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Optimizing Municipal Solid Waste Pyrolysis for Sustainable Fuel Production: A Review of Technologies and Operating Parameters

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Abstract

Municipal solid waste (MSW) is a growing global challenge driven by urbanization, consumption, and limited landfill capacity. Pyrolysis offers a promising route to reduce volume while recovering fuels and chemicals. This review synthesizes recent advances in MSW pyrolysis, emphasizing operating parameters, reaction mechanisms, and process optimization. We examine catalytic systems, product distribution, and how source-segregation shifts feedstock composition. Industrial case studies—including failures—are used to surface practical constraints. Beyond technology, economic viability, regulatory compliance, and public acceptance are critical for deployment. We conclude with research priorities to bridge lab-scale progress and sustainable, industrial implementation.

Keywords: Municipal solid waste (MSW); Pyrolysis; Waste-to-energy; Bio-oil; Renewable fuels; Feedstock composition; Energy recovery; Circular economy.
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1. Introduction

As fossil-fuel reserves decline and their environmental impacts become clearer, research into alternative energy sources has accelerated. MSW and other low-grade fuels can be converted to bio-oil (pyrolysis oil), which can then be used for energy. Since the early 1900s, numerous studies have sought to optimize fuel production from MSW (Municipal Solid Waste). Pyrolysis is one of the most promising processes for this purpose.[1,2] Pyrolysis addresses limitations of alternative methods and can produce high-quality bio-oil while reducing production costs.[3–5] Recent review articles have examined MSW management and thermochemical conversion from different perspectives. Sipra *et al*. focused on MSW pyrolysis for bio-fuel production, emphasising the influence of individual waste components and catalyst selection.[3] Other works assessed waste-to-energy technologies more broadly, often prioritising incineration and integrated WtE plants rather than stand-alone pyrolysis units.[6–8] Additional reviews concentrated on specific streams such as food waste, paper sludge or biomass residues, or on generic biomass pyrolysis instead of real mixed MSW.[9,10] However, these studies do not provide a systematic comparison of slow, intermediate and fast MSW pyrolysis technologies that simultaneously considers feedstock composition, operating windows, product quality for fuel applications and lessons from pilot and industrial deployment.

Imports of crude oil have become difficult in recent years due to rising oil prices, the volatile political environment in the Middle East and the unpredictability of the global oil market. The combustion of fossil fuels harms the environment—soil, water, and air. Fossil-fuel use contributes to climate change. Even small changes in climate can negatively affect agriculture around the world.[11,12] The combustion of fossil fuels produces energy and chemical compounds, which results in the release of various greenhouse gases such as carbon dioxide, nitrogen oxides and other toxic volatile compounds into the atmosphere.[13,14] Studies conducted show that the combustion of fossil fuels results in a net increase of 10.65 billion tons of atmospheric carbon dioxide annually.[15]

This article examines the global MSW situation to highlight the necessity of pyrolysis as a sustainable approach essential for global ecology and development. Annually, approximately 1.9 billion tons of MSW are produced

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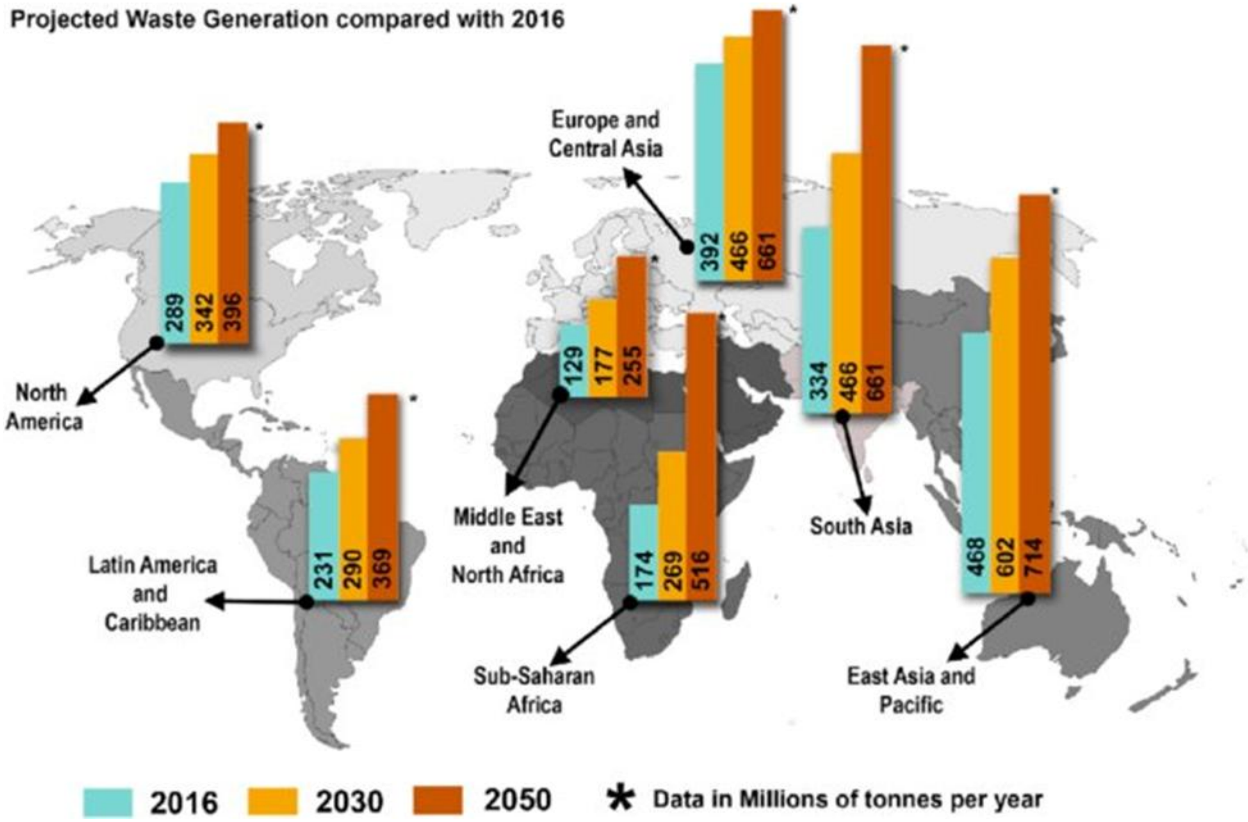

Fig. 1: Annual waste generation and its prediction in near future in the different regions of the world. Reproduced from.[18]

worldwide, equating to about 218 kg per person each year.[16] Literature data indicate that 19% of collected MSW is recycled, 11% is used in energy recovery processes, and the remainder is sent to landfills.[17] Owing to extensive plastic usage, World Bank statistics show that between 8% and 12% of total MSW globally is plastic waste, with projections indicating an increase to 9-13% by 2025, varying geographically.[18] In Europe, although efforts have led to the recovery of 50% of plastic waste, the remainder continues to be discarded, leading to substantial environmental impacts.[19] According to 2022 data, Sweden generated 4.5 million tons (460 kg/person) of MSW annually, with 32% recycled, 15% biologically treated, and 52% utilized for energy recovery.[6–8] Additionally, considering the MSW management situation in Europe, Finland also contributes significantly through effective waste management and energy recovery initiatives, further underscoring regional efforts toward sustainable practices. In the European Union, extensive source-segregation policies have significantly modified the composition of residual MSW, typically reducing the biogenic fraction and increasing the relative share of plastics and packaging materials.[20] Therefore, this review emphasises mixed MSW and its core segregated fractions, while non-MSW or industrial by-products are treated only peripherally to maintain relevance to municipal solid waste management. Polyvinyl chloride (PVC) is common in the dry part of municipal waste containing 90% chlorine.[21–23] Chlorine is catastrophic to health and the environment, so MSW must be carefully recycled to overcome the negative effects. Referring to the Middle East, Saudi Arabia is the second largest waste management country, producing approximately 6 million metric tons of plastic annually.[18] For the Asian region, China has 81.64% average physical combustible and 18.36% non-combustible materials. In China, residents often do not adequately separate MSW, and it is frequently mixed with food waste. Food waste contributes soluble chlorides and has a relatively high salt content. Because of this, the characteristics of MSW in China have low calorific value and high moisture content.[24] In general, the moisture content of MSW in America and Europe (only 10-30%) is lower compared to China.[8] This is due to the variable climatic conditions and lifestyle. However, in Taiwan, MSW consists of paper (28.95%), cellulose fabric (8.11%), garden waste (3.10%), food (23.18%), plastic (19.59%), leather and rubber (0.43%), metals (7.89%), glass (6.98%) and ceramics, land ma00terials and other (1.77%). Literature shows that paper is the major component of paper waste MSW.[9,10] Paper waste has a high heating value of about 17 MJ/kg and thus has the potential to be converted into commercial fuels.[25] Thus, it can be seen that MSW utilization is a serious concern worldwide and research is directed towards developing improved and cost effective technologies to solve this problem.[8,26] Fig. 1 illustrates annual waste generation trends and future

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projections across various global regions, demonstrating the urgency of adopting sustainable waste-to-energy technologies such as pyrolysis.

Analyzing the data on the movement of hazardous waste, we can conclude that the volume of generated waste in 2022 compared to 2021 increased by 83.5% globally.[27]

In many upper-middle-income countries, MSW management still relies heavily on landfilling, with limited diversion to recycling and energy recovery. As an illustrative example, official statistics for Kazakhstan report annual MSW generation of approximately 4.5 Mt, while only a minor share is currently recycled or used for energy recovery, and roughly one fifth of registered landfills meet environmental and sanitary requirements.[28,29] National policy documents set targets for universal access to waste collection services and a substantial increase in recycling rates, but similar gaps between policy goals and real performance are observed in other transition economies across Eastern Europe, Central Asia and parts of the Middle East and North Africa. Hence, rather than focusing exclusively on the Kazakhstani context, this review uses it as a representative case to formulate recommendations that are transferable to a wide range of countries facing comparable institutional, economic and technical constraints. Fig. 2 shows the total volume of municipal solid waste generated in Kazakhstan in 2022, highlighting the scale of the national waste management challenge.

Recent segregation policies in the European Union and other regions have significantly altered MSW composition, resulting in higher shares of plastics and reduced biogenic fractions.[20] This shift underscores the importance of focusing on mixed MSW and its principal fractions (plastics, organics, paper, textiles), which are the actual feedstocks encountered in practice. Accordingly, this review emphasizes comparative evaluation of pyrolysis technologies applied to mixed MSW, rather than unrelated waste streams such as sludge or agro-residues.

