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Opportunities and Challenges in Thermochemical Conversion of Municipal Solid Waste: A Comprehensive Review

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Abstract

Recent advancements in thermochemical conversion processes have elucidated new pathways for converting municipal solid waste into valuable resources. This review explores the primary thermochemical conversion methods, including combustion, gasification, pyrolysis, torrefaction, hydrothermal carbonization, and hydrothermal liquefaction, emphasizing their potential roles in waste management and energy recovery. Key challenges including feedstock variability, ash behavior, and scale-up limitations are discussed alongside opportunities for hybrid systems and circular economy integration. A comparative analysis of research publications indicates a significant focus on thermochemical pathways within the broader context of municipal solid waste research, underscoring the growing interest in these technologies. Recent advancements in each thermochemical process, alongside their operational, technical, and economic challenges, are discussed. Comparative data reveal that torrefaction enhances the hydrophobicity and grindability of municipal solid waste components, though its energy densification benefits are more modest than those observed in biomass. Hydrothermal carbonization and liquefaction are highlighted for their ability to process high-moisture and heterogeneous waste streams. The review also synthesizes recent findings on reactor configurations, emissions control, and synergistic effects in co-processing municipal solid waste fractions. The findings underscore the importance of developing standardized protocols for municipal solid waste characterization and the need for innovative hybrid systems to improve efficiency.

Keywords: Municipal solid waste; Feedstock variability; Thermochemical conversion; Waste-to-energy; Waste management.

1 Introduction

Municipal Solid Waste (MSW) management has evolved into a formidable challenge in the contemporary urban landscape, driven by population growth, urbanization, and changing consumption patterns. According to the United States Environment Protection Agency (US EPA), 292.4 million tons of MSW had been generated globally in 2018 which equivalent to 4.9 pounds per person per day [1]. Out of 292.4 million tons, about 32.1% were recycled and composted, and 18.8% were combusted for energy recovery while the rest 50% were sent to landfill which releases up to 193 million metric tons of carbon dioxide equivalent ($MMTCO_2E$) greenhouse gas to the environment [1]. The escalating volumes of waste and resulting greenhouse gas emission necessitate innovative and sustainable waste-to-energy (WtE) solutions. As the world grapples with the pressing need to reduce reliance on finite fossil fuel resources and curb environmental degradation, the role of MSW in the energy matrix gains prominence. Thermochemical conversion processes, including pyrolysis, gasification, and combustion, have emerged as promising technologies capable of transforming MSW into energy and value-added products. This review examines the key thermochemical conversion pathways for MSW, with a focus on their potential for energy and chemical recovery.

In recent years, the acceleration of research and technological developments in thermochemical conversion has opened up new avenues for turning waste into a valuable resource. From producing syngas for electricity generation to yielding biochar for soil improvement, thermochemical conversion technologies hold the potential to redefine the utilization of MSW. However, the journey from theoretical promise to practical implementation is fraught with challenges, ranging from feedstock variability to stringent environmental regulations. Figure 1 presents a comparative analysis of the total number of research publications related to MSW and those specifically

addressing thermochemical conversion of MSW. The data indicates that, proportionally, a significant part of MSW-related research is concentrated on thermochemical pathways, suggesting a growing interest in these technologies for waste valorization.

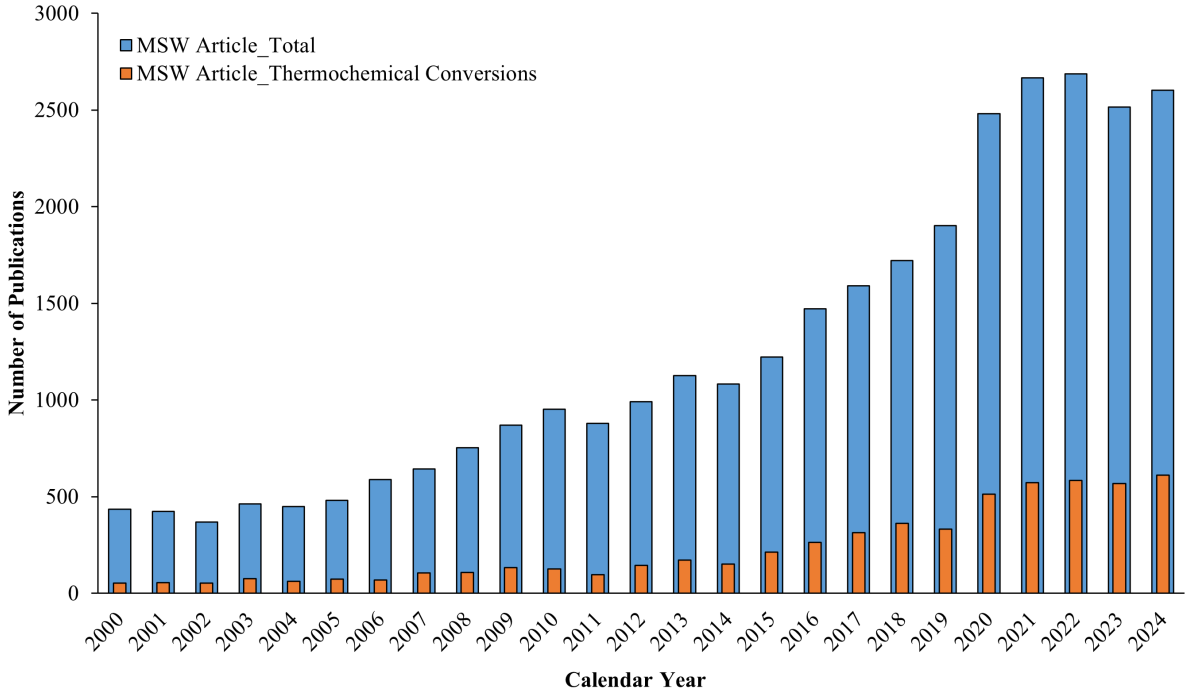

Figure 1: Publications on MSW and thermochemical conversions of MSW since 2000. The "Web of Science" platform was used to compile this list. The key words, such as torrefaction, pyrolysis, gasification, combustion, hydrothermal carbonization and hydrothermal liquefaction were used for the thermochemical conversion related publications.

While numerous review articles have examined individual thermochemical pathways such as pyrolysis or gasification, a comprehensive synthesis that integrates both dry and wet thermochemical processes for MSW remains limited. Existing reviews often focus on specific technologies or narrowly defined feedstocks, without addressing the interplay between feedstock variability, preprocessing requirements, and hybrid system design. This review distinguishes itself by (i) systematically comparing dry and wet thermochemical pathways under a unified framework, (ii) emphasizing the role of MSW heterogeneity on process performance, and (iii) identifying opportunities for integrating multiple conversion technologies to enhance efficiency and

circularity. It evaluates the technical and operational challenges that hinder the widespread implementation of these technologies within waste-to-energy and waste-to-chemicals systems. The analysis includes recent technological developments, environmental impacts, and relevant economic and policy considerations. In the context of global efforts to achieve sustainability targets, the assessment of thermochemical strategies for MSW treatment is increasingly relevant. The following sections provide a detailed evaluation of the major thermochemical conversion technologies, identify key opportunities and limitations, and outline the regulatory and societal factors that influence their adoption. This review aims to offer a structured and evidence-based reference for researchers, policymakers, and industry professionals engaged in advancing thermochemical solutions for MSW valorization.

2 Thermochemical conversion of MSW: opportunities and challenges

Thermochemical conversion technologies encompass a diverse array of processes designed to extract energy and produce chemicals from MSW. Generally, thermochemical conversions can be categorized into two types: (i) dry conversions (*e.g.,* combustion, gasification, pyrolysis, torrefaction) and (ii) wet conversions (*e.g.,* hydrothermal carbonization and liquefaction). Figure 2 illustrates the major differences among various thermochemical conversion processes regarding operating conditions and conversion products. Although thermochemical processes such as pyrolysis are often categorized based on dominant products (*e.g.,* carbonization vs. liquefaction), hydrothermal processes are treated separately in this review due to their fundamentally different reaction media and mechanisms. Hydrothermal carbonization and liquefaction occur in aqueous environments under subcritical conditions, leading to distinct reaction pathways compared to dry pyrolysis. Furthermore, hydrothermal carbonization predominantly yields solid hydrochar, whereas hydrothermal liquefaction targets liquid biocrude production. This distinction is

particularly important for MSW, where high moisture content favors hydrothermal routes over conventional pyrolysis classifications.

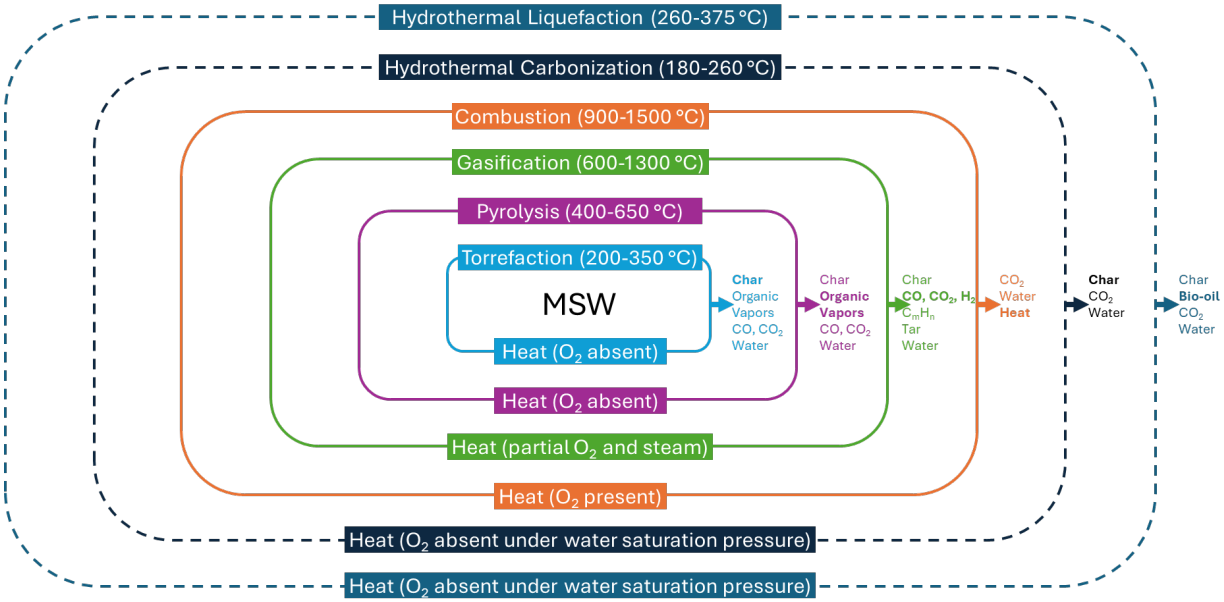

Figure 2: Comparison of various thermochemical conversions with potential projects. The products mentioned in bold characters are the major products(s) from that specific process. The dashed line indicates the wet process while solid lines represent dry processes (figure modified from Matsakas, et al. [2]).

2.1 Characteristics of MSW

MSW is a highly heterogeneous and complex feedstock composed of a wide range of organic and inorganic materials, including food waste, paper, plastics, yard waste, textiles, metals, glass, and inert residues [3]. The composition of MSW varies significantly depending on geographical location, socioeconomic conditions, seasonal variations, and waste management practices, making it inherently difficult to characterize and process consistently[3-7]. This variability directly impacts the performance, efficiency, and product distribution of thermochemical conversion technologies. Therefore, robust feedstock characterization and preprocessing strategies are essential to ensure consistent process performance.

The physical composition of MSW typically includes a large fraction of biodegradable materials (*e.g.,* food and yard waste), along with recyclable components such as paper and plastics, and non-

combustible materials such as metals and glass. Studies have shown that organic fractions can account for 30-60 wt% of MSW, while plastics and paper contribute significantly to the energy content due to their higher carbon and hydrogen content[3, 4, 8]. The ultimate analysis of MSW generally indicates carbon contents of 30-45 wt%, hydrogen 4-7 wt%, and oxygen 25-40 wt%, reflecting its partially biogenic nature [4, 8]. Nitrogen and sulfur contents are typically low (<1 wt%), although they can vary depending on waste composition and influence emissions such as NO_x and SO_x during thermochemical processing [9, 10].

Moisture content is one of the most critical parameters influencing MSW conversion. Depending on the fraction of food and organic waste, moisture content can range from 20 to 60 wt% [6]. High moisture content reduces the effective heating value and increases the energy required for drying, thereby negatively affecting the efficiency of dry thermochemical processes such as combustion, gasification, and pyrolysis. In contrast, wet thermochemical processes such as hydrothermal carbonization and liquefaction are better suited for high-moisture feedstocks, as they utilize water as a reaction medium.

The higher heating value (HHV) of MSW typically ranges from 6 to 20 MJ/kg, depending on the relative proportions of combustible and non-combustible components [11]. Plastic-rich fractions tend to exhibit higher HHVs due to their elevated carbon and hydrogen content, whereas food waste and other oxygen-rich materials generally lower the overall energy density.

