produced in several manufacturing processes. The process of gasifying biomass results in the production of syngas (synthesis gas), which is largely composed of CO, H <sub>2</sub> , and CH <sub>4</sub> .	(Capodaglio and Bolognesi, 2019)
4.	Heat	Energy is preserved in biomass. After burning, this energy is released as heat. Heating processes take advantage of the released heat.	(Perera et al., 2021; Vrabie, 2021; Yang et al., 2009)
5.	Chemicals and commercial grade fuels	Today's petroleum refineries can process bio-oils from waste or renewable biomass using new techniques to deliver commercial-grade fuels and some high-value compounds.	(Zhou and Hu, 2020; Mohan et al., 2006)
6.	Methanol	High pressures and low temperatures are advantageous for the production of methanol. Methanol is a secure fuel. The level of toxicity is comparable to that of gasoline. Additionally, if spilled, it degrades swiftly.	(Perera et al., 2021; Vrabie, 2021; Mussatto et al., 2022)

#### 7. Current studies, possibilities for the future, and challenges

Over the past few decades, there has been an enormous increase in the demand for energy due to the overpopulation, urbanisation, and industrialization. Currently, biomass serves as the world's primary source of bio-energy and is the most significant renewable energy source. Advanced conversion technologies must be carefully coordinated with biomass feed-stocks designed for the purpose in order to transform biomass into energy effectively. An increasingly feasible method for providing energy is the thermo-chemical conversion of naturally abundant waste biomass. In the last two years, some of the biomass, such as algal, wood, grass, cellulose, sugarcane, etc., have been successfully converted into various products (Table 2).

A feasible approach for completely transforming biomass into bio-

#### Table 2

Thermochemical processes used in the conversion of different waste biomass.

S. No.	Thermo- chemical process	Biomass	Products	References
1.	Pyrolysis	Algal	Volatile	(López-Aguilar
		-	compounds	et al., 2022)
2.	Pyrolysis	Algal	Biochar and bio-	(Chernova et al.,
			oil	2022)
3.	Pyrolysis	Wood	Bio-oil	(Wang and
		biomass		Brown, 2013)
4.	Pyrolysis	Sugarcane	Biochar and bio-	(Kumar et al.,
			oil	2022b)
5.	Combustion	Wheat straw	Heat	(El-Sayed et al.,
		biomass		2023)
6.	Combustion	Charcoal	Heat	(Otieno et al.,
				2022)
7.	Gasification	Wood	Syngas	(Boujjat et al.,
		biomass		2020)
8.	Gasification	Coconut shell	Producer gas	(Sivaraman et al.,
				2022)
9.	Gasification	Napier grass	Syngas	(Qatan et al.,
				2023)
10.	HTL	Wood bark	Bio crude oil	(Jokinen et al.,
				2023)
11.	HTL	Wood chips	5-hydroxymethyl	(Tumuluru et al.,
			furfural	2021)
12.	HTL	Cellulose	Advanced porous	(Kryeziu et al.,
			carbon	2022)
13.	Torrefaction	Wood	Gases	(Riaz et al.,
		biomass		2023)
14.	Torrefaction	Sesame stalks	Biochar	(Khairy et al.,
		and bean husk		2023)

energy and different bioproducts is to make use of biomass-derived bio-refineries. Nevertheless, the source, composition, and competence of the biomass feedstock have significant effects on the quality of the final product and the bio-processing techniques. In comparison to the other renewable energy sources, biomass is one of the largest and most common carbon sources used for producing renewable energy, fuels, and useful chemicals. Although there are still lots of challenges in commercialising thermo-chemical processes, also they have many other advantages, such as high efficiencies, a high rate of conversion, and the ability to produce a wide range of products (Asghar et al., 2022; Park et al., 2018; Ben and Ragauskas, 2017; Jha et al., 2022). Products obtained through these thermo-chemical conversions can be used as a sustainable bio-energy source, and aids in supplying the expanding energy demand in a variety of societal sectors. To make the technology profitable as well as socially acceptable, however, systematic research has to be conducted in a variety of areas, such as feedstock selection, pre-treatment, reactor design, optimisation of reaction parameters, separation of products, utilisation, and finally a business model (Kundu et al., 2018).

#### 8. Conclusions

This study reviews recent research and advances on production of valuable compounds using waste biomass as a substrate. On the basis of the above review, it is concluded that waste biomass cannot any more be seen as the culprit of environmental pollution but rather as a source of valuable intermediate products like biochar, bio-oil, heat, energy and syngas. Valorization of solid waste for production of valuable products puts forward an opportunity for the efficient utilization of unutilized resources and environmental trade-offs. Nonetheless, the implementation of emerging thermochemical conversion processes for converting waste biomass into valuable products holds a promising future for society globally. However, these thermochemical technologies are still in their research, development and prototyping phase. Moreover, the quality of the final product is influenced by a number of factors such as composition and source of biomass feedstock, type of thermochemical

process employed, processing cost and many more. Therefore, additional efforts are still demanded for enabling the large-scale commercialization of different thermochemical techniques thus facilitating appropriate conversion of biomass to intermediate products. In addition, there is a requirement of more technical routes for investigating the generation of highly valuable products from waste biomass feedstock.

#### **Ethics** approval

This article does not contain any studies with human participants or animals performed by the author.

#### Funding

This work receives no funding.

#### **CRediT** authorship contribution statement

Naveen Chandra Joshi: Conceptualization, Writing - original draft. Somva Sinha: Data curation, Writing - review & editing. Pooja Bhatnagar: Data curation, Writing – original draft. Yogesh Nath: Writing – review & editing. Bhavya Negi: Writing - review & editing. Vinod Kumar: Supervision, Data curation, Writing - review & editing. Prateek Gururani: Supervision, Data curation, Writing - review & editing.

#### Declaration of competing interest

The authors have no conflicts of interest to declare.

#### Data availability

All relevant data is included in the manuscript. Data will be made available on request.

#### Acknowledgement

We are thankful to the Division of Research and Innovation for their encouragement and support during the writing of the manuscript. Authors also want to thank Graphic Era (Demmed to be university) for their valuable support.

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