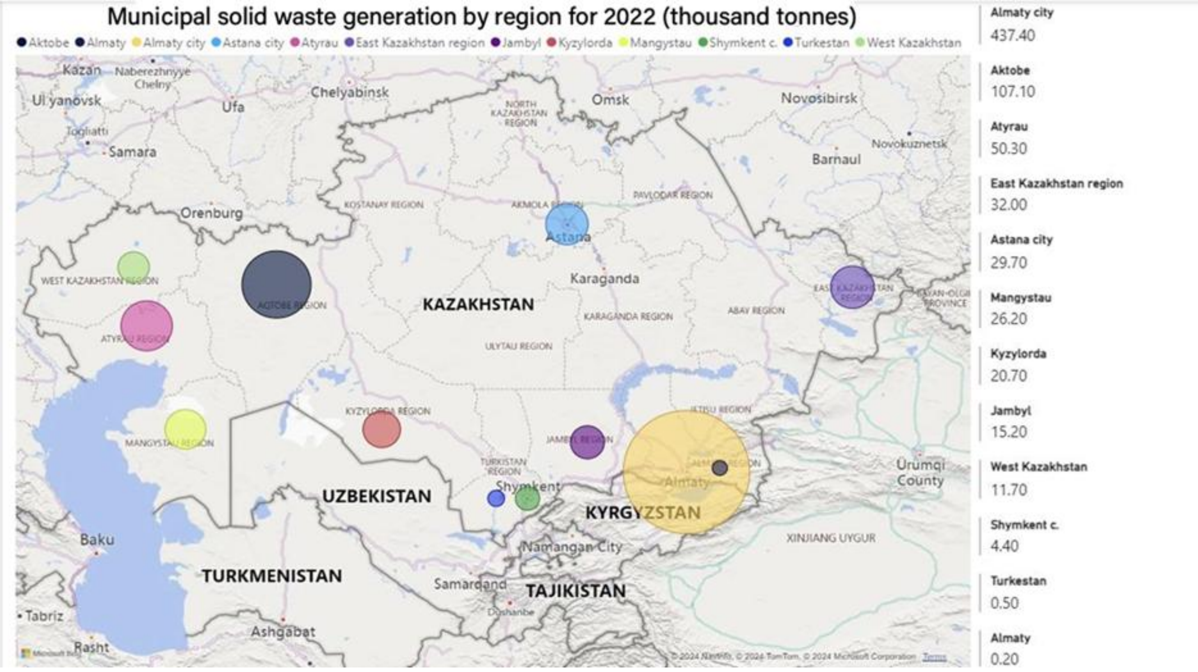

Fig. 2: Volume of municipal waste generation for 2022 in Kazakhstan. Reproduced from.[30]

Unlike previous reviews, this paper focuses exclusively on post-sorted mixed MSW and its main fractions (plastics, food waste, paper, textiles), rather than biomass or other wastes. It introduces quantitative comparison of bio-oil characteristics (Table 1), defines operating and heating rate bands (Tables 2, 4), and includes catalyst placement strategy (Table 9). Furthermore, it integrates case-based industrial insights and implementation challenges (Tables 10–11), contributing a decision-support tool for process and system design.

Compared to Lee *et al*. (2020), which emphasizes co-pyrolysis synergy between MSW fractions, our review concentrates on real-world mixed MSW post-separation.[31] Lu *et al*. (2020) narrows in on slow pyrolysis; our review compares slow, intermediate, and fast pyrolysis with consistent reference to heating rate regimes.[32] Lamba *et al*. (2025) provides a broad overview of plastic pyrolysis, while we focus on plastic-rich MSW as part of the actual urban waste

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stream, integrating other fractions and their effect on product quality.[33] Additionally, this paper introduces a structured industrial decision matrix and a commercialization roadmap absent from those prior works.

To ensure comprehensive coverage, literature was retrieved primarily from the Web of Science database, with complementary searches in Scopus and ScienceDirect. Keywords included "municipal solid waste pyrolysis," "MSW fast pyrolysis," "bio-oil from MSW," "catalytic pyrolysis," and "plastic-rich MSW." The search focused on peer-reviewed publications between 2015 and 2025. Inclusion criteria required that studies addressed MSW or its major fractions (plastics, food waste, paper, textiles) and reported relevant process data such as operating conditions, product yields, or bio-oil characteristics. In total, approximately 200 papers were screened, of which ~140 studies met the criteria and were synthesized in this review.

This structured approach provides both breadth and focus, ensuring that the analysis highlights the most relevant evidence for MSW pyrolysis technologies.

2. Literature search methods

The literature survey underlying this review was conducted between January 2023 and October 2025 using the Scopus, Web of Science, ScienceDirect and Google Scholar databases, as well as the Engineered Science publisher's journal platform. The primary time window covered the period 2000–2025, with earlier seminal works on pyrolysis included when necessary to clarify fundamental concepts.

Search queries combined terms related to municipal solid waste and pyrolysis technologies, for example: "municipal solid waste" AND pyrolysis; "MSW" AND ("fast pyrolysis" OR "intermediate pyrolysis" OR "rotary kiln" OR "microwave pyrolysis"); "mixed municipal waste" AND "co-pyrolysis"; "plastic waste" AND catalytic pyrolysis; "bio-oil upgrading" AND ("MSW" OR "solid waste"). Additional keywords such as "fluidized-bed reactor", "spouted-bed reactor", "fixed-bed", "thermo-economic analysis" and "waste-to-energy" were used to identify studies relevant to reactor design and techno-economic performance.

Publications were screened based on title and abstract, and full texts were then evaluated according to their relevance to mixed MSW or realistic MSW-derived streams (including refuse-derived fuel and source-segregated fractions). Priority was given to peer-reviewed journal articles reporting quantitative data on feedstock composition, operating conditions, product yields and properties, as well as to review articles that synthesise broader experimental evidence. Grey literature, such as technical reports and policy documents, was used selectively to provide context on waste generation trends, regulatory frameworks and national case studies.

3. Physico-chemical characteristics and structure of heating oil

The conversion of municipal solid waste into heating oil is considered an important substitute for traditional fossil fuels due to growing concerns about long-term environmental and climate impacts. As a promising energy, synthetic fuels are expected to partially replace petroleum-based liquids and can be produced by thermal conversion methods typically consisting of pyrolysis, thermal decomposition, gasification, and liquefaction.[34,35] Thermal decomposition is an almost simple method of converting feedstock into synthetic gas and oil. However, the disadvantages of this method are low efficiency, emissions and ash handling, which causes environmental problems and limits its wide application. Gasification is an interesting technology to produce environmentally friendly gases and fuel products.[36,37] However, gasification requires large investment in equipment, and the resulting gases are difficult to store and transport and require immediate use. In addition, gasification produces unwanted tars, which are the most problematic by-products in any gasification system, resulting in production disruptions.[38,39] In contrast, liquefaction is a process of converting waste to energy products at relatively low temperatures (about 300 °C) and high pressure (520 MPa), which can be used to convert high moisture biomass to bio-oil, but this method is not suitable for processing some municipal solid wastes.[40–42] The requirement of high pressure also leads to high cost and low efficiency of the process. Thus, pyrolysis appears to be the most efficient thermal decomposition method for processing feedstock in an oxygen-free atmosphere into liquid bio-oil, solid biochar and synthetic gas. In this regard, pyrolysis has recently attracted attention because of its potential cost-effectiveness.[43,44] In addition, interesting synergistic interactions have been reported in the joint valorization by pyrolysis of different feedstocks as biomass, plastics or coal mixtures,[10,21,45–47] in fact, pyrolysis has a higher thermochemical conversion efficiency compared to the other thermal conversion methods, *i.e.*, torrefaction and gasification technologies.[48–50]

Bio-oil derived from municipal solid waste exhibits considerable variability in its physical and chemical properties, influenced largely by feedstock composition and the specific conditions of pyrolysis such as temperature, heating rate, and the reactor type. The primary physico-chemical properties relevant for evaluating bio-oil quality as a fuel include heating value (calorific value), elemental composition, and density.

The heating value, typically expressed in megajoules per kilogram (MJ/kg), directly indicates the energy content of bio-oil, making it a critical parameter for assessing fuel potential. Elemental composition (carbon, hydrogen, oxygen, nitrogen, and sulfur content) impacts the combustion efficiency, emissions profile, and corrosiveness of bio-oils. Density affects handling and storage logistics, influencing the fuel's transportability and compatibility with existing infrastructure.

Table 1 summarizes relevant results from recent literature on bio-oil produced from different types of MSW under varying pyrolysis conditions, providing a comparative perspective on how feedstock and process parameters influence key oil characteristics.

The exact percentage composition of the MSW feedstock was not reported in several of the studies summarized in Table 1. To address this, the typical composition ranges of municipal solid waste presented in Table 7 can be used as a reference. In general, MSW consists of plastics (10–25 wt.%, occasionally up to ~30% in urban areas), food and organics (20–40 wt.%), paper (10–20 wt.%), textiles (2–5 wt.%), and wood (5–15 wt.%). These proportions influence the quality and yield of the pyrolysis products and help contextualize the bio-oil properties listed in Table 1.

Table 1 focuses on mixed MSW and its principal fractions (plastics, organics/food, paper, textiles), which remain the dominant feedstocks for pyrolysis after source-segregation practices. Other waste streams such as sewage sludge, rubber, or agricultural residues are excluded here, as their inclusion could obscure the evaluation of pyrolysis performance for municipal solid waste itself.

Table 1: Physico-chemical characteristics of liquid bio-oils obtained from key MSW fractions (post-segregation).