Ash content in MSW varies widely (typically 5-50 wt%) and is strongly influenced by the presence of inorganic materials such as dirt, metals, glass, and mineral residues [3, 12]. The inorganic fraction contains elements such as sodium, potassium, calcium, silicon, chlorine, and trace heavy metals, which play a critical role in thermochemical processes. For example, alkali and alkaline earth metals can promote slagging, fouling, and bed agglomeration in gasification and combustion

systems, while chlorine can lead to corrosion and the formation of hazardous compounds such as HCl and dioxins [13-15]. The presence of heavy metals also raises environmental concerns related to ash disposal and leachability, necessitating careful management and potential stabilization treatments [16, 17].

The physicochemical characteristics of MSW strongly influence the selection and performance of thermochemical conversion technologies. Dry processes such as combustion, gasification, and pyrolysis require relatively low moisture content and benefit from higher energy density feedstocks. In contrast, wet processes such as hydrothermal carbonization and liquefaction are more suitable for high-moisture, organic-rich waste streams. Additionally, the heterogeneous nature of MSW necessitates preprocessing steps such as sorting, size reduction, drying, and blending to improve feedstock uniformity and enhance conversion efficiency [18, 19]. Thermal pretreatment methods such as torrefaction and hydrothermal processing can further modify feedstock properties, improving grindability, energy density, and reactivity [20, 21].

Overall, a comprehensive understanding of MSW characteristics is essential for designing efficient and reliable thermochemical conversion systems. The following sections will elaborate on the various thermochemical conversions of MSW.

2.2 Dry processes

2.2.1 Combustion

Combustion, the most traditional form of WtE conversion, involves the direct burning of MSW to generate heat and subsequently produce steam for electricity generation through turbines. It remains the most established thermochemical conversion pathway for MSW worldwide, particularly in urban areas where land is limited and waste volumes are high. The process not only reduces the waste by mass about 70-80% and volume up to 90% but also generates useful energy

in the form of electricity and heat [22]. In modern WtE facilities, MSW is typically burned in large-scale grate furnaces, which can handle heterogeneous feedstocks with little preprocessing [23]. This robustness has contributed to the widespread deployment of incineration plants in Europe, Japan, and parts of China [24].

For most of these facilities, the most important parameter for energy generation is the heating value or energy density in the feedstock, which is largely dictated by the proportions of combustible and non-combustible mass. Figure 3 illustrates an inverse relationship between ash content and HHV, demonstrating why they are critically linked. Higher heating values reported in these studies range from 6.3 to 19.1 MJ/kg [11]. Volatile matter content in MSW is also consistently high, typically exceeding 59%, which supports rapid ignition and stable flame propagation [8]. Fixed carbon values vary between 15% and 20%, providing sufficient energy density to sustain combustion across staged chambers [12]. The ultimate analysis shows that carbon content generally falls between 36% and 41%, hydrogen between 4.9% and 6.1%, and oxygen between 32% and 34%, highlighting the semi-biogenic composition of MSW that includes food waste, paper, yard debris, and plastics [25]. Nitrogen and sulfur contents remain relatively low, around 1.0% and below 0.5%, respectively, which is advantageous in mitigating NO_x and SO_x formation during combustion [9]. Furthermore, seasonal variations in MSW composition have been shown to alter proximate and ultimate analysis results, with food waste-rich streams yielding higher oxygen content and lower HHVs, while plastic-rich fractions provide increased carbon and hydrogen contents that improve energy recovery potential [6]. Comparative analyses have also highlighted that the biogenic fraction of MSW contributes positively to renewable energy credits, making combustion performance data critical for life-cycle assessment (LCA) of WtE systems [26, 27]. These values indicate that MSW, although less energy-dense than fossil fuels, is a viable feedstock

for heat and power generation when processed in optimized incineration systems. Other studies have also emphasized that trace elements such as chlorine, potassium, and sodium, present in varying amounts depending on regional waste composition, can influence slagging, fouling, and corrosion tendencies in combustion systems [13, 14]. In addition, chlorine contents exceeding 0.3% have been correlated with enhanced formation of HCl and dioxins, which require additional flue gas treatment steps [15].

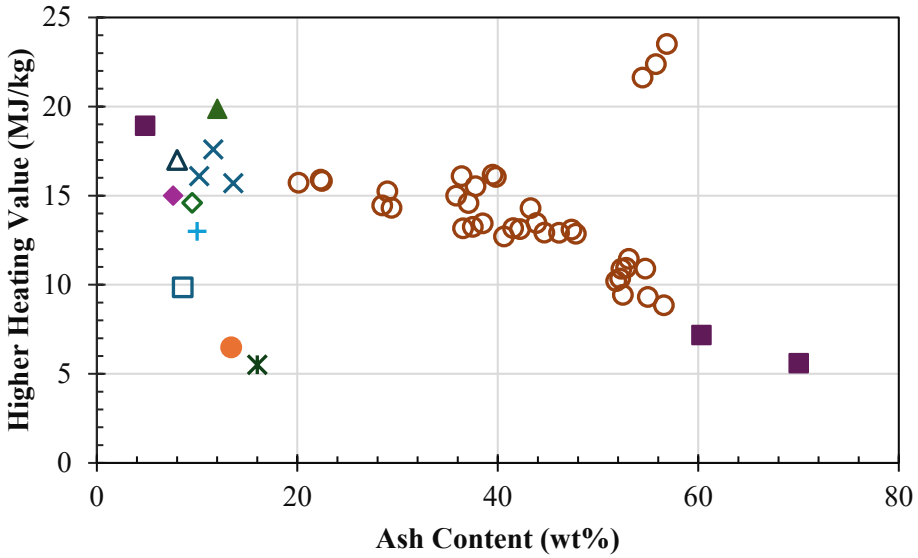

Figure 3: The relationship between ash content and higher heating value is illustrated using data compiled from multiple literature sources [11, 12, 25, 28-34], with distinct markers denoting individual data sets from each reference.

Although technologies have been created and adapted to accommodate the heterogeneous nature of MSW for combustion, most facilities are unique and inefficient due to the need to accommodate a wide range of fuel properties, slagging and fouling discussed above, and overall thermal inertia and energy transients in the plant [35]. These factors generally lead to a maximum thermal efficiency of 65-70% even in ideal operation [35]. As a result of this, a significant portion of active work in literature focuses on multi-phase modeling of combustion processes, particularly for grate-fired and fluidized bed incinerators [36-44]. These studies use computational fluid dynamics

(CFD) simulations to model airflow, volatile release, char oxidation, and temperature profiles to better understand, design, and optimize these combustion processes. Research by Wang *et al.* [45] demonstrated how integrating radiative heat transfer models into CFD platforms can better predict flame propagation and help redesign combustion chambers for temperature field flux influenced by gas radiation. Similar efforts by McPhali *et al.* [46] aim to incorporate feedstock-specific data, including proximate and ultimate analysis, into Aspen plus combustion models that calculate and respond to changes in feedstock properties. Emerging studies are also exploring the co-combustion of MSW with engineering fuels, such as hydrochar, biochar, coal, and refuse-derived fuel (RDF) [47-50]. These co-firing strategies are being tested to address combustion inefficiencies associated with low calorific value or high ash content in raw MSW. For instance, co-combustion with hydrothermally treated MSW and coal has shown promising results decreasing polycyclic aromatic hydrocarbons emissions compared to non-hydrothermally treated MSW as shown in work by Peng *et al.* [48]. Additionally, the co-incineration of plastic-rich fractions is being actively studied for both its energy contribution and its impact on synergy and ash residues [51]. Recent advancements in process control and combustion efficiency have been achieved through the application of numerical modeling and real-time control systems. Wu *et al.* [52] provide an in-depth analysis of combustion simulation techniques, revealing how CFD models are used to optimize furnace geometry, residence time, and air staging. These models allow plant operators to anticipate flame instability, slagging, or incomplete combustion based on feedstock variability and adjust air distribution accordingly [53]. In addition to conventional modeling approaches, Recent studies have demonstrated the effectiveness of machine learning approaches for real-time prediction and control of emissions in MSW combustion systems. For example, deep learning models such as long short-term memory (LSTM) and hybrid neural networks have been successfully applied to

predict dioxin formation and NO_x emissions with high accuracy, enabling improved process control under variable operating conditions [54, 55]. In addition, data-driven optimization frameworks have shown the ability to adjust air distribution and key operating parameters dynamically, resulting in enhanced combustion efficiency and reduced pollutant formation [56]. The integration of machine learning with combustion diagnostics further allows adaptive control systems to maintain optimal combustion temperatures and reduce harmful emissions under varying load conditions [56].

Another growing area of research is focused on combustion by-products, particularly bottom ash and fly ash. The bottom ash produced from MSW combustion typically represents about 20% of the input waste by mass and contains a mixture of glass, metals, ceramics, and mineral ash [57]. Depending on its composition, this ash can be used in construction applications such as road base materials or concrete additives, provided it meets leachability and toxicity criteria [16]. Fly ash, however, often contains higher concentrations of heavy metals and dioxins and is usually treated as hazardous waste [42]. Li *et al.* [58] have explored methods to stabilize or vitrify fly ash to make it safe for landfilling or recycling, including melting or sintering techniques that immobilize toxic species. From a circular economy perspective, incineration has traditionally been criticized for its "end-of-pipe" approach that seemingly conflicts with principles of material recovery. However, recent strategies aim to integrate incineration into resource recovery loops. For example, metals such as aluminum and iron are increasingly recovered from bottom ash via mechanical separation [59]. Additionally, flue gas condensation systems enable heat recovery for district heating, improving overall plant energy efficiency [60]. There is also growing interest in recovering phosphorus and other critical materials from MSW combustion residues, especially as global demand for fertilizers increases [61]. Studies now emphasize not only reducing their volume and

toxicity but also valorizing them as secondary resources [62-64]. Researchers are using analytical techniques such as X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and leaching tests to assess the suitability of ash for use in concrete, road base materials, or as sources of critical elements such as zinc, aluminum, or rare earth metals [17, 63]. Recent investigations are also evaluating ash aging and weathering behavior, recognizing that long-term exposure to atmospheric CO_2 or water can alter ash mineralogy and leachability [17]. In parallel, studies are optimizing vitrification and carbonation processes to stabilize hazardous fly ash and enhance its environmental compatibility [65].

A critical research area in MSW combustion is emissions control. Modern incineration plants must comply with stringent environmental regulations regarding the release of NO_x, SO_x, dioxins, furans, and heavy metals [66]. Emission formation depends heavily on combustion temperature, oxygen availability, and residence time [67]. For instance, excessive temperature spikes or poor mixing can lead to incomplete combustion and formation of dioxins [68]. To counter this, many facilities employ selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) systems for NO_x control, coupled with activated carbon injection and high-efficiency particulate arresters (HEPA filters) to trap heavy metals and acid gases [69]. The development of smart incinerators using sensor arrays and machine learning algorithms is gaining traction for regulatory compliance and safe facility operation. These systems continuously monitor temperature, oxygen levels, and flue gas composition to adjust fuel feeding rates and airflow in real time [70]. Rahat *et al.* [70] have demonstrated that data-driven multi-objective combustion management systems can significantly reduce NO_x emissions while improving boiler efficiency. Integrating such systems can enable emissions traceability and regulatory compliance, as demonstrated in emerging pilot projects across East Asia and the European Union [71, 72].

Oxy-fuel combustion has emerged as a promising enhancement to conventional incineration, particularly in the context of carbon neutrality goals. In oxy-combustion, oxygen replaces air as the oxidizer, producing flue gas stream composed primarily of CO_2 and water vapor, which is conducive to post-combustion carbon capture [73]. Becidan *et al.* [74] demonstrated that oxy-fuel combustion of MSW does not significantly compromise combustion efficiency and can be integrated into BECCS (bioenergy with carbon capture and storage) systems. This has important implications for MSW management, especially given that over 50% of typical MSW is biogenic in origin, enabling negative carbon emissions [75].

Public perception and policy also play a significant role in the development and deployment of MSW combustion technologies. In many regions, incineration faces public resistance due to concerns over health risks and emissions, even though modern plants operate well within regulatory limits [76]. Transparent monitoring, community engagement, and investment in state-of-the-art emissions control technologies are essential to overcoming these barriers. Policy developments such as carbon pricing, renewable energy incentives, and landfill taxes can help level the playing field between incineration and other waste treatment options.

2.2.2 Gasification

Gasification is a thermochemical process that transforms carbonaceous materials into a syngas (synthesis gas) consisting of CO, H_2, and CH_4 along with other low-molecular-weight hydrocarbons. The products may also contain several undesired components such as particulate matter, tar, alkali metals, chlorine, and sulfide depending on the feedstock quality [77]. The process occurs at high temperatures, typically exceeding 700 °C, and involves a controlled reaction with a limited oxygen supply.

Fixed bed gasifiers, including updraft and downdraft configurations, are among the earliest gasification systems adapted for MSW. These systems are characterized by a relatively simple design and operation, making them suitable for small-scale or decentralized applications. However, they are limited by feedstock heterogeneity and are prone to tar formation, particularly in updraft systems. Downdraft gasifiers, while producing cleaner syngas, require more uniform feedstock and are sensitive to moisture content, which is a common challenge with MSW. On the other hand, fluidized bed gasifiers, both bubbling and circulating types, offer improved feedstock flexibility and better temperature uniformity due to enhanced mixing. These systems are well-suited for MSW, which is often heterogeneous and contains varying moisture levels. Fluidized beds can accommodate a wide range of particle sizes and compositions, making them attractive for large-scale WtE applications.