Feedstock (MSW fraction)	Typical pyrolysis conditions	HHV (MJ/kg)	C (%)	H (%)	O (%)	N (%)	S (%)	Density (kg/m³)	Moisture (%)	Ash (%)	pH	Ref.
Mixed MSW	500 °C, fluidized bed, fast	23.5	58.7	7.8	32.0	1.0	0.5	1120	15.0	0.2	3.8	[62]
Plastic-rich MSW	550 °C, catalytic fixed bed	35.2	77.2	11.5	10.5	0.3	0.5	980	1.2	0.05	4.7	[63]
Biomass-rich MSW (organics/paper)	500 °C, fixed bed, slow	19.7	54.0	6.3	38.8	0.7	0.2	1200	25.0	0.5	3.2	[64]
Food waste	450 °C, rotary kiln	20.1	50.5	7.0	40.5	1.5	0.5	1230	28.0	0.8	2.8	[28]
Paper/Cardboard	500 °C, fixed bed	18.5	52.3	5.7	41.2	0.7	0.1	1190	22.0	0.3	3.5	[65]
Textiles (MSW)	550 °C, microwave	24.3	63.4	7.9	27.8	0.8	0.1	1075	12.5	0.1	4.1	[66]

Many feedstocks ranging from woody and herbaceous biomass (sawdust, hardwood, needles and sugarcane) to municipal solid waste (used tires and plastic), food industry residues (soybean cake and waste oil) and industrial waste (sewage sludge and waste paper) have been pyrolyzed to produce value-added energy products.[51–53] Recently, significant progress has been made in the development of pyrolysis technologies,[54] moreover, the produced synthetic oils can be transported and used in biorefineries and subsequently refined to produce transportation fuels.[55,56]

In addition to the type and properties of the feedstock affecting the bio-oil yield, the bio-oil yield is significantly affected by the operating conditions such as process temperature/time, heating rate and carrier gas flow rate.[57] Since the final temperature and heating rate play an important role in bio-oil yield and are controllable in the pyrolysis process, this review focuses on the effect of operating temperature and heating rate on bio-oil yields.[58] Since the operating temperature and heating rate mainly depend on the heating sources (*e.g.*, direct heating, solar, infrared, and microwave (MW) radiation), this review also considers the effect of the heat source. For example, the pyrolysis temperature and heating rate, which depend on the heat source, affect the pyrolysis products yield and their quality. Compared with conventional direct heating, MW and solar heating can significantly increase the pyrolysis temperature and pyrolysis heating rate.[59] Wang *et al*.[4] improved the yield and quality of bio-oil by using MW heating combined with microwave-assisted SiC absorbent.

There are several articles that discuss operating parameters that affect the yield of synthetic oil. Bio-oil yield and composition are determined by reactor design, feedstock type/characteristics such as mineral content, particle size and moisture content, and operating parameters including heating rate, final pyrolysis temperature, residence time and inert gas supply.[60] When the feedstock is decomposed using a heat energy source, temperature is the most important parameter characterizing the reaction conditions.[61,62] Above 550 °C, severe decomposition occurs, causing bio-oil cracking and gas product formation. Temperature control in the reactor was found to regulate the secondary decomposition processes towards the production of high quality liquids. The oil yield was significantly dependent on the final temperature.[61] The maximum oil yield was reached at temperatures between 450 and 550 °C and then decreased.[63,64] The volatile yield can be increased due to rapid fragmentation caused by high heating rate. The higher volatile yield may be due to decomposition of excess resins at high heating rates. Rapid endothermic decomposition creates an abundance of volatiles and in turn minimizes the time available for secondary reactions such as repolymerization of raw materials and volatiles.[65]

It is desirable to evaluate the cost-effectiveness of pyrolysis systems for potential scale-up and commercialization. In particular, the properties of the feedstock, such as moisture content, inorganic and organic composition, and heating characteristics, significantly influence the efficiency of thermal degradation and product distribution.

Although significant technological progress has been achieved and numerous pyrolysis experiments have been conducted, there is still debate regarding the fundamental degradation mechanisms that control product yields. For example, the effects of heating rate and operating temperature on bio-oil yield remain controversial. Some studies report that increasing temperature and heating rate leads to higher synthesis gas production and lower oil yields, while others claim that the oil yield remains relatively stable.[66] These inconsistencies are likely due to secondary reactions, interfacial molecular processes, and differences in reactor design and operating parameters.

Microwave-assisted pyrolysis (MWP), which offers advantages such as volumetric heating and rapid thermal response, is discussed in detail in a separate section of this article.

Further research is needed to clarify the mechanisms governing oil formation, optimize process parameters, and improve the energy efficiency of waste-to-fuel technologies.

4. MSW pyrolysis technology development

Pyrolysis technologies have been widely investigated as effective methods to convert municipal solid waste into valuable energy products, mainly liquid bio-oil, gaseous fuels, and solid char. To provide a clearer comparison and avoid overly descriptive repetition, the main types of MSW pyrolysis technologies are summarised in Table 2. The table highlights operating windows, strengths, and limitations, alongside a critical assessment of their industrial relevance.

Table 2 shows that slow pyrolysis is technologically simple and robust but yields low amounts of oil, making it unsuitable for large-scale fuel production. Intermediate systems such as rotary kilns or microwave reactors offer higher flexibility, yet face limitations due to energy consumption, mechanical wear, or poor scalability. Fast pyrolysis remains the most efficient option for liquid fuel production from MSW, though it requires strict feedstock pre-treatment and advanced control systems.

4.1. Slow pyrolysis (Fixed-Bed Pyrolysis)

This technology has been extensively studied due to its simplicity, cost-effectiveness, and robustness, making it particularly suitable for processing heterogeneous and bulky MSW materials such as wood residues, agricultural wastes,

Table 2: Comparative overview of MSW pyrolysis technologies with critical assessment.

Technology	Typical reactor types	Operating window	Target product	Strengths	Limitations / Critical remarks	Industrial readiness	Ref.
Slow pyrolysis	Fixed-bed	350–600 °C; low heating rate; minutes–hours	Char	Simple, robust, low cost; tolerant to heterogeneous feed	Very low oil yield; tar issues; poor throughput; not scalable for fuels	Mature for char production; limited for fuels	[67–71]
Intermediate pyrolysis (rotary kiln)	Rotary kiln	400–700 °C; moderate rate; residence time minutes–1 h	Balanced oil/char/gas	Handles bulky, heterogeneous MSW; continuous operation	High energy consumption; mechanical wear; tar and gas-cleaning challenges	Commercial-scale possible in WtE	[2,72–75]
Intermediate pyrolysis (microwave)	Microwave reactor	400–800 °C; fast heating; residence time minutes	Bio-oil	Rapid heating; better oil quality (low O, less tar)	High capital cost; scale-up problems; feed must be homogeneous in dielectric properties	Pilot/demonstration stage	[76–79]
Fast pyrolysis	Fluidized-bed, spouted-bed	450–600 °C; >1000 °C/s; vapour residence <2 s	Bio-oil	Highest oil yield; suitable for large-scale continuous operation	Requires dry, size-reduced feed; oil unstable without upgrading; complex controls	Pilot-to-industrial level, early commercial	[80–87]

Note: Low heating rate in slow pyrolysis typically refers to 0.1–10 °C/min, moderate heating rate in intermediate pyrolysis to 10–100 °C/min, while fast pyrolysis exceeds 1000 °C/s.

municipal biomass, and other similar waste streams.[69]

Fixed-bed reactors typically consist of a stationary reactor chamber loaded with feedstock.[67,68] Heat is supplied externally through electrical heaters or gas-fired burners, allowing slow and controlled heating.[69] The feedstock is heated in an oxygen-limited or inert atmosphere, gradually decomposing to yield solid char, liquid bio-oil, and gaseous products. The simplicity of the reactor design, along with its low mechanical complexity, contributes to lower capital investment and operational ease, making it accessible for small to medium-scale installations. The layout of slow pyrolysis process is shown in Fig. 3.

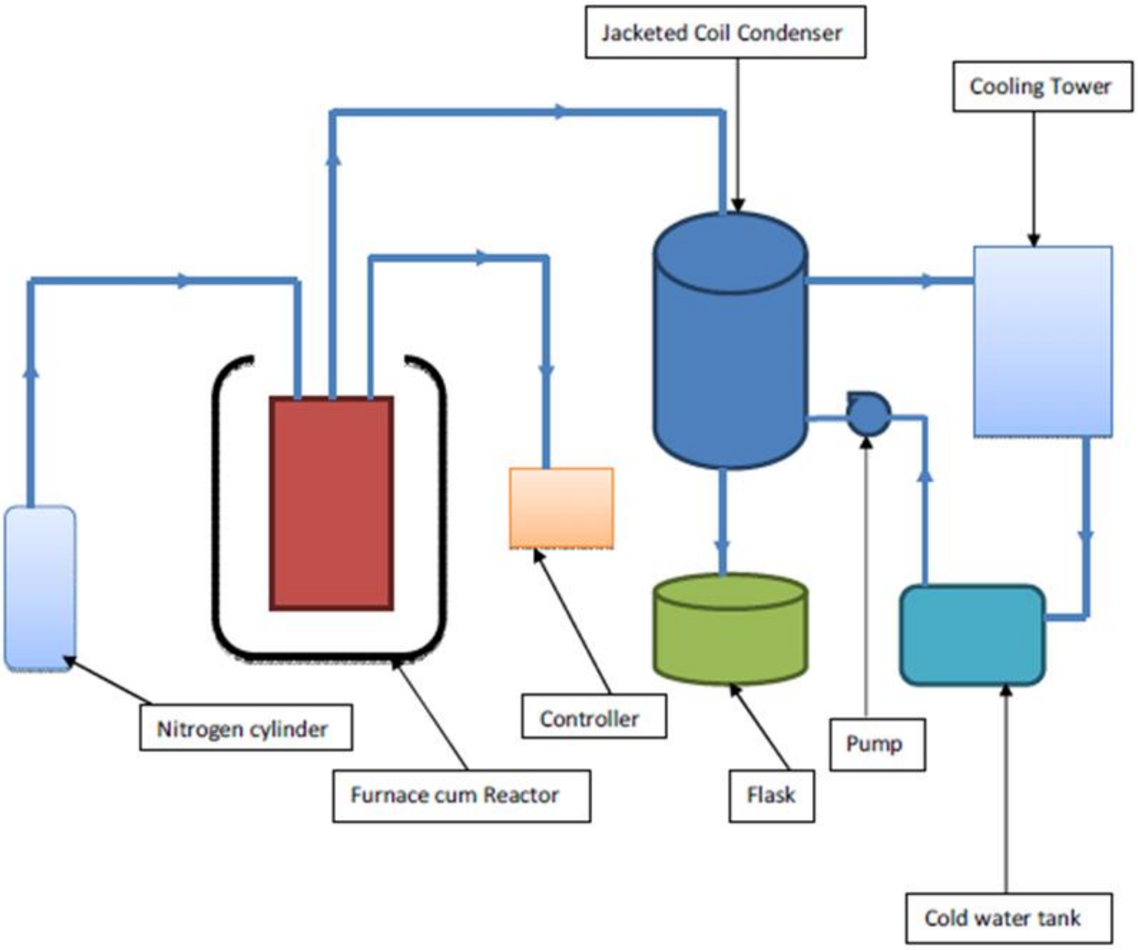

Fig. 3: General layout of slow pyrolysis process.[88]

Slow pyrolysis primarily aims at the production of high-quality char, which accounts for approximately 30–40% of the output.[70] Bio-oil yields usually range between 25–35%, and gaseous products, primarily consisting of CO, CO_2, CH_4, and H_2, are about 25–35%.[71] The produced char exhibits excellent characteristics for applications such as soil amendment, activated carbon, and pollutant adsorption. Typical product distributions for slow pyrolysis of MSW components are summarised in Table 3.

Slow pyrolysis consistently produces a high share of solid char (30–40%) but only 25–35% oil. This technology is economically justified only when char is the target product (biochar, activated carbon). Its limitations (tar formation, low throughput) make it unsuitable as a stand-alone route for MSW-to-fuel conversion. While Table 3 presents data for individual fractions for comparison, the row for *Mixed MSW* provides representative yields relevant to this review's focus.

Table 3: Typical Product Yields from Slow Pyrolysis of MSW Components.

Feedstock Type	Temperature (°C)	Char (%)	Bio-oil (%)	Syngas (%)	Ref.
Woody biomass	500	35–40	25–30	30–35	[89]
Agricultural residues	450	30–35	30–35	30–35	[90]
Paper waste	550	25–30	30–35	30–35	[10]

Slow pyrolysis offers numerous advantages due to its inherent simplicity and practicality. One significant advantage is the straightforward reactor design, which requires minimal mechanical components and operational complexity, making it particularly suitable for smaller-scale or decentralized waste management facilities.[91] This technology can efficiently process a broad spectrum of feedstocks, including large particle sizes and mixed waste streams, offering flexibility in waste management practices. Another notable benefit of slow pyrolysis is the production of high-quality char with desirable physicochemical properties, including high carbon content, large specific surface area, well-developed porosity, abundant surface functional groups (–OH, –COOH, –C=O), high cation exchange capacity, and alkaline character. These characteristics make the char suitable for multiple applications such as soil amendments (enhancing nutrient retention and pH regulation), activated carbon production, and pollutant adsorption in environmental management. Furthermore, the relatively lower initial capital investment, operational, and maintenance costs compared to more advanced pyrolysis technologies enhance its economic viability and accessibility.[70]

Slow pyrolysis is a well-established and cost-effective technology particularly suitable for decentralized waste management solutions, where the production of high-value char products is prioritized.[91] Continued research and technological advancements will further improve its efficiency, product quality, and broaden its applicability to diverse MSW streams.

The char produced through slow pyrolysis has extensive environmental applications including soil remediation, pollutant adsorption, and improving soil fertility as biochar. Additionally, the solid char can be used as a precursor for activated carbon production, offering economic advantages.[70] Beyond environmental uses, mineral-rich residues from thermal conversion processes have also been successfully employed as supplementary cementitious materials and composite binders in high-performance concretes and protective structures, as demonstrated for thermal power-plant wastes and composite binders with enhanced mechanical strength, reduced permeability and improved shock resistance.[92–94] Current research is increasingly directed towards optimizing operational parameters to enhance char quality, improve reactor efficiency, and reduce tar formation.[67,68] Further development in reactor design, such as staged pyrolysis systems or integrated post-treatment solutions, offers promising avenues for overcoming current technological limitations.

Despite robustness and low capital intensity, slow pyrolysis is ill-suited for large-throughput liquid-fuel production from mixed MSW due to inherently low oil yields and persistent tar formation.[1,95] Lab-scale reports often understate continuous tar management, hot-vapor filtration, and solids (char/ash) removal, which become limiting at scale and depress net liquid recovery.[49,96] The technology's industrial niche is therefore char-oriented (soil amendment/activated carbon) rather than oil-oriented; using slow pyrolysis as the lead route for bio-oil from mixed MSW is rarely economical without extensive upgrading. In integrated schemes, slow pyrolysis can play a complementary role for difficult residues, but should not anchor a fuels-centric MSW valorisation pathway.

4.2 Intermediate pyrolysis (Rotary Kiln and Microwave Pyrolysis)

Intermediate pyrolysis is positioned between slow and fast pyrolysis in terms of heating rates, reaction times, and product distribution, providing a balanced approach for efficient thermal conversion of municipal solid waste. This category encompasses mainly rotary kiln and microwave-assisted pyrolysis technologies, both distinguished by specific operational characteristics and unique advantages, suitable for diverse MSW feedstocks and varied end-use applications.[97–99]

Rotary kiln reactors are highly effective for processing heterogeneous MSW mixtures of varying size, density, and moisture.[2,72] Continuous mixing and rotation ensure efficient heat transfer and uniform pyrolysis products. Their ability to handle large particles and contaminants (metals, glass, stones) makes them suitable for large-scale facilities.[73,74] Moreover, their continuous operation enhances scalability and commercial viability for municipal waste treatment.

Microwave-assisted pyrolysis offers significant advantages, particularly due to rapid heat transfer and uniform temperature distribution within the feedstock.[77] This mechanism significantly reduces processing time compared to traditional methods, increasing overall throughput and process efficiency.[78] The rapid and selective heating provided by microwaves enhances product quality, yielding higher-quality bio-oils with lower oxygen content and reduced formation of undesirable by-products such as tar.[79,100] Additionally, the microwave process is more responsive and controllable, enabling rapid start-up and shutdown operations, making it suitable for applications where operational flexibility and fast response to feedstock variability are required.

However, despite these advantages, intermediate pyrolysis technologies also face certain limitations that must be considered. For rotary kilns, one challenge is relatively high energy consumption due to continuous rotation and heating of a large thermal mass, potentially impacting operational costs.[101] Additionally, significant mechanical wear can occur due to prolonged reactor rotation and abrasive feedstock materials, resulting in higher maintenance demands and operational downtime.

Microwave pyrolysis, despite its innovative advantages, also presents operational limitations, including high initial capital costs associated with specialized microwave generation and waveguide equipment.[102] Furthermore, microwave reactors generally require homogeneous feedstock with uniform dielectric properties for optimal energy absorption and efficient pyrolysis, posing challenges when processing highly heterogeneous MSW mixtures. Another technical constraint is related to scalability; microwave pyrolysis units currently demonstrate limitations in scaling to industrial-size operations due to the complexity of uniformly distributing microwave energy over large reactor volumes.

To clearly illustrate differences and complement textual information, a summary of rotary kiln and microwave pyrolysis operational parameters and product distributions is presented in Table 4.

Table 4: Typical Operational Parameters and Product Distribution for Rotary Kiln and Microwave Pyrolysis.

Parameter	Rotary Kiln Pyrolysis	Microwave Pyrolysis
Temperature Range (°C)	400–700	400–800
Heating Rate	~10–50 °C/min	~50–200 °C/min
Residence Time	Minutes to ~1 hour	Typically minutes
Feedstock Suitability	Highly heterogeneous, large particles	Homogeneous feedstock, smaller particles
Bio-oil Yield (wt.%)	35–45	40–60
Char Yield (wt.%)	25–35	15–30
Syngas Yield (wt.%)	25–35	25–35
Quality of Bio-oil	Moderate, high moisture content	Good, lower moisture and oxygen content
Complexity and Investment	Moderate	High
Scalability	Good	Moderate (limited by technical factors)
Reference	[74,103]	[77,104]

Critical assessment (Table 4):

- Rotary kilns tolerate heterogeneous MSW but suffer from high energy use and mechanical wear.
- Microwave pyrolysis improves oil quality (lower oxygen and moisture), but is capital-intensive and not yet scalable.
- Both approaches require robust gas cleaning and integration with upgrading processes to be viable at larger scales.

Future research and technological development directions for intermediate pyrolysis technologies include optimization of process parameters, improvements in reactor design to enhance energy efficiency, and effective integration with downstream processes (such as catalytic upgrading of bio-oils). Innovative research into microwave-absorbent materials and microwave distribution systems may address scalability and feedstock variability constraints, enhancing the commercial viability of microwave pyrolysis. For rotary kiln pyrolysis, continued development focuses on reactor durability, energy efficiency improvement, and reduction of operating and maintenance costs through advanced materials and reactor configurations.

In conclusion, intermediate pyrolysis techniques, including rotary kiln and microwave pyrolysis, offer a balanced approach between product quality, throughput, and operational complexity, potentially bridging the gap between slow and fast pyrolysis. Advancements in operational efficiency, feedstock versatility, and scalability will be crucial for broader commercial adoption and implementation in environmentally MSW management and renewable energy production.

Rotary kilns offer feed tolerance and continuous operation, but suffer from high energy consumption and mechanical wear, while microwave systems deliver improved oil quality yet face scale-up challenges and high capital costs. In practice, both technologies demand front-end sorting, drying, and robust gas cleaning to avoid tar fouling and corrosion. Industrial application of rotary kilns is feasible in waste-to-energy plants, whereas microwave pyrolysis remains largely pilot-scale.

4.3 Fast pyrolysis (Fluidized-bed and spouted-bed reactors)

Fast pyrolysis maximises liquid yields through very high heating rates and short vapor residence times.[80,81] Among the most widely used configurations for fast pyrolysis are fluidized-bed reactors and spouted-bed reactors,[82–84] both of which allow excellent heat and mass transfer due to intense mixing of solid particles and efficient contact between feedstock and heat source. The fast pyrolysis process is illustrated in the diagram in Fig. 4.