Entrained flow gasifier, traditionally used for coal, operates at higher temperatures (1200-1600 °C) and require finely pulverized feedstock. Using MSW in entrained flow gasifiers is gaining interest due to their high carbon conversion efficiency and low tar output. However, even after extensive pre-treatment, the MSW may not meet the quality to feed into the entrained flow gasifier. In recent years, plasma gasification showed the capability of handling highly heterogeneous and hazardous MSW streams. By generating extremely high temperatures (>3000 °C) using plasma torches, this technology ensures complete breakdown of organic matter and vitrification of inorganic residues [78]. Recent reviews have highlighted advancements in plasma torch design, reactor configurations, and system integration, leading to improved process efficiency and syngas production [79, 80]. In addition, plasma-assisted reforming has been shown to effectively reduce tar formation through the generation of reactive species such as OH and O radicals, enhancing syngas cleanliness and downstream usability [81]. Modeling and experimental studies further

demonstrate that plasma gasification can achieve high syngas yields and improved carbon conversion efficiency through optimization of operating parameters and gasifying agents [82]. Despite these advantages, challenges related to high energy demand, capital cost, and system scalability remain key barriers to widespread commercialization [78].

Different components of MSW, including organic materials like food waste, and inorganic materials such as plastics and metals, possess unique gasification characteristics. For instance, Xiao *et al.* [83] reported that biomass components, such as paper and wood, yield high quality syngas due to their favorable chemical structures for gasification. In contrast, materials like waste plastics offer higher gas yields due to their high carbon and hydrogen content, but the resulting syngas can be of lower quality if contaminants from additives or incomplete conversion are present. Kitchen waste, often rich in moisture and organic content, typically exhibits the lowest gasification performance, resulting in lower syngas yields and heating values. This variability necessitates tailored gasification strategies to optimize syngas production based on the specific composition of the waste being processed. Gasification temperature is a critical factor affecting syngas composition and yield. As the temperature increases, it promotes several key reactions that enhance gas production, including the Boudouard reaction, steam methane reforming, and the water-gas shift reaction [84]. For instance, studies have shown that raising the temperature from 700 °C to 900 °C can significantly increase the production of H_2 and CO [85]. Higher gasification temperatures facilitate the breakdown of complex organic molecules and promote secondary reactions that yield more valuable gas products. However, temperatures exceeding 900 °C can lead to a decrease in H_2 production due to competing reactions that favor CO formation, highlighting the delicate balance required in gasification temperature management [84]. The choice of gasification medium, such as air, steam, or CO_2 plays a significant role in determining the quality

and composition of the produced syngas [86]. Air gasification typically leads to lower heating values (LHV) of syngas in the range of 4 to 7 MJ/m³, primarily due to the dilution effect of nitrogen present in the air [87, 88]. Conversely, steam gasification tends to yield hydrogen-rich syngas, achieving syngas LHVs between 8 and 12 MJ/m³ [89]. The steam-to-MSW ratio is crucial, as optimal ratios enhance syngas production by promoting steam reforming reactions. Research suggests that an increase in steam-to-MSW ratio correlates with higher concentrations of H_2 and CO, while excessive steam can inadvertently lower system temperatures and reduce overall gasification efficiency. Studies have also shown that the addition of steam can improve carbon conversion efficiency by facilitating the reactions necessary for syngas production [90].

The oxidant-to-MSW ratio is identified a key parameter in gasification that influences the partial combustion of waste and the resulting syngas composition [91-93]. An optimal oxidant-to-MSW ratio typically falls within the range of 0.1 to 0.4 for air gasification, balancing the combustion and gasification reactions to maximize syngas yield while minimizing the production of unwanted by-products [84]. Studies indicate that maintaining an optimal oxidant-to-MSW ratio can enhance the overall carbon conversion efficiency [91]. However, as the oxidant ratio increases, it can lead to a rise in combustion reactions at the expense of syngas quality, necessitating careful monitoring and adjustment of the oxidant-to-MSW ratio to ensure efficient gasification. Zheng *et al.* [91] reported that maintaining a carbon dioxide-to-MSW ratio around 0.83 during CO_2 gasification improve syngas yield by promoting the thermal cracking of char, thereby increasing the overall efficiency of the gasification process.

In addition to temperature and oxidant ratios, reactor configuration exerts a strong influence on tar levels, carbon conversion, and syngas quality. Fixed-bed (updraft/downdraft) systems are mechanically simple and suited for smaller scales but can exhibit higher tar unless operated at

364 elevated temperatures or with downstream cracking [94-97]. Bubbling and circulating fluidized
365 beds provide superior mixing and heat transfer, enabling more uniform temperatures, lower tar,
366 and higher cold gas efficiency across heterogenous MSW feeds [98, 99]. Entrained flow gasifiers
367 including plasma-assisted designs can achieve very low tar and high carbon conversion at ≥1200
368 °C with fine feed sizes, at the expense of higher O_2 or energy demand and tighter feed preparation
369 requirements [100-102]. Catalytic and sorbent-assisted routes are increasingly reported to suppress
370 tar and tune syngas properties. Natural olivine and calcined dolomite crack tars and capture alkali
371 or chlorine species, while Ni-based catalysts often supported on Al_2O_3, $MgAl_2O_4$, or CeO_2-ZrO_2
372 drive steam and shift reactions to elevate H_2 yield. Deactivation via sulfur/chlorine/alkali
373 poisoning can be mitigated using guard beds or periodic regeneration [103-106]. Active-bed
374 additives such as CaO can capture CO_2 in sorption-enhanced gasification, increasing apparent H_2
375 concentration and improving cold gas efficiency under steam-rich conditions [107].

376 Table 1 demonstrates the combined influence of feedstock composition and gasifier configuration
377 on syngas quality, tar formation, and solid residue yields in MSW gasification. Updraft fixed-bed
378 gasifiers operating at 800 °C with plastic packaging mixture (PPM), solid recovered fuel (SRF),
379 and waste fraction after drum separator sorting (FDS) MSW streams produce comparable specific
380 syngas yields; however, they exhibit lower H_2/CO ratios and tar yields that vary with feedstock
381 characteristics. Notably, FDS generates more char due to its higher ash and fines content. In
382 contrast, downdraft gasifiers operated at 1000 °C with engineered blend pellets of paper-mill
383 rejects sourced from two different mills, such as newsprint mill (AN) and brown paper mill (SSK),
384 along with de-inking sludge, and wood chips showed higher gas yield, elevated H_2/CO ratios, and
385 reduced tar content, underscoring the advantages of fiber-rich MSW streams. Plasma moving-bed
386 and bubbling fluidized-bed systems treating unsorted MSW further illustrate that increased

operating temperatures and enhanced mixing intensities can elevate the H_2/CO ratio, even though at the expense of higher energy input and, in some cases, increased char production. These observations reinforce the conclusion that both feedstock fractionation and reactor design must be co-optimized to achieve desired syngas quality and minimize undesirable by-products. This aligns with findings from Gao et al. [108], who emphasize that feedstock properties (e.g., ash and volatile content), gasifier type, and operating conditions (temperature, equivalence ratio) collectively determine syngas composition and conversion efficiency in biomass and MSW gasification systems.

Table 1: An overview of MSW gasification in various gasifiers. NR indicates "not reported" in the literature.

Gasifier type	Operating temperature (°C)	Feedstock	Equivalence ratio	Product (wt%)			Syngas quality (H_2/CO)	Ref.
				Gas	Tar	Char		
Fixed-bed updraft	800	PPM	0.15	94.48	2.76	2.76	1.32	[96]
			0.21	95.81	1.86	2.33	1.02	
		SRF	0.15	86.25	3.50	10.25	0.49	
			0.21	88.87	2.83	8.30	0.56	
		FDS	0.15	73.17	1.61	25.23	0.55	
			0.21	81.97	1.08	16.96	0.50	
Fixed-bed downdraft	853	Refuse-derived fuel	0.30	NR	NR	NR	0.92	[109]
	918	MSW	0.40	NR	NR	NR	0.57	[110]
	1090	Mixed MSW	0.35	NR	NR	NR	1.11	[111]
Fixed-bed downdraft	1000	20% AN reject pellets, 80% wood chips	0.36	98.72	0.43	0.85	0.66	[112]
		10% AN reject pellets, 10% de-inking sludge, 80% wood chips	0.53	97.82	0.22	1.96	0.59	
		15% AN reject pellets, 20% de-inking sludge, 65% wood chips	0.36	96.01	0.50	3.49	0.61	
		10% AN reject pellets, 40% de-inking sludge, 50% wood chips	0.27	89.25	0.19	10.56	0.53	
		20% SSK reject pellets, 80% wood chips	0.28	98.98	0.25	0.76	0.58	
		50% SSK reject pellets, 50% wood chips	0.24	98.27	0.10	1.63	0.51	
		70% SSK reject pellets, 30% wood chips	0.34	97.90	0.56	1.55	0.68	
		80% SSK reject pellets, 20% wood chips	0.22	96.50	0.64	2.86	0.70	
Plasma moving-bed updraft	1000-1200	MSW+plastics	NR	~85	<1.0	~10-15	1.0-1.2	[78]
Bubbling fluidized bed	400-700	Mixed MSW	0.25-0.35	80-90	2-5	5-15	1.78 (steam), 0.64 (CO_2)	[113]
Entrained flow	1200-1500	MSW, refuse-derived fuel	0.25-0.35	>90.0	<1.0	<5.0	1.0-1.5	[84]

Despite these advancements, challenges remain in managing ash chemistry, mitigating corrosion and fouling, and ensuring consistent syngas quality from variable MSW feedstocks. For example, moisture contents greater than 25-30 wt% typically depress reactor temperature, raising tar formation, and decreasing H_2/CO production. Hence, feedstock pre-conditioning plays a significant role in gasification operability. Drying or mild torrefaction 200-300 ℃ can remedy this while also improving grindability, reducing O/C ratio, and stabilizes feed quality [18, 114]. In addition, mechanical preprocessing focusing on size classification and removal of inert or metals enhances gasifier throughput and reduces bed agglomeration risks in fluidized beds [19]. Beyond air or steam, CO_2 as a gasifying agent, dry reforming, or Boudouard pathways can upgrade plastic-rich fractions, while co-gasification with biomass, sewage sludge, or paper rejects can balance H/C ratios and ash behavior. Several studies show synergistic effects that reduce tar and raise H_2/CO at optimized blend ratios [115-118]. Pressure up to 30-60 bars can facilitate downstream synthesis of methanol, though it may increase methane formation and impose stricter tar control because it can foul the equipment and poison the catalyst [119, 120]. Ash chemistry such as alkali, chlorine, silica, and metals governs slagging, fouling, and bed agglomeration. High K/Na with silica can form low-melting silicates, with mitigation strategies including bed material selection (i.e., bauxite, olivine), temperature windows avoiding sticky phases, and upstream removal of fines and glassy fractions [121-123]. In chlorine-bearing MSW, volatilization of alkali chlorides contributes to corrosion and particulate emissions; sorbents such as kaolin and limestone optimize quench and cleanup to reduce these risks [124].

Tar formation remains a significant challenge, potentially leading to blocking, fouling, and corrosion [2]. Various methods exist for tar removal, including physical processes like filters, scrubbers, and wet electrostatic precipitators, and chemical processes such as thermal and catalytic

cracking. Hu *et al.* [108] found that tar can be completely decomposed at elevated temperatures of 950 °C. Recent advancements in steam gasification show promise for high hydrogen yield with reduced tar formation. He *et al.* [109] observed that steam gasification at 850-950 °C in the presence of a calcined dolomite catalyst can completely decompose tar. Different gasifier types also influence tar formation, with entrained flow gasifiers demonstrating reduced tar production due to their higher operating temperatures compared to fluidized bed and fixed bed gasifiers [110-112]. However, feeding non-traditional feedstocks into entrained flow gasifiers presents its own set of challenges.

The advantages of MSW gasification over combustion include the potential to produce syngas, which can be utilized in conventional burners. However, syngas may contain particulate matter, acid gases, and organic pollutants due to the heterogeneous and contaminated nature of MSW (*e.g.,* halogenated plastics, glass, dirt). The costs associated with cleaning gasification-derived syngas may exceed those of incineration, which limits the commercial availability of MSW gasification plants in the United States [104]. Additionally, the composition variability of MSW, which can differ regionally and seasonally, impacts both the gasification efficiency and syngas quality [105]. Robust pre-treatment processes, including mechanical sorting, shredding, and blending, can enhance feedstock homogeneity, thereby improving gasification efficiency. Effective emission control technologies, such as electrostatic precipitators and scrubbers, are crucial for capturing harmful pollutants like particulate matter, dioxins, and heavy metal.