Fluidized-bed reactors consist of a bed of fine solid particles (typically sand or catalytic materials) that behave like a fluid when air or an inert gas is passed through them at sufficient velocity.[86] The feedstock is introduced into this bed, where it is rapidly heated to the desired temperature. The volatile products are carried away quickly by the fluidizing gas and rapidly condensed to form bio-oil, while non-condensable gases and char are separated.[71]

Spouted-bed reactors are similar in principle but use a central jet of gas to create a spouting action that circulates particles and feedstock in a toroidal pattern.[84] This

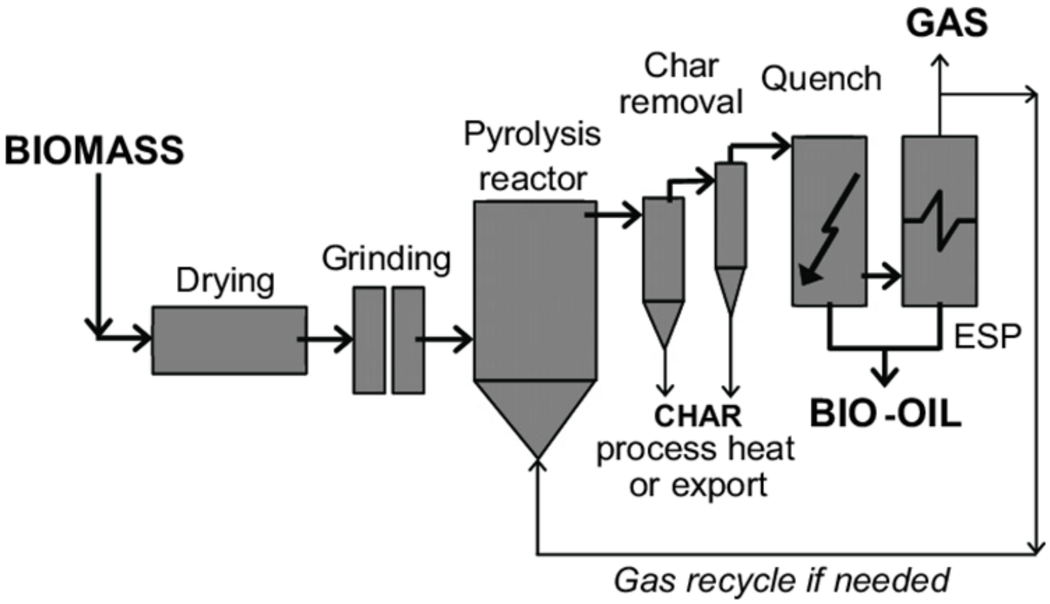

Fig. 4: Scheme of fast pyrolysis process. Reproduced from.[85]

configuration is particularly advantageous for handling sticky, fibrous, or large particles that may cause defluidization in conventional fluidized beds.

Both reactor types allow for precise temperature control, uniform heat distribution, and excellent scalability, making them suitable for industrial pyrolysis of MSW and biomass mixtures.[82–84]

Feedstock must be finely ground (usually <2 mm) to ensure rapid heat transfer, and moisture content is typically maintained below 10% to avoid excessive water in the bio-oil.[85,105]

Fast pyrolysis primarily aims at high bio-oil yields, typically ranging from 60% to 75% by weight, depending on feedstock and operating conditions.[106] The remaining products are char (10–20%) and syngas (10–20%).[107] The resulting bio-oil is a dark brown, low-viscosity liquid with high oxygen content, moderate heating value (16–19 MJ/kg), and water content of up to 25%.

The Table 5 summarizes typical product yields for fast pyrolysis of selected MSW components.

Table 5: Typical Product Yields from Fast Pyrolysis of MSW Components.

Feedstock Type	Reactor Type	Temperature (°C)	Bio-oil (%)	Char (%)	Syngas (%)	Ref.
Mixed MSW	Fluidized-bed	500	65–70	15–20	10–20	[4]
Plastic-rich MSW	Spouted-bed	550	60–65	10–15	20–25	[108]
Biomass (wood waste)	Fluidized-bed	500	70–75	12–15	10–15	[109]

However, the technology also faces several technical and economic challenges. First, the bio-oil produced is thermally and chemically unstable, requiring upgrading through catalytic hydrodeoxygenation or emulsification for long-term storage and engine use.[110,111] Second, feedstock must be finely ground and dried, increasing preprocessing costs.[4] Third, char separation and gas cleaning systems must be carefully engineered to avoid operational fouling and pressure drop. Finally, fluidized and spouted-bed systems are relatively complex and require advanced instrumentation and controls.

Fast pyrolysis has strong potential for deployment in integrated waste-to-energy systems, especially in urban regions with large volumes of MSW. Bio-oil derived from this process can be co-fired with fossil fuels, upgraded to transportation fuels, or used in distributed energy systems.[109] Moreover, the by-products - char and syngas - can be utilized as solid fuel or for electricity generation via gas engines and turbines, increasing the overall energy efficiency. Ongoing research focuses on: In-situ and ex-situ catalytic upgrading of bio-oil; Use of co-pyrolysis (*e.g.*, biomass + plastic) to improve oil properties; Integration with microwave-assisted heating or solar-driven pyrolysis; Advanced control systems for real-time monitoring and optimization.

The fast pyrolysis is a promising and rapidly developing technology for converting MSW into valuable liquid fuels. With advancements in bio-oil upgrading and reactor engineering, this method is expected to play a key role in future circular economy strategies and the transition to renewable energy systems.

Recent Engineered Science publications further illustrate how process parameters and catalytic systems can be tuned to improve bio-oil quality and yield from diverse feedstocks. Promsampao *et al.* optimised fast pyrolysis of palm kernel cake in a fluidized-bed reactor, demonstrating how particle size, carrier-gas flow and temperature jointly control liquid yield and fuel properties.[112] Pannucharoenwong *et al*. showed that natural zeolite and dolomite catalysts can increase the hydrocarbon content of products from sawdust pyrolysis, highlighting the role of inexpensive mineral catalysts in upgrading lignocellulosic feedstocks.[113] Singh and co-workers transformed waste plastics into petrochemical and diesel-range fractions via staged pyrolysis and upgrading, while Kapoor *et al*. evaluated co-pyrolysis of rice straw and groundnut shell, linking operating conditions to fuel properties of the resulting bio-oil.[114,115] Similar catalyst-driven optimisation was reported for spent coffee grounds, where the biomass-to-catalyst ratio significantly affected both bio-oil and char yields.[116] Together with studies on catalytic pyrolysis of plastic waste for diesel-engine fuels,[117] these results underscore the importance of matching catalyst type and loading to the specific MSW-derived fraction being processed.

The comparative analysis of slow, intermediate, and fast pyrolysis technologies highlights the diverse approaches available for the thermal conversion of municipal solid waste into valuable energy products. Each technology has specific operational principles, reactor designs, and product distributions that define its suitability for different applications and scales.

Slow pyrolysis, characterized by low heating rates and long residence times, primarily produces high-quality char. Its simplicity, cost-effectiveness, and ability to process a wide range of heterogeneous waste materials make it particularly suitable for decentralized or rural waste management systems, where solid char is the target product. However, its limitations in terms of low bio-oil yield and slow throughput reduce its attractiveness for large-scale energy recovery applications.

Intermediate pyrolysis, especially in rotary kilns and microwave-assisted systems, offers a balance between product yields and operational complexity. Rotary kilns are particularly effective for treating heterogeneous MSW without extensive preprocessing. Meanwhile, microwave pyrolysis stands out for its energy efficiency, rapid heating, and enhanced bio-oil quality, though its commercial application is still limited due to high capital costs and challenges in scaling.

Fast pyrolysis, particularly using fluidized-bed and spouted-bed reactors, delivers the highest bio-oil yields and is the most efficient method for large-scale MSW-to-liquid-fuel conversion. It offers the best energy recovery in terms of liquid product yield and can be integrated into existing energy infrastructure. However, it requires finely ground, dry, and relatively homogeneous feedstock, as well as advanced control systems, making it more complex and capital-intensive.

Based on the current technological maturity, scalability, and the need for high liquid fuel yield, fast pyrolysis emerges as the most optimal solution for large-scale valorization of MSW, especially in urban areas with high waste generation and access to preprocessing infrastructure. Nevertheless, a hybrid or integrated approach - combining pre-sorting, fast pyrolysis of organic fractions, and slow pyrolysis or rotary kiln treatment of residuals - could offer a more comprehensive and flexible waste management solution.

Slow pyrolysis is optimal for char-oriented applications, intermediate systems provide a compromise between oil and char but remain costly, while fast pyrolysis achieves the highest oil yields and scalability. However, without effective pre-sorting, drying, and upgrading, even fast pyrolysis faces operational barriers at the industrial level.

Table 6 shows general comparative characterisation of

Table 6: Comparative Summary of Pyrolysis Technologies for MSW Treatment.

Parameter / Feature	Slow Pyrolysis	Intermediate Pyrolysis	Fast Pyrolysis
Typical Reactor Types	Fixed-bed	Rotary kiln, Microwave reactor	Fluidized-bed, Spouted-bed
Heating Rate	Low (0.1–10 °C/min)	Medium (10–100 °C/min)	High (>1000 °C/s)
Operating Temperature (°C)	350–600	400–700	450–600
Residence Time	Long (minutes to hours)	Moderate (minutes)	Short (<2 seconds)
Main Product	Char	Balanced (bio-oil, gas, char)	Bio-oil
Bio-oil Yield (wt.%)	25–35	35–55	60–75
Char Yield (wt.%)	30–40	20–30	10–20
Syngas Yield (wt.%)	25–35	20–30	10–20
Feedstock Requirements	Low preprocessing	Moderate (moisture and size tolerance)	High (dry and finely ground)
Suitability for MSW	Very good (mixed, bulky waste)	Good (heterogeneous waste, flexible)	Best for organic and homogeneous waste
System Complexity	Low	Medium to High	High
Scalability	Medium	High (rotary kilns), Moderate (microwave)	High (especially fluidized-bed)

Parameter / Feature	Slow Pyrolysis	Intermediate Pyrolysis	Fast Pyrolysis
Capital Cost	Low	Moderate to High	High
Main Advantages	Simple, low cost, good char	Balanced yields, flexible feedstock handling	High bio-oil yield, fast processing
Main Limitations	Low oil yield, slow process	High maintenance (rotary), expensive (MW)	Complex, sensitive to feedstock quality
References	[118–120]	[97,121,122]	[4,123,124]

pyrolysis technologies for MSW processing. In summary, the optimal pyrolysis technology for MSW depends on the specific context, including feedstock composition, desired products, available infrastructure, and economic constraints. While fast pyrolysis offers the highest efficiency for bio-oil production, intermediate systems provide versatility, and slow pyrolysis remains a robust choice for char-focused applications. Future strategies should aim to tailor pyrolysis systems to local waste characteristics and energy needs, while also considering environmental impacts and economic feasibility.

Fast pyrolysis achieves the highest liquid yields (up to 60–75 %) and is the most scalable option for MSW valorisation, but its success depends on tight feed specifications (dry, size-reduced, homogeneous). Reported pilot plants often face oil instability, char fouling, and gas-cleaning challenges that are understated in lab studies. Without catalytic upgrading or hydrodeoxygenation, the oil is unsuitable for long-term storage or direct fuel use. Industrial feasibility therefore hinges on integrated systems with preprocessing, fast quenching, and downstream upgrading.

5. Discussion factors affecting physical and chemical properties of bio-oils

The physico-chemical properties of bio-oil derived from municipal solid waste are strongly influenced by a wide range of factors related both to the nature of the feedstock and the operational conditions of the pyrolysis process.[125] Key characteristics such as heating value, viscosity, elemental composition, water content, acidity (pH), chemical stability, and the presence of oxygenated compounds directly affect the usability of bio-oil as a fuel, chemical feedstock, or energy carrier.[31] However, these properties can vary significantly depending on the specific parameters of the process and the composition of the input material.

MSW presents a particularly complex challenge due to its heterogeneous nature, consisting of various organic (*e.g.*, paper, food waste, wood) and synthetic (*e.g.*, plastics, textiles) components, as well as inorganic contaminants.[3] The composition of the feedstock not only determines the product yields but also heavily influences product quality—for example, plastic-rich fractions may increase the calorific value of the resulting oil, but also introduce chlorine and other contaminants that affect environmental performance and stability.

In addition to feedstock variability, technological parameters such as pyrolysis temperature, heating rate, vapor residence time, and the presence or absence of catalysts are critical determinants of oil properties. Higher pyrolysis temperatures tend to favor gas production and the formation of more carbon-rich products, while moderate temperatures (typically 450–550 °C) are generally optimal for maximizing oil yield and quality.[86,126] The heating rate governs the thermal decomposition pathway, and the use of catalysts can help reduce oxygen content, improve chemical stability, and selectively promote the formation of desirable compounds.[61,127]

This section provides a comprehensive overview of the main factors affecting the physical and chemical properties of bio-oils produced from MSW. Particular focus is given to the composition of the feedstock, the influence of temperature and heating rate, and the role of catalytic pyrolysis. Understanding these parameters is essential for process optimization and for enhancing the value and performance of pyrolysis-derived fuels and chemicals.

5.1 Composition of municipal solid waste

The highly heterogeneous composition of MSW strongly influences pyrolysis behavior. A comparative overview of major fractions, their pyrolysis characteristics, and critical implications is presented in Table 7.

Plastic-rich fractions yield the highest amounts of energy-dense oils, but require strict chlorine and tar control. Paper and biomass fractions contribute to unstable, acidic oils with lower heating values. Rubber and textiles introduce nitrogen- and sulfur-containing volatiles, complicating upgrading. Food waste and sludge fractions lower oil yield and increase process instability, highlighting the need for segregation and pre-treatment.

Plastic fractions typically account for 10–25 wt.% of MSW globally, with higher shares (up to ~30%) in urbanized regions. The main types are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS).

Overall, these data confirm that plastic-rich MSW streams offer the highest potential for pyrolytic liquid recovery, whereas food waste and sludge-rich compositions reduce oil yields and increase process instability. This underlines the necessity of segregation and pre-treatment for successful large-scale MSW pyrolysis.

In summary, the composition of MSW is one of the key

Table 7: Typical Composition of MSW and Implications for Pyrolysis.

Component	Typical share (wt.%)	Pyrolysis behavior	Critical assessment	Ref.
Food waste	20–40 %	High moisture, low calorific value, yields more char and gas	Decreases oil yield; drying required; better suited for anaerobic digestion than pyrolysis	[73,76,102]
Plastics (PE, PP, PET)	10–25 %	High oil yields, but with waxy/tarry fractions	Valuable for liquid recovery but cause operational fouling; requires sorting	[85,104]
Paper & cardboard	10–20 %	Oxygenated volatiles, unstable oils	Contributes to acidity and instability of oils; blending with plastics improves balance	[77,82]
Yard waste/wood	5–15 %	Lignocellulosic, forms char and phenolic oils	Useful for biochar, but liquids require upgrading	[79,101]
Textiles	2–5 %	Mixed behavior; can yield N/S-containing volatiles	Increases heteroatom load, complicates oil upgrading	[81]
Rubber/tires	2–5 %	Yields aromatic oils and char	High soot and PAHs; needs emission control	[84,103]
Sludge/agro-residues	<5 %	Variable; often high ash	Ash catalyzes secondary reactions, reduces oil yield	[77,80]

determining factors in bio-oil production. Plastic-rich wastes tend to yield higher quantities of energy-dense, hydrocarbon-rich oils, while biomass and paper components contribute to higher oxygen content and acidity.[91] Understanding these differences is essential for process optimization, especially when designing pyrolysis systems for specific waste streams or when evaluating the feasibility of co-processing mixed fractions. Future advancements in feedstock characterization, blending strategies, and preprocessing technologies will be essential to improve the reliability and efficiency of MSW pyrolysis for liquid fuel production.

5.2 Temperature and heating rate

Pyrolysis temperature has a strong impact on both the quantity of oil produced and its chemical makeup. Oil yield generally rises with temperature up to an optimal range, then declines at higher temperatures as secondary cracking of vapors becomes significant. For example, in the pyrolysis of paper waste (mostly cellulose), Biswal *et al*.[128] reported a maximum liquid yield of about 50–52 wt.% at ~400 C. Below that temperature, thermal decomposition is incomplete (yielding less volatiles), while above ~400–450 °C the oil yield began to drop as more of the paper volatiles cracked into permanent gases.[128] This behavior is typical for biomass-based MSW components: an optimal temperature around 450–500 °C often maximizes bio-oil output.[105] If the temperature is raised further, additional volatiles are produced but tend to break down into lighter gases rather than condense as oil, thus reducing the oil fraction.[62]

Mixed MSW feedstocks show similar trends. Velghe *et al*.[61] observed that pyrolyzing a MSW-derived feed at 450°C (slow pyrolysis) gave only ~21–32 wt.% liquids (including water) because the chosen temperature was slightly below the optimum for maximum oil. In a study on refuse-derived fuel (RDF) – a processed MSW blend of paper, plastics, *etc*.[62] found that increasing the final temperature from 700 °C to 800 C led to the oil yield dropping (with oil/tar decreasing from roughly ~27 wt.% down to ~23 wt.%) while non-condensable gas yield rose (from 43.6% to 46.9%).[61] At an even higher temperature of 900 C, the gas production further increased (gas >52 wt.%) at the expense of solids, but the oil yield remained near 23 wt.% – essentially, beyond ~800 °C any additional volatiles were immediately cracked to gas rather than condensing to liquids. These results reinforce that excessively high temperatures favor gas formation and diminish the liquid product.[61,62] Extremely high thermal severity can also alter the oil's chemistry: higher temperatures produce smaller, more aromatic molecules in the oil, whereas lower temperatures favor heavier fractions.[129] In the RDF study, oils produced at 800–900°C contained more light aromatic compounds, while pyrolysis at 700°C (a lower severity condition) would allow larger aliphatic compounds to persist in the oil.[61]

Different MSW components have different optimal temperature ranges due to their varying thermal stability. Plastic wastes (*e.g.* polyolefins like polyethylene and polypropylene) typically require ~400–500 °C to fully depolymerize. Below ~400 °C, plastic pyrolysis is incomplete (yielding waxes or solid residue), but raising the temperature increases oil output up to a point. Prurapark *et al*. demonstrated this with high-density polyethylene (HDPE): at 400 C, HDPE yielded about 22.5 L of oil per 100 kg feed, whereas at 450 °C it yielded 40.5 L – nearly doubling the oil volume.[130] They identified 450 °C as the best temperature in their setup for maximum oil from HDPE.[108,130] Other studies using longer residence times or catalysts have found slightly higher optimum temperatures for plastics; for instance, Faisal *et al*.[131] achieved 75.1 wt.% oil yield from mixed plastic waste at an optimized temperature of ~536 C (with 150 min residence). Above ~550°C, plastics start yielding more light gases (H_2, CH_4, C_2–C_4) due to over-cracking,[131] so oil yield plateaus or drops. Not all plastics behave equally: in the case of PET (polyethylene terephthalate, a polyester found in bottles), pyrolysis tends to produce mostly solid char/coke and very little oil – one experiment noted that PET yielded predominantly solid residue that even clogged the reactor, whereas HDPE under the same conditions produced mainly liquid.[108,130] This is because PET's aromatic-ring structure favors char formation (and yields benzoic acid and gases) rather than volatilization.[130]

Wet organic wastes (food scraps, yard waste) also show temperature-dependent yields. Food waste pyrolysis (once dried) can generate substantial bio-oil at sufficient temperatures. A recent study on vegetable wastes found that increasing the pyrolysis temperature from 300 °C to 500 °C boosted the oil yield from ~39% to ~55% (dry basis).[132] The devolatilization of food biomass is largely complete by ~500 °C,[132] so higher temperatures mainly drive secondary reactions. Some highly oxygenated biomass feeds might exhibit a slightly higher optimal temperature if fast heating minimizes secondary cracking – for example, pyrolysis of tomato peels showed oil yields rising from 14% at 450 °C to 32% at 550 °C and 40% at 600 °C when using a very short residence time process.[132] In general, however, most MSW components reach peak oil production in the mid-400 to 500 °C range, and beyond that the incremental oil from further heating is offset by greater gas production.[62] Thus, controlling the reactor temperature to an appropriate range is critical for maximizing oil yield.

Temperature also influences oil composition. Lower pyrolysis temperatures favor heavier molecular-weight compounds and oxygenates in the oil (since cracking is limited). Oils produced at 350–400 °C from biomass often contain larger sugar-derived oligomers, carboxylic acids, and other oxygenated tars. At higher temperatures (500 °C+), these unstable heavy compounds break apart into smaller fragments: the bio-oils shift toward phenolic and aromatic compounds, and eventually more of the carbon is diverted to permanent gases (CO, CO_2, light hydrocarbons) rather than remaining in the liquid. For instance, co-pyrolysis of food waste (rich in carbohydrates) with plastics showed that at 350 °C the bio-oil contained a high content of carboxylic acids (up to 42% if PET was present) along with furans and other oxygenates.[133] If the temperature were increased, one would expect these oxygenates to crack into smaller hydrocarbons and gases, reducing acid content.[134] In the RDF pyrolysis study, the oils from 800–900 °C contained a higher proportion of aromatic hydrocarbons (from secondary recombination reactions like Diels–Alder) compared to oils from slower, lower-temperature pyrolysis which retained more long-chain aliphatic compounds and oxygenated species.[62] In summary, a higher pyrolysis temperature leads to oil that is chemically "lighter" (lower molecular weight) – containing more aromatic and gaseous fractions – while a lower temperature produces a heavier, more oxygenated oil (often with higher viscosity and boiling range). The trade-off is that some oxygenated heavy compounds at low T boost oil yield (since they stay in the liquid phase) but lower its quality as a fuel, whereas very high T yields a cleaner, more aromatic oil but in smaller quantity.