Integrating gasification with advanced cleanup systems and downstream synthesis processes underscores its potential in circular economy frameworks, but economic and scale-up hurdles persist. Recent advancements in gasification have incorporated machine learning and data-driven techniques to optimize process parameters, predict syngas composition, and manage operational

variability associated with heterogeneous MSW feedstocks [56, 108]. These tools facilitate improved control over key variables such as temperature, equivalence ratio, and gasifying agent selection, leading to enhanced syngas quality and overall process efficiency [90, 108]. The adoption of such digital optimization strategies represents a growing trend toward more intelligent and adaptive thermochemical conversion systems. Ongoing research into co-gasification strategies, pressure effects, and digital optimization tools (*e.g.,* CFD, machine learning) will be essential for improving efficiency and enabling broader deployment of MSW gasification as a sustainable WtE technology.

2.2.3 Pyrolysis

Pyrolysis involves the thermal decomposition of organic materials in the absence of oxygen, resulting in the production of three primary products, such as char, liquid bio-oil, and gases. The process operates at moderate temperatures, typically between 400 and 800 °C, promoting the breakdown of complex polymers into simpler, energy-rich compounds.

Lu *et al.* [125] recently compiled many literature sources concerning slow pyrolysis of MSW [126-133]. Their review looked at pyrolysis of many feedstock including plastics (Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyethylene terephthalate (PET)), paper and cardboard (office paper, newspaper, corrugated cardboard, mixed paper products), wood and woody biomass (woodchips, sawdust, branches and twigs, forestry residues), food and organic wastes (food scraps, vegetable peels, fruit waste, expired food products), yard and green waste (grass clippings, leaves, tree trimmings, garden waste), agricultural residues (straw, corn stover, rice husks, wheat husks), mixed MSW (household waste (after sorting and pre-treatment), municipal solid waste streams, mixed recyclables), and specialty organic wastes (rubber (*e.g.,* tires), textile waste (natural fibers), sewage sludge, industrial organic waste (*e.g.,* food processing waste)). While each feedstock/study

has unique and valuable findings, these diversity of feed materials used in MSW pyrolysis can be grouped into several categories based on common compositions, yield patterns, waste quality improvements, and beneficial end uses. High carbon content feed materials like plastics and rubber, along with high cellulosic content materials such as paper, cardboard, and woody biomass, exhibit similar compositions, leading to high yields of bio-oil and syngas. On the other hand, organic-rich materials such as food waste, yard waste, and green waste typically produce substantial amounts of biochar, which can be used for soil amendment and carbon sequestration. Mixed organic and inorganic content feeds like municipal sludge and industrial organic waste, after sorting and contaminant removal, provide a balanced yield and contribute to waste volume reduction and material recycling. Homogenized and dried waste streams such as shredded mixed MSW, dried food waste, and dried yard waste are often pre-treated to achieve uniformity and moisture reduction, enhancing pyrolysis efficiency. These feed materials, along with sorted plastics and paper, tend to produce balanced yields of bio-oil, syngas, and biochar, making them versatile for energy production, chemical feedstocks, and waste minimization.

Different feed materials for MSW pyrolysis can be grouped based on their compositional makeup, such as carbon, hydrogen, and oxygen content, carbohydrate concertation, etc. to reflect feedstock quality similarities. These similarities influence the pyrolysis process and the types of products generated. High carbon content materials include plastics like PE and PP, rubber (*e.g.,* tires), and coal-derived products. Feed materials with high cellulosic content encompass paper and cardboard, wood and woody biomass such as wood chips and sawdust, and agricultural residues like straw and husks. High moisture and organic content feed materials are typically food waste, yard waste including grass clippings and leaves, and green waste such as vegetable scraps and garden waste. Mixed organic and inorganic content materials include mixed MSW after sorting, municipal

sludge, and industrial organic waste. High lignin content materials consist of woody biomass like wood chips and branches, agricultural residues with high lignin content such as corn stover and rice husks, as well as bark and forestry residues.

Though yields can vary depending on specific feed characteristics and pyrolysis conditions like temperature and residence time, feedstock qualities often lead to similar pyrolysis yield patterns of products (bio-oil, syngas, and biochar) derived from pyrolysis. For instance, feed materials that typically produce high bio-oil (liquid) yields include plastics such as PE and PP, rubber materials like tires, and certain types of biomass such as wood chips and sawdust. Materials that yield a high amount of syngas include mixed MSW with a high proportion of organic waste, food waste, and agricultural residues like corn stover and rice husks. High biochar yields are commonly associated with woody biomass such as wood chips and branches, agricultural residues like straw and husks, and yard waste including leaves and grass clippings, derived from higher fixed carbon contents. Some feed materials produce a balanced yield of bio-oil, syngas, and biochar, such as mixed organic waste, paper and cardboard, and certain combinations of plastics and organic materials.

The diverse material fractions in MSW lead to a variety of beneficial uses for MSW pyrolysis, optimizing waste management and resource recovery. Different feed materials used in MSW pyrolysis can be grouped based on their beneficial end uses. For energy production, feed materials such as mixed MSW (after sorting and pre-treatment), plastics like PET and High-density polyethylene (HDPE), paper and cardboard, yard waste including grass clippings and leaves, and food waste are commonly used. These materials are optimized to produce bio-oil, syngas, or biochar, which can be used as fuel or energy sources. As chemical feedstocks, plastics such as PET and HDPE can produce valuable chemicals like hydrocarbons and monomers, while wood and yard waste can yield chemicals like acetic acid and methanol. Paper and cardboard can also be

converted into valuable chemicals such as furans and levoglucosan through pyrolysis. For soil amendment purposes, organic waste including food waste and yard waste, as well as agricultural residues like straw and husks, are used to produce biochar, which enhances soil quality and sequesters carbon. In terms of waste minimization and recycling, mixed MSW can significantly reduce overall waste volume and allow for the recovery of metals. Plastics can be processed to reduce plastic waste and recover monomers or hydrocarbons, while paper and cardboard can be recycled to reduce waste and recover fibers.

Due to the complex nature of MSW as a mixture, it is perhaps unsurprising that different samples of MSW as well as the various components and their mixtures can behave very differently during pyrolysis. Synergistic co-pyrolysis involves the interaction of various MSW components during pyrolysis, which can significantly impact reaction rates and product yields. When different constituents are combined during pyrolysis, complex reactions between the intermediates can lead to synergistic effects that alter the rate of pyrolysis and the quantity and quality of the end products. For example, co-pyrolyzing food waste with other MSW components like lignocellulosic materials can accelerate pyrolysis rates and alter product distributions. The presence of excess oxygen in food waste typically results in pyrolysis oils with high oxygenate levels but combining it with low oxygen/carbon (O/C) ratio materials can improve the quality of the oils. For example, Chen *et al.* [134] noted a more than double increase in hydrocarbon olefin production for comingled food waste and tires. Co-pyrolysis of food waste with lignocellulosic materials can lead to increased hydrocarbon production and reduced non-hydrocarbon content [135]. Furthermore, combining food waste with algae biomass can increase gas yield while reducing oil yield but improve the heating value of the oil [136].

Plastic waste, characterized by high carbon and hydrogen content and negligible oxygen content, also exhibits significant synergistic effects during co-pyrolysis with other MSW constituents. For instance, co-pyrolyzing plastic waste with biomass [137] can enhance oil yield and improve its heating value. Different plastics exhibit varying interactions with biomass, with some combinations promoting hydrocarbon production [138] and others influencing char formation [139, 140].

Biomass waste, consisting of cellulose, hemicellulose, and lignin, shows diverse thermal degradation behaviors [141, 142]. Co-pyrolysis of biomass with plastics or other organic materials can shift product distribution from char to pyrolysis oil and syngas. For instance, co-pyrolyzing biomass with short-chain organic compounds can increase oil and syngas yields, while lignin presence can enhance product quality under certain conditions [143].

Other review articles discussing the pyrolysis of MSW and components have documented additional insights and applicability in various regions around the globe [7, 144]. For example, Du *et al.* [7] reviewed waste compositions from cities in eastern China in addition to Tokyo, Singapore, Berlin, and MSW that could be excavated from long-standing landfills from China, Sweeden, Belgium, Australia, Thailand, Estonia, Finland, and India. In general, it was concluded that legacy wastes had much different composition than landfill inbound waste, primarily due to the decay and loss of organics. Most locations reported plastic, rubber, and stones/aggregate to be major contributing factors in landfill resources. Wood and paper still existed in larger quantities in Finland, as well as site specific locations in Sweeden and Austria, with larger proportions of wood. Thailand, China, and Estonia also had notable fraction of glass. For these minable resources, the largest fraction (39-71%) was attributed to ‘fines’, or otherwise small, undefined/undefinable fractions, highlight the lack of definition and understanding that yet remains about these resources.

Other studies form additional insight for a more comprehensive global view of MSW compositions [4, 5]. Based on average pyrolysis performance data reported in [125, 128, 132, 145-151], and using location-based compositional data from [4, 7, 152], a summary of MSW compositions and expected pyrolysis results are presented in Figure 4. Although few if any distinct trends can be noted from this wealth of data, there is ample indication that their processes such as pyrolysis can take advantage of these resources around the globe. In addition, the wide scatter in waste fractions and resulting yields indicate that future work in the area of waste sortation, processing, and upgrading could significantly improve the performance and uniformity of MSW pyrolysis.

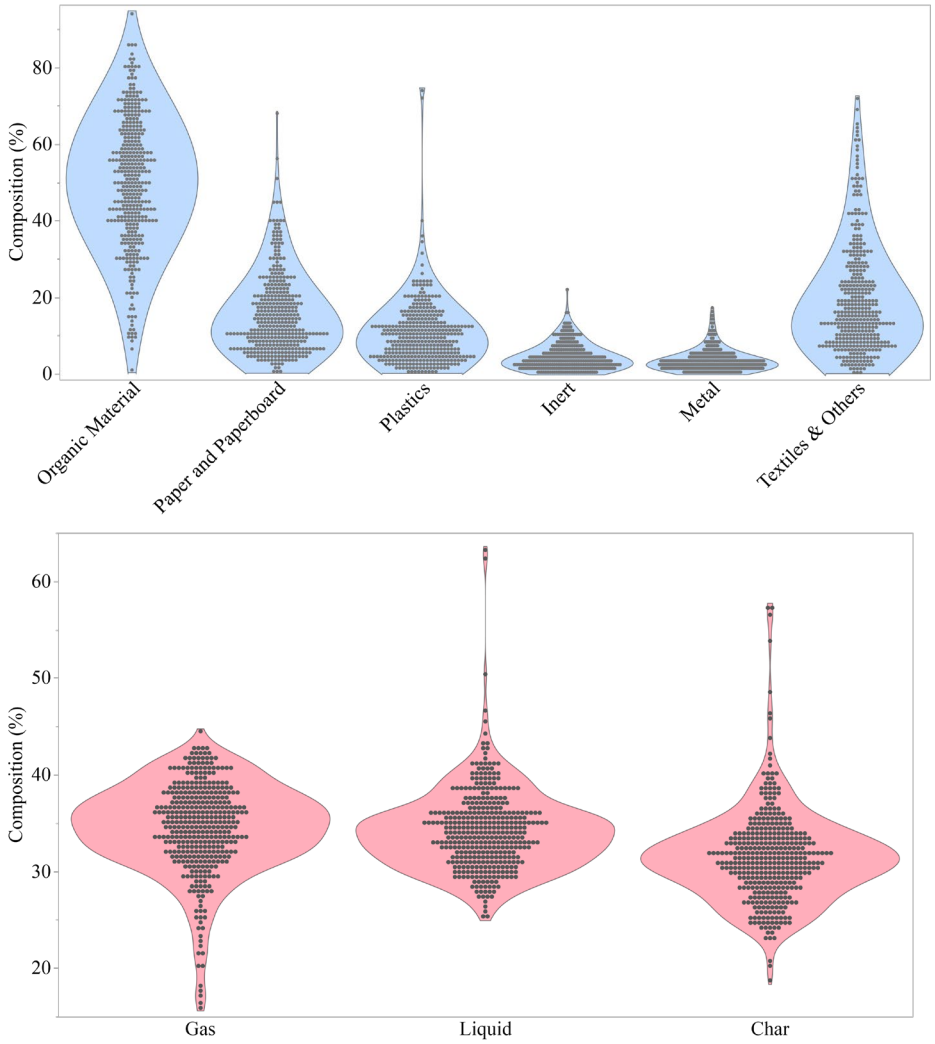

Figure 4: Variability of components in MSW (top) along with their impact in product yields (bottom).

Many proposed technologies and reactor styles for pyrolysis of MSW have been recently summarized [153]. At the forefront of these technologies are different types of reactors. Fixed-bed reactors, while commonly used in laboratory settings, exhibit low heat transfer efficiency and are not suitable for large-scale applications due to their poor heat distribution and lengthy processing times [154]. In contrast, rotary kiln reactors are more prevalent in industrial settings. They facilitate good mixing of waste and allow for flexible adjustments in residence time, though they still operate under slower heating rates, resulting in significant char production. For example, Li *et al.* [155] strived to measure and model MSW pyrolysis for a variety of configurations and operational conditions. Although their findings well document the residence time as a function of drum rotation frequency, surface roughness, etc., they found that there are significant distributions to residence times, as well as significant differences when compared to normal distribution curves. Fluidized-bed reactors offer higher heat transfer rates and better mixing, making them ideal for fast pyrolysis [153]. Dai *et al.*[156], for example, studied the pyrolysis of waste tires in a recirculating fluid bed. They found a multi-stage system was preferred for processing waste materials like tires to ensure adequate residence time as well control the decomposition in several stages to achieve high liquid yields. However, the application of fluid bed reactor in MSW is limited by complications in separating materials and maintaining operational efficiency. Tubular reactors present an innovative approach, allowing for continuous movement of material and improved heat transfer. They generally involve a tubular housing, are externally heated, and use mechanical transport of material down the length with a screw, scrapper, drag chain, etc. While promising for future applications, they require rigorous pre-treatment of feedstock to avoid operational challenges. Aguado *et al.* [157], for example, examined pyrolysis of low-density polyethylene (LDPE) in a screw reactor. They found acceptable conversion of the hydrocarbon

589 chain over an acidic cracking catalyst resulted in acceptable selectivity (over 80%) to gasoline fuel
590 ranges, with overall increase in olefins with increasing transport speed with decreasing amounts
591 of paraffins, isoparaffins, and somewhat unchanging amount of naphthalenes, and aromatics.
592 Despite the promise of these pyrolysis technologies, they often face limitations. Pre-treatment
593 steps, such as separating contaminants and reducing moisture content, adding complexity and
594 increasing costs. Additionally, the need for effective emissions control is paramount, particularly
595 for harmful substances like HCl and SO_2 that can arise from certain feedstock components, such
596 as polyvinyl chloride (PVC). Emissions from these processes can include harmful gases such as
597 HCl, SO_2, and NH_3, which require careful management to minimize their impact on the
598 environment. Commercial pyrolysis systems often incorporate advanced scrubbing and filtering
599 techniques to address these emissions, positioning themselves as cleaner alternatives to traditional
600 incineration methods.

601 *2.2.4 Torrefaction*

602 Torrefaction, a thermochemical conversion process, operates under mild pyrolysis conditions
603 typically ranging from 200 to 350 °C in an oxygen-depleted environment [158-160]. The resultant
604 torrefied product, often termed "biocoal", exhibits characteristics akin to traditional coal, rendering
605 it suitable for co-firing with coal in power plants or direct utilization in industrial processes. The
606 benefits of torrefaction include an augmentation in fixed carbon content, calorific value, and
607 energy density [20, 21, 161, 162]. Furthermore, torrefaction enhances the grindability and
608 hydrophobicity of the solid products while reducing susceptibility to microbial degradation as
609 torrefaction reduces the moisture content significantly [2, 21, 163]. Critical process parameters
610 such as temperature, residence time, feedstock type, particle size, reactor type, moisture content,

611 and heating rate influence the physicochemical properties of torrefied material, with temperature
612 being the most influential, followed by residence time [164-166].

613 While torrefaction has traditionally been employed for upgrading biomass feedstocks, its
614 application to other feedstock types, such as MSW, sewage sludge is gaining attention. Research
615 have mainly been conducted to investigate the physical and chemical properties of torrefied MSW
616 [167-170]. Although literature on torrefaction technologies for MSW treatment is relatively scarce
617 compared to gasification and pyrolysis, it presents a promising avenue for addressing the
618 challenges associated with the direct utilization of MSW in thermochemical processes, such as
619 generates tar in gasification, produces water and acid contents in pyrolysis bio-oil, and releases
620 secondary pollutants during combustion [20]. Torrefaction showed the potential to solve the issues
621 associated with direct utilization of MSW. Studies have indicated that torrefaction can enhance the
622 physicochemical properties of MSW to levels comparable to coal [171]. Investigation into the
623 behavior of organic and inorganic pollutants during torrefaction reveals that heavy metals with
624 high boiling points (*e.g.,* Pb and Zn) tend to be retained in the char fraction, whereas those with
625 low boiling points, such as Hg, Cl tended to enter the gas phase [168, 172]. On the other hand,
626 organic pollutants such as dioxins are predominantly found in the char, with minor amounts in the
627 volatile fractions [172].

628 The primary objective of the study by Ivanovski et al. [171] was to investigate the effects of
629 torrefaction on the thermochemical properties of MSW sourced from the Republic of Slovenia.
630 The elemental composition of the raw MSW revealed a carbon content of 43.2%, hydrogen at
631 8.1%, nitrogen at 0.8%, oxygen at 47.9%, and sulfur at 0.03%. Proximate analysis indicated a
632 moisture content of 44.3%, volatile matter of 54.9%, fixed carbon content of 6.7%, and ash content
633 of 3.1%. The HHV of the raw MSW was determined to be 24.3 MJ/kg. The study found that

torrefaction significantly affects mass yield (MY) and energy yield (EY), with MY and EY decreasing with increasing temperature: at 200°C, MY was 92.9% and EY 93.5%; at 250°C, MY decreased to 79.1% and EY to 79.8%; and at 300°C, MY fell to 65.8% and EY to 66.8%. Compared to traditional torrefaction literature, these trends in MY and EY are much different. While this study with MSW shows a near 1:1 trend of decreasing MY to EY, for example, many biomass torrefaction studies typically show more significant loss in MY with a relatively high retention in EY closer to 2:1 or 3:1 ratio for decreasing MY to EY [21, 164, 173], significantly improving the energy density. As a result, this suggests that while the properties of torrefied MSW chars may perform better in combustion, the energy density is not significantly improved upon. Interestingly, this seems to also be supported by investigations by Yuan *et al.* [167]. They note that although torrefaction had a significant impact on the structure and size reduction properties of MSW, they report very modest changes in ignition temperature, maximum weight loss, burnout temperature, mean combustion rate, as well as combustible and burnout indices with torrefaction extent. Again, biomass in comparison demonstrates more substantive changes in combustion properties with the application of torrefaction [21].

The elemental analysis post-torrefaction of MSW showed an increase in carbon content to 52.9% (at 300°C) and a decrease in hydrogen to 6.6%, while oxygen content declined to 39.5% [171]. The proximate analysis further revealed that fixed carbon increased to 10.1%, volatile matter decreased to 44.7%, ash content rose to 6.6%, and HHV increased marginally to 25.3 MJ/kg. The thermal analysis revealed distinct thermal stability zones for both raw and torrefied MSW samples. The initial mass loss for raw MSW occurred around 74°C, corresponding to moisture evaporation, followed by a significant degradation phase between 280°C and 360°C, where the weight loss was notable, particularly for samples torrefied at 200°C and 250°C. In the higher temperature range, a

steady degradation phase was observed between 375°C and 615°C for all samples, culminating in a final mass loss peak around 675-700°C, where the highest reaction intensity was recorded for the 300°C torrefied chars, indicating enhanced stability and thermal degradation characteristics with increasing torrefaction temperatures.

The study by Głód *et al.* [174] investigates the potential of torrefaction as a process to enhance the energy properties of MSW, with more of a focus on the physical and mechanical properties of the torrefied product. The findings demonstrate that torrefaction significantly improves the weather resistance and durability of MSW pellets, allowing them to withstand prolonged immersion in water without loss in structural integrity. Specifically, while untreated MSW pellets exhibited a maximum water uptake of 0.72 kg of water/kg of fuel (dry) after 72 hours, torrefied pellets only absorbed 0.34 kg of water/kg of fuel (dry), highlighting their enhanced hydrophobicity. These water-resistant properties were also observed elsewhere [20]. Haykiri-Acma *et al.*[175], looked at torrefaction following pelleltization of a textile-rich RDF and found that all ranges of torrefaction (230-290°C) improved water resistance time (maintaining pellet integrity) to >10 days, which was the maximum testing time for that property. They also found that after 25 days the HHV for all conditions changed less than 4%, with the most severe torrefaction case changing only 1% indicating great potential for weather resistance and storage performance. Recent study by Abdulyekeen *et al.* [20] demonstrated the efficacy of torrefaction in enhancing the hydrophobicity and grindability of MSW. They reported that the torrefied MSW generates finer particles compared to untreated samples, attributed to increased brittleness with torrefaction severity which agreed with other literature [21, 176]. Measurement of contact angles confirms the improvement in hydrophobicity, with torrefied MSW exhibiting significantly higher contact angles compared to untreated MSW. For example, the contact angles measured for untreated and torrefied (at 300 °C

for 50 min) MSW were measured as 114.3° and 173.3°, respectively. Głód *et al.* [174] went on to document that torrefaction leads to the production of stronger pellets with improved mechanical properties, such as higher durability, compressive strength (3.75 MPa compared to 2 MPa), and shear strength (34 MPa compared to 8 MPa), and as evidenced by values exceeding 99% durability and compressive strengths greater than 3 MPa for all torrefied pellets. Another study looked at extrusion, as another form of densification, of raw and torrefied combinations of waste plastics and biomass [21]. They found that torrefaction of the waste mixtures generally improves the shear strength of extruded filaments, but these properties were lower than those of virgin resins alone. They suggest that, depending on the plastic type(s), the unmodified plastic exhibits an initial brief elastic region followed by a prolonged strain hardening phase. When biomass fibers are added (or other MSW fiber components, by analogue), the material behavior changes to a rapid brittle failure with comparatively little strain. This suggests that the mixed pellets/filaments are much less flexible, likely due to an influence of short fiber length and ineffective reinforcement from interfacial shear stresses between the biomass and plastic regions. However, when pelletization is used before torrefaction, it was found that torrefaction can decrease the strength as measured through the compressive strength and hardness with increasing torrefaction[175]. For these torrefied RDF pellets, a low torrefaction condition (230 °C) did not change the strength properties from the raw RDF pellets drastically (1198 and 117 N/mm^2 for compressive strength and hardness respectively, compared to 1141 and 112 N/mm^2).

The milling of torrefied MSW also results in smaller average particle sizes and improved grindability, as indicated by reduced Hardgrove Grindability Index (HGI) values (17 compared to 22 for HGI and 6 compared to 12 following Thermally Treated Biomass Grindability Index (TTBGI) methods), suggesting a decrease in energy consumption during size reduction [174]. This

was also observed in simulated MSW streams and post-industrial wastes [20, 176]. Size reduction improvements were also observed for torrefaction of wood waste and garden wastes extracted from MSW streams [177]. Similar to the alteration of structural/strength properties discussed above, the authors attribute this to an embrittled structure and disrupted fibrous nature from partial degradation. In general, IR analysis of surface functional groups showed mostly loss of aliphatic and hydroxyl groups, while promoting increased aromatic groups. For example, increasing torrefaction severity showed less prominent bands (from dehydration reactions) at the 3500 and 3750 cm^{-1} regions, represents the stretching vibration of hydroxyl (O–H) [178]. Table 2 and Table 3 summarize the overall influences of torrefaction on waste feedstock size reduction and properties. These enhancements collectively indicate that torrefaction can effectively upgrade the physical and thermal characteristics of MSW, making it a more viable and efficient option for energy production.

Table 2: Grindability characteristics of torrefied MSW and component fractions.

Feedstock		Grindability Index (HGI/TTBGI)	Energy Consumption	Particle Size Distribution	Key Observations	Ref.
Biomass	Alder chips	HGI increased from ~20 to ~40	↓ by ~30–50% after torrefaction	Finer particles, narrower distribution	Significant improvement in grindability; suitable for vertical spindle mills	[179, 180]
	Willow chips	HGI increased from ~25 to ~45	↓ by ~40%	Improved uniformity	Excellent milling performance post-torrefaction	
	Palm kernel shells	HGI increased (exact values not given)	Not specified	Improved size reduction	High-density biomass showed better grindability after torrefaction	
	Biomass pellets (various)	Modified HGI used (varied by feedstock)	Cutting mill: 5.15 Wh/kg; Hammer mill: 5.24 Wh/kg; Impact mill: 8.23 Wh/kg	Cutting mill: 0.62 mm; Hammer mill: 0.51 mm; Impact mill: 0.41 mm	Impact mill produced finest particles; energy use varied by mill type	[181, 182]
MSW and Wastes	Mixed MSW (general)	TTBGI ↓ from 22 to 17	↓ (qualitative)	Smaller average particle size	Embrittlement improved grindability and reduced energy input	[20]
	Textile-rich RDF	TTBGI ↓ from 12 to 6	↓ (qualitative)	Maintained pellet integrity >10 days	Improved grindability and water resistance of RDF pellets	
	Wood/Garden waste	Not specified	↓ (qualitative)	Improved brittleness and size reduction	Fibrous structure disrupted, aiding mechanical processing	
	Paper/Cardboard	Not specified	↓ (qualitative)	Uniform particle size after pelleting	Pellets achieved >99% durability and >300 kg/m³ density	[183]
	Thin plastics	Not suitable for pelleting	Not reported	Poor grindability	High moisture and elasticity hindered	

					densification and grinding	
	Thick plastics	Not specified	Moisture ↓ by 30% (screw press)	Limited grindability improvement	Mechanical preprocessing improved dewatering but not grindability	
	Paper-plastic blend	Similar to PRB coal (qualitative)	Not specified	Fiber → fine fraction; plastic → coarse	Torrefied blend showed coal-like grinding behavior; fiber and plastic separated by size	[176]
	C&D waste	Not specified	3862–4338 MJ/t (torrefaction energy)	Improved grindability with power level ↑	Higher torrefaction power improved grindability and carbon content	[170]
	Grass clippings	Not specified	↓ with higher moisture	Improved grindability at 64% m.c.	High moisture enhanced torrefaction efficiency and grindability	
	MSW-derived pellets	Not specified	↓ by ~30–50%	Narrower particle size distribution	Torrefaction improved pellet brittleness and reduced milling energy	[20, 176]

716

717 The grindability of torrefied materials varies significantly between biomass and MSW
718 components, reflecting differences in composition, structure, and response to thermal treatment.
719 For biomass, torrefaction consistently improves grindability, as evidenced by substantial increases
720 in HGI. For example, alder and willow chips show increases from ~20–25 to ~40–45—and
721 reductions in energy consumption by 30–50%. These improvements are accompanied by finer and
722 more uniform particle size distributions, making torrefied biomass more suitable for pulverized
723 fuel systems. In contrast, MSW components exhibit more heterogeneous responses. Mixed MSW
724 and textile-rich RDF show notable improvements in grindability, with TTBGI values decreasing
725 from 22 to 17 and 12 to 6, respectively, and enhanced brittleness facilitating size reduction. Paper
726 and cardboard fractions form durable, uniform pellets, while plastics, especially thin films, remain
727 challenging due to poor densification and elasticity. Blends of paper and plastic exhibit coal-like
728 grinding behavior, with fiber and plastic separating into fine and coarse fractions, respectively.
729 Other MSW-derived materials, such as construction and demolition waste or grass clippings, also
730 benefit from torrefaction, particularly under optimized moisture and power conditions. Overall,
731 while torrefaction enhances grindability across most MSW fractions, the degree of improvement
732 is highly dependent on feedstock type, preprocessing, and torrefaction severity.