The heating rate (rate of temperature ramping in the reactor) determines how quickly the waste particles reach the pyrolysis temperature. It governs the residence time of solids during active devolatilization and the extent of secondary reactions on the volatiles. In general, slow pyrolysis (low heating rate, *e.g.* a few °C per minute) favors production of char, whereas fast or flash pyrolysis (high heating rate, *e.g.* hundreds of °C per minute) favors production of liquids at the expense of char.[135] This is because rapid heating causes the waste to devolatilize quickly, releasing vapors that can be swiftly cooled to liquids before they have time to break down or repolymerize. Slow heating, on the other hand, allows prolonged solid-phase reactions and the repolymerization of intermediates into char, reducing the oil yield. Studies on MSW-derived feeds confirm this behavior, although the final outcome also depends on the chosen temperature and vapor residence.

At moderate pyrolysis temperatures (~450–500 °C), a higher heating rate is generally beneficial for oil yield. Velghe *et al*.[61] observed that for sewage sludge (as a proxy for wet MSW organics) pyrolyzed at 450 °C, the fast-heating condition produced less total liquid than slow heating, but this was mainly because less water condensed – the organic oil fraction was actually higher in the fast pyrolysis case. In slow pyrolysis, more water and light volatiles remained with the oil, inflating the "liquid yield" but yielding a dilute oil. Fast heating of the same material gave slightly lower overall liquid yield (more of the biomass carbon went to gas), yet the oil that did form was drier and of better quality (discussed more below).[61] In essence, high heating rates shorten the contact time between volatile products and the hot reactor zone, thereby reducing secondary reactions like cracking or polymerization. This tends to increase the yield of condensable volatiles (bio-oil) relative to char for biomass. Garcia *et al*.[62] found that for MSW, short vapor residence times (<1 s, effectively achieved by fast heating and quick removal) limited secondary pyrolytic cracking and gave higher oil yields, whereas longer exposure led to more gas. Fast pyrolysis processes of wood waste in fluidized beds (heating rates >100 °C/s) can recover up to ~60 wt.% bio-oil in some cases, versus only ~30% in slow pyrolysis of the same biomass.[61]

However, at very high temperatures or prolonged high-temperature exposure, increasing the heating rate can actually reduce oil yield by promoting excessive cracking. This was clearly shown in the RDF pyrolysis study at 800 °C: when the heating rate was increased stepwise from 5 °C/min (very slow) to 20, 90, and 350 °C/min (fast), the bio-oil yield plummeted from ~55 wt.% down to ~23 wt.%. Correspondingly, the gas yield surged (from ~14% up to ~47%) as more of the volatiles were broken into non-condensable gases at the highest heating rate.[62] The char yield decreased with faster heating (since more feed volatilized), but most of that extra volatilization went into gas, not liquid, under these severe conditions.[62] In this case, the combination of high heating rate and high final temperature caused substantial secondary thermal cracking of primary vapors, leading to smaller molecules that remained gaseous.[62] It highlights that heating rate effects are coupled with temperature: fast heating is essential for maximizing oils in typical fast pyrolysis (~500 °C),[136] but if the process temperature is too high (*e.g.* 800 °C), even fast heating yields mainly gas unless the vapors are very quickly quenched. Many plastics pyrolysis processes illustrate this balance as well. For polyolefin plastics, a moderately high heating rate is used to ensure the polymer quickly depolymerizes to oil vapors rather than forming char. If heating is too slow, some plastics (especially those with additives or multi-layer materials) might form more char or high-boiling tar. On the other hand, excessively fast heating of plastics in a high-temperature reactor can overshoot the optimal decomposition and crack the oil into light hydrocarbons. Marcilla *et al*.[137] observed that slow vs. fast pyrolysis of HDPE yielded similar total volatiles, but fast pyrolysis produced more low molecular weight gases while slow heating yielded more heavy oil/wax. The optimal heating rate thus depends on ensuring complete volatilization but minimal secondary breakdown.[37,110]

The heating rate also influences the chemical composition of the oil by altering secondary reaction pathways. Slow bio-oils (from low heating rates) tend to contain more large molecules, including heavier hydrocarbons and oxygenated oligomers, because vapors have a greater chance to undergo intermolecular reactions or to polymerize before leaving the hot zone. Interestingly, slow heating can allow some fractionation of volatiles within the reactor, which can result in the oil coming off in stages (water and light oxygenates first, heavier tars later). This was evidenced in a comparative study: slow bio-oils had higher carbon and lower oxygen content than fast bio-oils from the same feed, because much of the water and light oxygenates had time to separate out.[61] Velghe *et al*.[61] found the slow-bio-oils from sewage sludge had significantly lower O/C ratio and water content than the fast-bio-oils, making the slow oils more energy-dense (weighing in at ~33 MJ/kg vs ~25 MJ/kg for fast-bio-oil). The slow heating allowed formation of some long-chain aliphatics and retained more heavy oil, whereas fast heating produced more oxygenated compounds (*e.g.* alcohols, furans) that ended up either in the aqueous phase or as lower-energy oil.[61] On the other hand, fast bio-oils typically show higher contents of single-ring aromatics and phenolics (especially from lignin or plastics) because rapid vapor release and quenching "freeze in" these intermediates before they repolymerize. In the RDF experiments, the slow heating (5 °C/min) oil contained a greater fraction of long-chain alkanes and alkenes (C_8–C_{39} range) as well as oxygenates, while the fast-heating oil was richer in aromatic hydrocarbons. The authors attributed the aromatic increase to in-situ Diels–Alder cyclization of olefins at high heating rates and temperatures.[62] Similarly, fast pyrolysis of woody waste yields oil dominated by phenolic compounds (from lignin) and light oxygenates, whereas a very slow pyrolysis might produce heavier extractable tars or polycyclic aromatics if vapors spend more time reacting. In summary, high heating rates favor simpler, smaller molecules in the oil (aromatics, phenols, light olefins), while low heating rates can yield larger paraffins, olefins, and highly oxygenated oligomers – though some of those may segregate or end up as char.

The physicochemical properties of bio-oils from MSW depend on the feedstock composition and the process conditions as discussed. Two key properties for evaluating the oil as a fuel are its chemical composition (*e.g.* dominant compound types, elemental makeup) and its energy content (heating value). Table 8 compiles representative data from

Table 8: Representative bio-oil yields, compositions, and heating values for MSW and its components under different conditions.

Feedstock & Conditions	Oil Yield (wt.%)	Dominant Oil Compounds	Heating Value (MJ/kg)	Ref.
Mixed MSW, 800 °C, slow heating (5 °C/min)	55	Long-chain aliphatic hydrocarbons, oxygenates	Not reported	[62]
Mixed MSW, 800 °C, fast heating (350 °C/min)	23	Aromatic hydrocarbons, cracked products	Not reported	[62]
Paper waste, ~400 °C, 20 °C/min	50–52	Oxygenated organics (aldehydes, acids, ketones)	25–30 (est.)	[128]
Plastic waste (HDPE/PP/PS), ~536 °C, 150 min	75.1	Hydrocarbons C10–C25 (paraffins, olefins)	40	[131]
Plastic (HDPE), 450 °C, batch	~28	Aliphatic hydrocarbons (kerosene range)	44 (approx.)	[130]
Food waste, 500 °C, fast pyrolysis	~55	Oxygenated compounds (acids, phenols, furans)	20–25	[133]
Green wood waste, 500 °C, auger reactor	39.9	Phenolics, aromatics, ketones	25.5	[138]

various studies, showing how pyrolysis temperature and heating regime impacted oil yield, major compound types, and fuel quality indicators for different MSW-derived feeds.

Optimal oil yields are generally obtained at 450–550 °C; excessively high temperatures (>800 °C) favor gas formation. High heating rates increase oil yield and reduce char, but may lead to secondary cracking at severe conditions. Plastic-rich feeds produce hydrocarbon-rich, high-HHV oils, while biomass-derived feeds yield oxygenated, unstable oils. Co-processing plastics with biomass improves oil stability through hydrogen-rich radical transfer.

As Table 8 shows, plastic-rich wastes yield oils that are high in hydrocarbons and energy content, whereas biomass-derived wastes yield more oxygenated oils with lower heating value. For instance, a mixed polyolefin plastic waste can produce an oil with HHV around 40 MJ/kg – comparable to diesel – because it is almost entirely composed of C_{10}–C_{25} hydrocarbons and virtually no water.[131] In contrast, bio-oil from paper or food waste contains a substantial fraction of oxygenated compounds (acids, sugars, guaiacols, *etc*.) and water, resulting in HHVs closer to ~20 MJ/kg.[61] The presence of plastics in MSW can significantly upgrade the oil quality: Chua *et al*.[139] reported an oil from mixed MSW (containing paper, plastics, organic waste) with 75.17% C and only 12.83% O, yielding an HHV of ~35.5 MJ/kg. By contrast, a typical fast-pyrolysis bio-oil from pure wood might be ~55–60% C and 30–40% O with HHV ~20 MJ/kg.