Table 3: Torrefaction performance metrics by MSW component.

MSW Component	MY (%)	EY (%)	HHV Improvement (MJ/kg)	Hydrophobicity	Grindability	Ref.
Food waste	34–66	83–97	+5.9 (e.g., 11.1 → 17.0)	Improved (moisture resistance ↑)	Improved (due to embrittlement)	[184]
Plastics (LDPE, PET)	14–15	High (inert)	+5.3 (e.g., 19.2 → 24.5)	Low (hydrophobic by nature)	Low (no significant change)	[185]
Paper/Cardboard	~50–70	~60–80	+3–5	Moderate	Moderate	[20, 176]
Textiles (cotton/polyester)	40–60 (cotton-based)	50–70	+4–6 (lignite-equivalent)	Moderate	Improved (cotton-rich blends)	[186]
Yard waste	50–70	70–98	+6.6 (e.g., 15.6 → 22.2)	High (OH group loss)	High (fibrous structure breaks down)	[187]
Mixed MSW	51–70	65–85	+4–8 (e.g., 17.9 → 25.9)	Improved (O/C ↓)	Improved (ash and fiber breakdown)	[20]

Torrefaction performance varies significantly across different MSW components due to their diverse physical and chemical compositions. MY typically decreases with increasing torrefaction severity, with values ranging from 34–66% for food waste and up to 70% for yard waste and mixed MSW. However, EY often remains relatively high (65–97%), particularly for food waste and yard waste, due to the retention of energy-dense carbon fractions. HHV improvements are most pronounced in lignocellulosic materials such as yard waste and paper/cardboard, where increases of 4–6 MJ/kg are common, while plastics and textiles show more modest gains or inert behavior. Hydrophobicity generally improves across all organic MSW types due to the loss of hydroxyl groups and reduction in oxygen content, with torrefied food waste and yard waste exhibiting enhanced moisture resistance. Grindability is also enhanced in fibrous or brittle materials like yard waste and textiles, where torrefaction disrupts the structural integrity and facilitates size reduction. In contrast, plastics such as LDPE and PET remain largely inert under typical torrefaction conditions, showing minimal changes in grindability or hydrophobicity. These findings underscore the importance of feedstock-specific strategies when applying torrefaction to MSW, particularly when targeting downstream applications such as co-firing, pelletization, or gasification.

During torrefaction of comingled wastes, Rago *et al.*[188] documented synergistic interactions between components. The study investigates the torrefaction of waste biomass, newspaper, and low-density polyethylene, and their blends at 300°C. Notable synergistic interactions were observed between the biomass and newspaper, leading to improved fuel properties in the resulting char, such as increased HHV, higher carbon content, and reduced volatile matter content. These interactions were statistically significant and resulted in enhanced devolatilization reactions, which contributed to the improved fuel characteristics of the torrefied blend. In contrast, LDPE remained largely inert at the torrefaction temperature, leading to inhibited mass transfer during co-torrefaction with biomass. This resulted in higher char yield and HHV for biomass-LDPE blends, but also in higher volatile matter content. They suggest that the plastic melt formed a coating around biomass particles, which blocked the pores in the char matrix and limited the release of volatiles, thereby promoting secondary char formation. Saha et al., also investigated synergistic interactions of torrefied components in a study look at torrefaction (200-250°C) of mixed biomasses (corn stover and loblolly pine) and various plastics (PET, HDPE, PVC, LDPE, PP, PS, Polyurethane (PU), Nylon 6/6 (N66), Acrylonitrile butadiene styrene (ABS), and Polycarbonate (PC)) [189]. Similar to the work of Rago, they also concluded that LDPE was effectively inert during torrefaction and did not accelerate decomposition. However, they did not report that certain plastics, namely PVC and PU, were most commonly associated with enhanced and degraded reaction rates (synergy) respectively. In the case of negative synergy, they theorized that, similar to Rago's conclusions [188], the degradation of PU formed a boundary layer (of char in this case) around the fiber particles, reducing the overall volatile release rated. On the other hand, positive synergy was noted to occur due to the formation of reactive intermediates that could catalyze decomposition. HCl formation from dehydrochlorination, or formation of allylic radicals from

773 dehydrochlorination or hydrogen abstraction could enhance the breakdown of biomass through
774 attacking hydroxyl sites along the biopolymers. Similar effects were also noted by Zhu *et al.* [190]
775 in a kinetic study of mixed waste paper and plastics.

776 Torrefaction approaches for MSW present various advantages and limitations that influence their
777 effectiveness as a pretreatment method. Unfortunately, much existing literature knowledge is
778 based on biomass which has significantly different compositions, contaminations, physical
779 properties and formats [174]. Nevertheless, there are some technological advantages and shortfalls
780 that can be gained from existing work. Dry torrefaction significantly enhances the heating value
781 and energy density of biomass [191], while improving combustion stability and gasification quality
782 [192, 193]. However, it requires pre-drying of high-moisture feedstocks, which can be energy-
783 intensive, and may result in increased ash content, potentially leading to ash-related issues during
784 combustion [192, 194]. On the other hand, wet torrefaction eliminates the need for pre-drying,
785 thereby saving energy consumption and reducing ash content, which improves overall fuel
786 properties [195, 196]. Despite these benefits, wet torrefaction poses challenges such as equipment
787 corrosion, clogging, and the necessity for wastewater treatment and management, along with
788 producing a lower yield of torrefied product [193, 197]. Ionic-liquid-assisted torrefaction enhances
789 the rate and quality of biomass processing while utilizing environmentally friendly and recyclable
790 ionic liquids [198, 199], yet it is hindered by lower energy yields compared to dry torrefaction,
791 high operational costs, and limited commercial applicability. Super-heated steam torrefaction
792 minimizes carrier gas usage and enhances product uniformity, reducing explosion risks [200];
793 however, it necessitates specialized equipment for steam generation and control, which can be
794 costly and limit scalability. Lastly, microwave-assisted torrefaction improves energy yield,
795 grindability, and energy density of torrefied biomass with faster processing times and more

uniform product distribution [201]. Nevertheless, this method requires careful optimization of microwave power and processing parameters, and it faces limitations in scalability due to the complexity and costs of the necessary equipment.

From the above discussion, it can be summarized that although torrefaction is being widely used as conversion pathway for biomass to produce high value fuels or products, for MSW it would be better suited as a preprocessing step.

2.3 Wet processes

2.3.1 Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC) is an emerging thermal conversion process that holds promise for converting organic waste into an aqueous environment at elevated temperatures typically 180-260°C and saturated pressures [202-206]. One of the main advantages of HTC is that it does not require removing moisture from the feedstock to be processed. Unlike conventional torrefaction, HTC is carried out in presence of subcritical water [207]. Under these conditions, organic compounds undergo hydrolysis, dehydration, decarboxylation, and polymerization reactions. These chemical transformations reduce the hydrogen and oxygen content in the feedstock while concentrating carbon in the formation of a carbonaceous solid known as hydrochar, along with aqueous by-products [208]. Batch experiments have shown that 45-75% of the carbon initially present in the MSW feedstock is retained in the hydrochar [209]. The hydrochar produced exhibits properties similar to lignite coal, with high carbon content and energy density [210]. If the hydrochar is applied in scenarios involving long-term carbon storage, the overall greenhouse gas emissions are typically lower than those associated with conventional waste management options such as landfilling, composting, or incineration [211]. This makes HTC particularly attractive for both energy recovery and carbon sequestration purposes.

Process conditions such as temperature and residence time play a critical role in determining the yield and quality of the hydrochar. Increasing the severity of HTC (*i.e.,* higher temperatures or longer reaction times) typically reduces solid yields but increases the fixed carbon content, HHV, and degree of carbonization. Lucian *et al.* [212] demonstrated that under intermediate HTC conditions 220-240 °C, secondary chars can condense on the surface of primary hydrochar. These secondary chars, extractable with organic solvents, are rich in compounds such as phenols, furfurals, and organic acids. They may enhance the reactivity and energy content of the final product but also present potential challenges for product purity and downstream processing.

In support of these observations, a comparison of key literature values related to hydrochar properties under different HTC conditions is presented in Table 4. The table includes data on elemental composition C, H, N, S, O wt%, proximate analysis including volatile matter, fixed carbon, ash wt%, and HHV, as functions of process temperature and duration. Notably, increasing the HTC temperature results in higher carbon content and HHV while reducing oxygen content. For instance, at 230 °C for 45 minutes, the hydrochar in Abdoli *et al.* [213] reached 66.6 wt% C and an HHV of 27.64 MJ/kg, compared to only 43.5 wt% C and 19.5 MJ/kg at 180 °C for 60 minutes reported by Lucian *et al.* [214]. This aligns with the chemical transformations that remove oxygen-containing functional groups and enhance energy density. Additionally, fixed carbon increases with severity, from 35.1 wt% at 180 °C to 49.2 wt% at 260 °C, while volatile matter decreases, indicating improved combustion behavior. Ash content remains relatively stable across conditions 6-9 wt%, though feedstock variability may influence this. Nitrogen and sulfur contents were low across all studies reported here, although it will change with feedstock type. These studies typically showed decreasing S and increasing N with more intense processing.

HTC has also demonstrated versatility in handling the heterogenous and variable nature of MSW. Researchers have investigated the carbonization of individual MSW components such as food waste, paper, wood, rubber, and plastics to better understand how each behaves under hydrothermal conditions. Lin *et al.* [215] found that HTC significantly improves fuel properties and thermal stability of lignocellulosic components such as paper and wood. However, food waste undergoes extensive solubilization and decomposition, which diminishes the combustion improvement of the resulting hydrochar. Additionally, polymers such as PP and PE undergo minimal chemical transformation during HTC, indicating that HTC is better suited to biogenic fractions of MSW [216].

Environmental assessments have shown that HTC may provide sustainable performance compared to other waste management strategies. A recent LCA study by Mannarino *et al.* [217] evaluated the integration of HTC into a water resource recovery facility treating sewage sludge. The study compared four HTC-based scenarios with a benchmark composting strategy and found that HTC could reduce climate change impacts by up to 98% relative to composting. Moreover, when the process water from HTC was subjected to anaerobic digestion (AD) for biogas recovery, environmental performance improved across 11 of 16 impact categories. Furthermore, when hydrochar is combusted for energy recovery, the net calorific value often exceeds that of biogas generated via AD or the direct incineration of raw MSW [213]. Moreover, HTC produces fewer emissions than incineration and offers solid fuel that is more hydrophobic, dense, and stable, improving its storage, handling, and transport properties [209, 215].

An increasingly popular direction involves the integration of HTC with AD, a biological process where microorganisms break down organic matter in the absence of oxygen. In such hybrid systems, the digestate produced from AD can undergo HTC to generate additional hydrochar,

while the process water from HTC can still retain biodegradable compounds that support further methane production [218]. In typical AD-only configurations for treatment of MSW, 305-3850 mg/L of the influent chemical oxygen demand (COD) remains in the digestate, whereas HTC of this digestate can recover 64-88% of its dry mass as hydrochar and transfer 9.58-72.3 g/L of soluble organics into the process water, when this HTC liquid or slurry is recycled to AD, Aragón-Briceño et al. [219] and others report biomethane increases of up to 80% in HTC process water, compared with untreated organic fraction substrates [220, 221]. This coupling enhances recourse recovery and promotes a more circular treatment pathway. For example, *Lucian et al.* [214] and Sharma et al. [222] reported that HTC of the organic fraction solid digestate produced after AD of the organic fraction of municipal solid waste, containing a stabilized but still organic-rich fraction along an inorganic/ash fraction not only improved hydrochar quality but also yielded process water suitable for subsequent AD, by partially depolymerizing residual solids, increasing soluble COD and volatile fatty acids, and generating an aqueous phase that remained biodegradable even though the parent solids had already undergone AD, enabling multiple valorization routes within the same waste stream [222]. In this context, HTC acts as a post-treatment that disrupts lignocellulosic and microbial structures left in the digestate, converting hard-to-digest solids into more enzyme accessible substrates for a second AD step rather than simply retreating fully stabilized material.

882 *Table 4: Characteristics of MSW derived hydrochar at different conditions. NR indicates "not reported" in the literature.*

HTC condition		Ultimate analysis, db (%)					Proximate analysis, db (%)			HHV, db (MJ/kg)	Ref.
Temp. (°C)	Time (min)	C	H	N	S	O	VM	FC	Ash		
200	30	49.19	6.36	2.06	0.33	42.06	88.21	10.18	1.61	NR	[48]
200	30	35.5 ± 8.1	4.57 ± 0.7	1.5 ± 0.3	<0.1	34.6 ± 1.8	62.5 ± 1.1	11.1 ± 2.5	26.4 ± 1.4	17.4 ± 0.6	[223]
200	120	45.4 ± 9.8	5.01 ± 0.2	1.5 ± 0.4	<0.1	35.1 ± 0.7	65.0 ± 0.9	10.9 ± 1.7	24.1 ± 0.8	16.8 ± 0.5	
250	30	39.9 ± 4.7	4.76 ± 0.3	1.9 ± 0.3	<0.1	25.5 ± 1.4	47.0 ± 0.8	16.4 ± 3.4	36.6 ± 2.6	18.0 ± 0.8	
250	120	42.6 ± 2.2	4.38 ± 0.0	2.2 ± 0.1	<0.1	19.0 ± 1.0	43.4 ± 1.0	17.5 ± 2.6	39.1 ± 1.6	18.9 ± 2.7	
300	30	42.5 ± 5.6	4.54 ± 0.2	2.3 ± 0.3	<0.1	15.7 ± 1.6	41.3 ± 3.9	15.6 ± 4.0	46.1 ± 5.1	20.7 ± 1.7	
300	120	43.9 ± 0.1	4.00 ± 0.1	2.3 ± 0.0	<0.1	15.7 ± 0.6	40.2 ± 1.5	20.3 ± 4.9	39.5 ± 3.4	21.0 ± 0.6	
190	30	56.85	7.33	0.97	0.08	32.59	75.16	23.76	1.09	19.05	[224]
250	1200	33.5	2.7	0.63	0.05	14.2	35.7	5.5	48.8	20.0	[225]
NR	NR	23.63	1.07	2.60	NR	35.04	52.99	9.35	37.66	NR	[225]
NR	NR	47.36	8.56	1.78	0.38	23.01	69.71	11.38	18.91	NR	[226]
150	30	60.87	8.35	0.79	0.11	29.88	80.77	13.24	5.99	30.17	[227]
175	30	63.81	8.81	0.72	0.11	26.55	79.27	14.58	6.15	30.77	
200	30	66.55	8.78	0.70	0.10	23.87	76.16	18.39	5.45	33.01	
225	30	70.54	8.97	0.60	0.08	19.81	78.75	15.92	5.33	36.69	
210	30	33.89	4.63	1.42	1.09	15.12	43.3 ± 0.5	12.8 ± 0.5	43.9 ± 0.7	13.5 ± 0.1	[228]
230	30	34.39	4.76	1.04	0.74	13.98	41.5 ± 0.7	13.4 ± 0.8	45.1 ± 0.5	14.2 ± 0.0	
250	30	35.04	4.57	1.41	0.67	5.37	34.4 ± 0.4	12.6 ± 0.9	53.0 ± 0.6	14.6 ± 0.1	
280	30	35.58	4.19	1.54	0.43	3.34	33.0 ± 0.8	12.1 ± 1.4	54.9 ± 0.9	15.2 ± 0.0	
210	60	33.61	4.24	1.13	0.92	14.16	41.5 ± 0.3	12.5 ± 0.3	45.9 ± 0.4	13.7 ± 0.0	
230	60	34.81	4.74	1.09	0.57	9.57	38.1 ± 0.2	12.7 ± 0.3	49.2 ± 0.3	14.3 ± 0.0	
250	60	34.71	3.45	1.31	0.54	6.09	34.3 ± 0.2	11.8 ± 0.6	53.9 ± 0.7	14.7 ± 0.1	
280	60	35.69	3.33	1.54	0.43	4.36	33.2 ± 0.9	12.2 ± 1.0	54.7 ± 0.5	15.4 ± 0.1	
210	90	33.15	4.26	0.86	0.83	12.14	39.7 ± 0.3	11.6 ± 0.4	48.8 ± 0.6	14.1 ± 0.1	
230	90	36.58	4.32	1.34	0.52	6.39	36.9 ± 0.3	12.2 ± 1.0	50.9 ± 0.7	14.3 ± 0.1	
250	90	30.45	3.30	1.38	0.5	4.00	29.9 ± 0.2	9.7 ± 1.0	60.4 ± 0.8	14.6 ± 0.1	
280	90	28.90	3.28	1.42	0.33	3.96	28.6 ± 0.4	9.3 ± 0.8	62.1 ± 1.2	14.8 ± 0.1	
180	60	43.3	5.4	1.4	NR	33.3	82.2	1.1	16.7	19.5	[229]
180	180	44.4	5.4	2.0	NR	29.0	78.3	2.4	19.3	18.9	
220	180	53.5	5.9	2.0	NR	20.8	71.1	11.1	17.8	22.2	
250	360	57.3	5.6	2.7	NR	6.2	55.0	16.8	28.2	25.6	

883

An emerging and underexplored opportunity is the use of HTC as a pretreatment step for high-temperature thermochemical conversions such as pyrolysis, gasification, or combustion. While direct studies on MSW are limited, there is compelling evidence from biomass-focused research that HTC-treated solids possess favorable structural and chemical characteristics that enhance performance in downstream thermal processes. Specifically, studies from, Islam *et al.* [230] and Fakudze *et al.* [231], demonstrate that HTC produces char with improved thermal stability, reduced reactivity to moisture, and higher aromaticity. These traits translate to better handling, reduced tar formation in gasifiers, and improved calorific content in combustion [232]. Furthermore, HTC offers partial demineralization and homogenization of heterogeneous feedstock, including waste and mixed biomasses, and MSW, facilitating smoother operation and longer lifespans for reactors used in pyrolysis or combustion [225]. Integrating HTC upstream of these high-temperature processes could represent a viable pathway to improve both operational efficiency and product quality but experimental data specifically applying this strategy to MSW remains a critical research gap.

Despite its promise, HTC is not without challenges. One major concern is the fate of inorganic components, such as chlorine, sodium, and potassium, which may remain in the hydrochar or leach into the process water. These inorganics can negatively affect the combustion characteristics or require additional downstream treatment to mitigate environmental risks. Furthermore, the aqueous phase contains a variety of dissolved organic compounds some of which may be inhibitory or difficult to degrade which complicates its treatment and potential reuse [233]. When processing MSW, there are components such as plastics rubber, synthetic textiles, etc. that are not significantly degraded [216]. As a result, the applications of MSW solid chars may need to be used differently than biomass derived chars. Lastly, scalability and economic viability of HTC remain

907 uncertain. Limited commercial-scale deployment exists, and questions remain regarding the cost
908 of reactor materials, heat recovery, process integration, and the market for hydrochar products.

909 *2.3.2 Hydrothermal liquefaction (HTL)*

910 Hydrothermal liquefaction (HTL) process can convert biomass, including the organic fraction of
911 MSW, into a crude-like bio-oil under subcritical water conditions, typically 260-375 °C and 10-
912 25 MPa [234-236]. Unlike pyrolysis and gasification, HTL operates in an aqueous medium,
913 making it especially suitable for wet feedstock without requiring energy-intensive drying. The
914 main products are biocrude oil, an aqueous phase rich in organic compounds, gaseous byproducts
915 (mainly CO_2), and solid char and ash residues [237].

916 HTL mimics natural petroleum formation on a vastly accelerated timescale by depolymerizing and
917 solubilizing organic polymers such as cellulose, hemicellulose, proteins, and lipids. The process
918 involves a series of reactions including hydrolysis, dehydration, decarboxylation, and cleavage of
919 carbon-nitrogen bonds [238]. When applied to MSW, HTL effectively reduces its volume and
920 converts its energy-rich organic fractions (*e.g.,* organic fraction, plastic) into a transportable and
921 upgradable biocrude. Importantly, HTL is tolerant of feedstock variability, accommodating a mix
922 of food waste, paper, yard waste, and biosolids, though optimal performance depends on proper
923 control of operating parameters such as temperature, residence time, and pH [239].

924 Macromolecular components of MSW, such as cellulose, hemicellulose, lignin, proteins, and lipids
925 undergo distinct transformation pathways [234, 235, 240]. Carbohydrates primarily hydrolyze into
926 sugars and subsequently dehydrate into furans and organic acids, while lignin decomposes into
927 phenolic compounds through cleavage of ether and carbon–carbon linkages. Proteins contribute to
928 nitrogen-containing intermediates, including amines and heterocyclic compounds, which can later

be incorporated into the biocrude. Lipids, when present, typically yield long-chain hydrocarbons via hydrolysis and decarboxylation, contributing positively to fuel quality.

Secondary reactions play a critical role in determining product distribution. These include polymerization and condensation reactions that convert reactive intermediates into heavier oil fractions or solid char [241]. The balance between depolymerization and repolymerization reactions is strongly influenced by temperature, residence time, and the presence of catalysts or co-solvents [236]. Higher temperatures generally favor depolymerization and oil formation, while excessive severity can promote gasification and char formation [237].

Several studies have explored the performance of HTL on MSW, examining not only yield but also the quality of the resulting biocrude and the properties of the residual phases. For instance, HTL applied to the organic fraction of MSW digestate, comprising primarily of anaerobically digested food waste and sewage sludge, resulted in the production of a biocrude with enhanced energy density (up to 34 MJ/kg), significantly reduced moisture content, and moderate heteroatom levels [242]. Elemental analysis of the biocrude revealed carbon, hydrogen, nitrogen, and oxygen contents of approximately 68.2%, 9.2%, 5.8%, and 15.3%, respectively, with sulfur content being negligible [243]. These heteroatoms, particularly nitrogen and oxygen, are known to originate from proteinaceous and carbohydrate-rich components of the feedstock and pose challenges for downstream upgrading due to their impact on stability and emissions [242]. Pre-treatment methods such as de-ashing and aqueous phase recirculation have also been found to influence biocrude properties, with improvements in oil stability and reduction in inorganic contaminants [244].

Table 5 summarizes key data from selected studies on HTL of MSW, comparing temperature, time, elemental composition, heating value, and yields. These results provide insight into how process conditions affect the quality and energy density of HTL products. As shown in the HTL

literature comparison in Table 5, there is no consistent correlation between temperature, residence time, and the HHV of biocrude when DI water is used as the sole solvent. For MSW feedstocks processed in DI water, biocrude HHVs span a broad range (25.2–37.0 MJ/kg) across temperatures of 200–360 °C and residence times of 20–60 minutes. These variations appear to be more strongly influenced by differences in feedstock composition and product distribution than by a direct dependence on temperature or time. In contrast, experiments employing a 1:1 DI water:glycerol co-solvent system exhibit a more discernible relationship between temperature and biocrude quality. At 300 °C, HHV remain relatively stable (28.5–30.7 MJ/kg) across residence times of 15-45 minutes. However, increasing the temperature to 325–350 °C results in higher HHV (33.3–35.6 MJ/kg), accompanied by increased carbon content and reduced oxygen content in the biocrude. These findings suggest that, within the co-solvent system, temperature exerts a more pronounced and positive influence on biocrude energy content than residence time. The high HHVs in these studies confirm that HTL biocrude is energetically competitive precursor compared to other pathways. Across all studies, the nitrogen content remained moderately high 3-5 wt%, reflective of the proteinaceous nature of food and green waste within MSW. Sulfur content was generally low <0.6 wt%, reducing the risk of SO_x emissions upon combustion.

Recent studies have increasingly focused on HTL of real MSW feedstocks, enabling more realistic evaluation of process performance, product quality, and operational challenges. These investigations demonstrate that feedstock heterogeneity significantly influences reaction pathways, biocrude yield, and composition, particularly due to the presence of mixed organic fractions and inorganic contaminants such as alkali metals and chlorine. For instance, recent studies on real MSW have shown that inorganic species can affect phase partitioning, promote side reactions, and contribute to catalyst deactivation and increased heteroatom content in biocrude,

thereby complicating downstream upgrading processes [245, 246]. In addition, these studies report that HTL of real MSW generates more complex aqueous and oil phases containing higher concentrations of oxygenated and nitrogen-containing compounds, which further challenges product stabilization and refining [244]. Overall, these recent advancements highlight that while HTL offers strong potential for valorizing wet and heterogeneous MSW streams, effective implementation requires improved understanding of feedstock variability, inorganic behavior, and integrated upgrading strategies under realistic operating conditions. Successful implementation at-scale will require holistic consideration of the inorganic fraction of its influence on oil quality, wastewater burden, and solid residue utilization. Continued research into feedstock preprocessing, catalytic stabilization, and circular economy integration will be essential to unlock the full potential of HTL in sustainable waste management systems.

The presence of heteroatoms, particularly nitrogen and oxygen, poses challenges for downstream upgrading. Nitrogen compounds can lead to NO_x emissions during combustion and catalyst poisoning during hydrotreating, while oxygenated species reduce thermal stability and increase acidity. As a result, upgrading processes such as hydrodeoxygenation and hydrodenitrogenation are typically required to produce transportation-grade fuels [237, 242]. In addition, the aqueous phase generated during HTL contains a significant fraction of dissolved organic compounds, including short-chain acids, alcohols, phenols, and nitrogenous species. This phase often exhibits high COD, which can complicate wastewater treatment but also presents opportunities for energy recovery via AD or nutrient recovery [244, 247].

A critical challenge in HTL of MSW lies in managing the inorganic fraction of the feedstock. MSW typically contains non-biodegradable components such as glass, metals, ceramics, and mineral impurities, which are not reactive under HTL conditions and accumulate in the residual

998 solid phase or migrate into aqueous and oil fractions. Common inorganics such as sodium,
999 potassium, calcium, chlorine, phosphorus, and trace metals (*e.g.,* zinc, copper, iron) can
1000 significantly affect both process performance and downstream upgrading [248]. In the biocrude,
1001 alkali and alkaline earth metals (AAEMs) may promote emulsification, cause corrosion in
1002 upgrading reactors, and poison catalysts during hydrotreating. Their presence often necessitates
1003 additional demineralization steps such as solvent washing, adsorption, or ion exchange prior to
1004 catalytic upgrading [249]. In some cases, the solid residue can be processed into biochar or ash
1005 suitable for use as soil amendments or construction materials, particularly if heavy metal
1006 concentrations remain within regulatory limits [250]. Meanwhile, inorganics that partition into the
1007 aqueous phase can increase COD and toxicity, complicating wastewater treatment and limiting
1008 opportunities for reuse or nutrient recovery [247]. In some cases, the inorganic phosphorus in the
1009 aqueous phase could be recovered as struvite or phosphates, integrating HTL into nutrient recovery
1010 systems [251], however, these applications require careful leachate testing and compliance with
1011 environmental standards. Several mitigation strategies have been explored. Mechanical pre-sorting
1012 and size reduction can remove large non-reactive particles, while chemical pre-treatment such as
1013 acid washing can reduce ash-forming minerals before liquefaction. Additionally, recirculation of
1014 the aqueous phase has been shown to reduce the overall process water requirements, though care
1015 must be taken to avoid the buildup of inhibitory compounds or salinity [252]. Treatment strategies
1016 include biological processes (e.g., AD), advanced oxidation, and membrane separation. In some
1017 cases, nutrient recovery, particularly phosphorus as struvite, can enhance the overall sustainability
1018 of the process.

1019 Although recent research has focused on improving HTL performance through catalytic systems
1020 and co-solvents, the integration of HTL with other thermochemical and biological processes

represents a promising pathway for maximizing resource recovery. For example, coupling HTL with AD allows for the valorization of both solid and aqueous fractions, improving overall energy recovery [218, 222]. Similarly, integrating HTL upstream of gasification or catalytic upgrading can enhance feedstock uniformity and reduce tar formation[84].

1026 *Table 5: Characteristics of MSW at different conditions. NR indicates "not reported" in the literature while b.d. represents "below detection limit".*

Reactants			HTL condition		HHV, db (MJ/kg)	Bio-oil ultimate analysis, db (%)					Mass yield, db (%)			Ref.
Feedstock	Solvent	Catalyst	Temp. (°C)	Time (min)		C	H	N	S	O	Solid	Oil	Gas	
Real-MSW	DI water	No	320	20	37.00	77.67 ± 0.68	8.90 ± 0.14	1.50 ± 0.10	NR	10.18 ± 0.22	12.9	26.8	14.1	[253]
Real-MSW	DI water	No	350	15	30.15	62.82	9.39	2.94	NR	24.86	54.17	10.57	NR	[245]
Real-MSW	DI water	Yes	350	15	28.61	60.28	9.20	3.36	NR	27.17	37.80	17.62	NR	
Real-MSW	DI water	No	200	60	33.5	57.40	12.80	4.90	0.50	24.40	NR	NR	NR	[239]
Biogenic-MSW	DI water	No	320	60	26.09 ± 1.65	62.50 ± 3.56	6.44 ± 0.65	7.31 ± 1.11	0.02 ± 0.02	23.73 ± 2.82	NR	NR	NR	[246]
Real-MSW	DI water	No	340	60	27.00 ± 1.72	64.90 ± 4.02	6.24 ± 0.90	7.27 ± 1.62	0.04 ± 0.02	21.55 ± 2.53	20.6	18.0	20.9	
Real-MSW	DI water	No	360	60	25.24 ± 1.59	63.50 ± 4.12	5.55 ± 0.72	7.67 ± 1.53	0.05 ± 0.01	23.23 ± 3.12	NR	NR	NR	
Real-MSW	DI water	No	300	30	NR	NR	NR	NR	NR	NR	90.4	6.0	3.6	[254]
Real-MSW	DI water	No	320	30	NR	NR	NR	NR	NR	NR	87.7	8.2	4.1	
Real-MSW	DI water	No	330	30	NR	NR	NR	NR	NR	NR	87.5	8.7	3.8	
Real-MSW	DI water	No	350	30	31.0	74.0	8.3	1.9	b.d.	14.8	81.4	15.2	3.4	
Real-MSW	1:1 DI water:Glycerol	No	300	15	30.7	67.4	7.6	0.6	b.d.	24.4	72.2	24.5	3.3	
Real-MSW	1:1 DI water:Glycerol	No	300	30	28.5	61.1	8.1	0.3	b.d.	30.5	68.5	26.2	5.3	
Real-MSW	1:1 DI water:Glycerol	No	300	45	28.7	62.3	7.8	0.4	b.d.	29.5	64.8	31.1	4.1	
Real-MSW	1:1 DI water:Glycerol	No	325	15	33.3	71.0	7.4	0.6	b.d.	21.0	46.2	48.1	5.7	
Real-MSW	1:1 DI water:Glycerol	No	325	30	33.5	73.0	7.6	0.8	b.d.	18.6	42.1	53.2	4.7	
Real-MSW	1:1 DI water:Glycerol	No	325	45	33.4	73.2	6.8	0.7	b.d.	19.3	40.4	55.8	3.8	
Real-MSW	1:1 DI water:Glycerol	No	350	15	33.4	74.2	7.7	0.8	b.d.	17.3	33.6	59.3	7.1	
Real-MSW	1:1 DI water:Glycerol	No	350	30	35.6	77.0	6.8	0.9	0.2	15.1	33.3	60.2	6.5	
Real-MSW	1:1 DI water:Glycerol	No	350	45	34.6	77.0	7.3	0.4	b.d.	15.3	32.1	61.6	6.3	

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3 Conclusions and future recommendations

This review highlights the potential of thermochemical conversion processes as innovative solutions for managing MSW while simultaneously generating energy and value-added products. The advantages of these technologies over traditional incineration methods include enhanced energy efficiency, the production of high-quality fuels, and the integration of sophisticated pollution control measures. However, the inherent variability in MSW composition presents substantial challenges in optimizing these conversion processes. The variability in MSW composition, influenced by factors such as population density, economic activity, and seasonal fluctuations, necessitates comprehensive characterization efforts across diverse geographical regions. Future research should prioritize the development of standardized protocols for the systematic evaluation of MSW feedstocks to facilitate the optimization of thermochemical conversion technologies.

Table 6 exhibits distinct trade-offs of thermochemical conversion technologies in terms of efficiency, scalability, product quality, and environmental performance. Combustion remains the most mature and scalable technology but is limited to energy recovery. In contrast, gasification and pyrolysis offer greater flexibility in producing fuels and chemicals, though they require more stringent feedstock control and downstream processing. Hydrothermal processes, particularly HTL, demonstrate strong potential for wet MSW streams by eliminating drying requirements and producing energy-dense fuels, but challenges related to inorganics, upgrading, and process integration still remain. Overall, no single technology is universally optimal; instead, hybrid systems that combine preprocessing (e.g., HTC or torrefaction) with high-temperature conversion pathways may offer the most effective route for maximizing resource recovery from MSW.

Table 6: Comparative assessment of thermochemical conversion technologies for MSW.

Technology	Scalability	Feedstock flexibility	Product quality	Environmental impact	Key challenges	Overall assessment
Combustion	Commercial, large-scale	Very high (handles mixed MSW)	Low (no chemical products)	High emissions (NOx, dioxins) but controlled in modern systems	Low efficiency for material recovery, public perception	Mature, reliable but limited to energy recovery
Gasification	Demonstration –commercial	Moderate (requires preprocessing)	High (flexible fuel/chemicals)	Lower emissions than combustion; tar issues	Tar formation, feedstock variability, gas cleanup cost	Promising for chemicals and hydrogen production
Pyrolysis	Pilot–demonstration	Moderate (needs sorting/drying)	Variable (bio-oil instability)	Lower emissions; requires upgrading	Oil quality, heterogeneity, scale-up challenges	Flexible but still developing for MSW
Torrefaction	Pilot scale	Moderate	Moderate (improved fuel properties)	Low emissions	Limited energy densification for MSW	Best as preprocessing step
HTC	Emerging	High (wet feedstocks)	Moderate (solid fuel)	Lower emissions, potential carbon sequestration	Wastewater treatment, limited plastic conversion	Strong for wet MSW pretreatment
HTL	Pilot–early commercial	High (wet, mixed organics)	High (energy-dense oil)	Lower air emissions; wastewater concerns	Heteroatoms, upgrading, inorganics, cost	Highly promising for fuel production from wet MSW

An integrated waste management system incorporating various pretreatments is often necessary, including mechanical, biological, and heat treatments. The objective of such preprocessing is to enhance waste combustibility and maximize the recovery of recyclable materials. In addition to these pretreatment methods, torrefaction can also be employed to reduce moisture content and produce MSW-derived fuel for subsequent thermochemical conversion. This integration of low temperature technologies such as HTC and HTL with traditional thermochemical conversion methods presents a promising avenue for improving feedstock quality. Future work should focus on specific hybrid system configurations, such as: (i) HTC coupled with gasification to improve feedstock uniformity and reduce tar formation, (ii) HTL integrated with catalytic upgrading or refinery co-processing to produce transportation-grade fuels, (iii) HTL combined with AD to valorize aqueous byproducts and enhance overall energy recovery, and (iv) pyrolysis systems coupled with catalytic reforming to improve bio-oil stability and quality. These targeted configurations provide a clearer pathway toward scalable and efficient MSW valorization systems.

Future studies should also explore the synergistic effects of these integrated approaches, with a focus on optimizing operating parameters to maximize efficiency and reduce pollutant formation.

Investigating these pathways will require experimental validation using real MSW feedstocks instead of synthetic and/or part of MSW, alongside techno-economic assessments to evaluate their feasibility and scalability.

While parametric and exploratory investigations of reaction conditions and various technologies are essential, there is an apparent gap in current literature that looks holistically at the impacts such systems could have. As much care should be taken into characterization, remediation, and demonstration of safe wasted disposal, greater attention must be given to key unresolved challenges, including: (i) the behavior and partitioning of inorganic species such as alkali metals, chlorine, and heavy metals and their impacts on corrosion, fouling, and catalyst deactivation; (ii) the upgrading of intermediate products such as bio-oil and biocrude, particularly with respect to heteroatom removal and fuel stability; and (iii) the treatment and valorization of aqueous byproducts from HTL and HTC, including opportunities for COD reduction, nutrient recovery, and integration with biological systems such as AD.

Further, the challenges associated with emissions control, particularly with respect to harmful pollutants generated during conversion processes, cannot be overlooked. Investment in advanced emission control technologies and the implementation of rigorous monitoring protocols will be critical to ensure compliance with environmental regulations and to build public trust in WtE facilities. In parallel, there is a growing need for integrated techno-economic and life-cycle assessment studies that evaluate entire systems rather than individual processes, incorporating feedstock variability and regional waste management conditions. Additionally, the application of digital tools such as machine learning and advanced process modeling offers promising opportunities for improving process control, optimizing operating conditions, and enhancing system reliability.

In conclusion, while the thermochemical conversion of MSW shows great promise for sustainable waste management and energy recovery, continued research must move beyond isolated process evaluation toward integrated, scalable, and system-level solutions. Collaborative efforts among researchers, policymakers, and industry stakeholders will be critical to promote innovation and facilitate the broader adoption of effective WtE strategies.

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