Dominant compounds in the bio-oil also differ by feedstock. Pyrolysis of wood and paper waste tends to generate phenolic derivatives (from lignin) and furans/ketones (from cellulose/hemi-cellulose). In the green waste oil example, phenolic compounds were the most abundant class.[127] These contribute to high viscosity and chemical instability (aging) of bio-oils. Food waste oils often contain short carboxylic acids (*e.g.* acetic acid), carbonyls, and sometimes nitrogen compounds if proteins are present. Co-pyrolysis of food waste with plastics showed oils rich in acids and furans when plastic content was lower,[133] but more aliphatic hydrocarbons when a higher ratio of plastic was present[133] – indicating plastics can supply hydrogen-rich radicals that stabilize the bio-oil into hydrocarbon chains. Plastic-derived oils are dominated by hydrocarbon fractions: polyolefins yield aliphatic chains (waxes, oils) that can range from gasoline-range molecules up to heavy waxes depending on cracking severity, while polystyrene yields aromatic compounds (styrene, ethylbenzene, *etc*.). In a HDPE pyrolysis study, distillation of the oil showed it consisted mainly of kerosene-range hydrocarbons, followed by fractions in the gasoline and diesel range.[130] The oil had a low density (0.68–0.74 g/mL) and viscosity (~3–5 cSt) similar to light fuels,[130] reflecting its paraffinic nature. Such oil is highly calorific but may have a low flash point if light fractions are present[131] (one plastic oil sample had flash point <20 °C due to volatile content). Nitrogen and sulfur content in MSW oils depends on the feed: plastics generally contain little N/S (and indeed one MSW study found ~0% of each in the oil),[139] but household waste can include proteins or rubber leading to some N/S in the oil. Fortunately, much of the N (from proteins) tends to end up in char or as ammonia in the gas phase, and S (from *e.g.* rubber or food) can convert to H_2S or stay in char, so MSW bio-oils often have low nitrogen/sulfur – *e.g.* the mixed MSW oil in one study had <0.01% S and no detectable N.[139]

From a fuel perspective, bio-oils from MSW require upgrading before they can be used in conventional engines, but their quality improves when more plastics (or other hydrogen-rich materials) are present. The high oxygen content in biomass-derived oil causes low stability, corrosiveness, and low heating value, so methods like hydrodeoxygenation, catalytic cracking, or emulsification are often applied to upgrade bio-oils.[61,127] The presence of plastics can mitigate these issues by contributing hydrogen and yielding more stable hydrocarbon compounds. In fact, slow bio-oils in one study (with less oxygen and water) had a higher calorific value (~33 MJ/kg) approaching that of fossil fuel, though they were still aromatic and required further treatment to improve ignition quality.[61] Fast bio-oils (oxygen-rich) had lower energy content (~25 MJ/kg) but came in higher yield.[61] Thus, there is a trade-off between quantity and quality of oil influenced by process conditions: milder, slower pyrolysis yields a smaller amount of more energy-dense oil, while fast/severe pyrolysis yields more oil that is less refined.

Overall, the research indicates that careful optimization of temperature and heating rate is crucial for MSW pyrolysis to maximize oil production without sacrificing too much quality. For a given MSW feed, an intermediate temperature (around 450–500 °C) with a rapid heating and short vapor residence time tends to give the best oil yields.[140] Under these conditions, one can obtain oil yields on the order of 40–60 wt.% from the biomass fractions and even higher (60–80%+) from plastic fractions.[131] If the temperature is pushed too high or heating is too prolonged, secondary cracking will lower the oil yield (as seen by the drop from 55% to 23% oil in Table 1 when heating rate increased at 800 °C).[62] On the other hand, if the process is too cold or slow, much of the material remains as char or un-vaporized tar (*e.g.* PET plastic or incomplete decomposition at 300 °C). By tailoring these parameters, one can influence the oil's makeup: lower-severity conditions give more heavy oils (higher yield, lower grade), while higher-severity conditions give lighter oils (lower yield, higher grade). In practice, a balance is struck to produce the maximum recoverable energy in the liquid product. The data gathered from MSW-specific studies provide valuable guidelines for optimizing pyrolysis systems to convert municipal waste into sustainable liquid fuels with improved yield and desirable properties.

5.3 Influence of the catalyst

Catalytic pyrolysis is an advanced modification of conventional thermal pyrolysis, in which specific catalysts are introduced to alter the reaction pathways, selectively break chemical bonds, and improve the quality of the resulting bio-oil.[141] While traditional pyrolysis often yields oils with high oxygen content, high acidity, and poor thermal stability - especially from biomass and paper-rich municipal solid waste - catalytic processes aim to reduce these limitations by enhancing deoxygenation, aromatization, and cracking reactions.[105]

In the context of MSW, catalytic pyrolysis is particularly valuable due to the heterogeneous and variable composition of the feedstock. Different MSW fractions - such as plastics, food waste, paper, and textiles - respond differently to catalysis, and selecting an appropriate catalyst is critical for targeting specific oil characteristics. For example, catalysts can help convert long-chain aliphatic hydrocarbons (from plastics) or oxygenates (from biomass) into more stable aromatic and olefinic compounds with higher calorific value and lower oxygen content.

Several types of catalysts have been studied in the catalytic pyrolysis of municipal solid waste and its individual components. Among the most commonly used are zeolites, such as HZSM-5, HY, and Beta.[142,143] These microporous aluminosilicate minerals are widely favored due to their strong acidity, shape-selectivity, and capacity to promote both aromatization and cracking reactions. Zeolites are particularly effective in converting oxygenated compounds derived from biomass into monocyclic aromatic hydrocarbons (MAHs), including benzene, toluene, and xylene (BTX), thereby reducing the overall oxygen content of the oil and improving its fuel quality.[144] Natural clays, such as bentonite and kaolinite, although less catalytically active than zeolites, are low-cost materials that can contribute to partial deoxygenation and reduction of tar and char formation.[145] Due to their economic feasibility, natural clays are often employed in large-scale systems where cost considerations are critical. Metal oxides, including calcium oxide (CaO),[146] magnesium oxide (MgO),[10,147] iron oxide (Fe_2O_3),[148,149] and aluminum oxide (Al_2O_3),[150] are another category of catalysts used for their basic or amphoteric properties.[151] These oxides effectively neutralize acidic intermediates and facilitate the removal of CO_2 and CO through decarboxylation reactions. For example, CaO has been applied in MSW pyrolysis to capture CO_2, promoting hydrocarbon enrichment in the pyrolysis vapors. Lastly, supported metal catalysts, such as nickel on ZSM-5 or iron on Al_2O_3, combine acidic and redox functionalities.[152] These catalysts enable more selective conversion of complex macromolecules, improving deoxygenation and promoting the formation of valuable hydrocarbons. Supported metal catalysts are especially effective when processing mixed MSW streams that contain both biomass and plastic components.[153]

The introduction of catalysts typically leads to a decrease in total oil yield but a significant improvement in oil quality. This is due to the enhanced cracking and deoxygenation reactions promoted by the catalyst, which convert heavy or oxygenated compounds into light hydrocarbons and gases.

Catalytic pyrolysis of plastic-rich MSW (*e.g.*, PE, PP, PS) enhances the breakdown of polymers into aromatic hydrocarbons rather than long-chain waxes. For instance, catalytic cracking of polystyrene using HZSM-5 converts a large fraction of the polymer into ethylbenzene and styrene monomers, while catalysts used with polyethylene yield more light alkanes and aromatics than thermal processes.[135]

With biomass-based MSW components, such as food waste or paper, catalytic pyrolysis facilitates the removal of oxygen through decarboxylation and dehydration reactions. This reduces acid and phenol formation and increases the presence of hydrocarbons suitable for fuel applications.

Table 9 illustrates how different types of catalysts affect the yield and composition of bio-oil produced from different MSW components.

Zeolite catalysts (*e.g.*, HZSM-5) improve oil quality by increasing aromatic hydrocarbons, but they are costly and

Table 9: Effect of Catalysts on Pyrolysis of MSW Components.

Feedstock	Catalyst Type	Catalyst Details	Oil Yield (%)	Key Effects on Oil Composition	Reference
Plastic-rich MSW	Zeolite (HZSM-5) in-situ (mixed with feed)	High acidity, Si/Al = 25	~50–60	High BTX content, increased aromatics	[154]
Food waste	CaO in-situ (bed additive)	Basic oxide	~35	Deoxygenation, less acetic acid	[49]
Paper/cardboard	HZSM-5 in-situ (mixed with feed)	Fluidized bed reactor	~40	Reduced levoglucosan, higher phenolics	[154]
Mixed MSW (plastic + biomass)	Ni/Al_2O_3 ex-situ (fixed downstream bed).	Supported metal catalyst	~45	High heating value, reduced O content	[155]
Waste textiles	Natural clay in-situ (mixed with MSW feedstock or used as bed material).	Activated bentonite	~30–40	Reduced tar, improved flowability	[156]

prone to deactivation. Metal oxides (*e.g.*, CaO, MgO) are low-cost options that enhance deoxygenation and reduce acidity, though oil yields may decline. Supported metal catalysts offer a balance between yield and quality, but scale-up remains challenging due to feedstock heterogeneity and catalyst fouling.

Despite its many benefits, catalytic pyrolysis has some limitations. Catalysts can be expensive, especially zeolites and noble metal-supported variants, and they are subject to deactivation due to coke formation, sintering, or contamination by metals and chlorine compounds found in MSW.[156] Regeneration of catalysts (*e.g.*, via calcination) adds operational complexity. Moreover, the variability in MSW composition can result in inconsistent catalyst performance, requiring system-specific optimization.

There are also scale-up challenges: ensuring uniform contact between solid MSW particles and catalysts in large-scale reactors is not trivial, especially when dealing with bulky or mixed waste streams. Fixed-bed and fluidized-bed catalytic pyrolysis systems are currently being piloted for MSW conversion, but further development is needed for commercial viability.[157]

Catalytic pyrolysis is a promising strategy for upgrading the quality of bio-oils derived from MSW.[140,141] By selecting appropriate catalysts, it is possible to enhance the deoxygenation and cracking of complex compounds, thereby improving fuel properties and increasing the value of the final product. Although oil yields may slightly decrease, the overall energy content, stability, and composition of the oil are greatly improved. Future research should focus on catalyst durability, regeneration methods, and reactor design tailored to the heterogeneous nature of MSW.

To consolidate the comparative evaluation, a critical scoring matrix was developed (Table 10). This table summarizes the relative performance of slow, rotary kiln, microwave, and fast pyrolysis across key criteria such as oil yield, oil quality, feedstock tolerance, energy efficiency, economic viability (CAPEX/OPEX), operational complexity, scalability, and technology readiness level (TRL). Table 11 provides a concise decision-support framework that highlights the trade-offs and practical limitations of each technology.

Table 10: Critical scoring matrix for MSW pyrolysis technologies (Scale 1–5, where 1 = very poor, 5 = excellent).

Criterion	Slow pyrolysis	Rotary kiln	Microwave pyrolysis	Fast pyrolysis
Oil yield	2	3	4	5
Oil quality	2	3	4	4
Feedstock tolerance	5	4	2	3
Energy efficiency	3	2	2	4
CAPEX/OPEX	4	3	2	3
Operational complexity	2	3	2	4
Scalability	5	4	2	4
TRL (Technology Readiness Level)	5	4	2	4

Note: Scores are semi-quantitative, derived from literature trends and industrial reports. They reflect relative performance rather than absolute values.

Slow pyrolysis is the most robust and scalable technology but produces oil of insufficient quality for fuel markets. Microwave pyrolysis offers improved oil properties but remains limited by high costs and low TRL. Rotary kilns provide moderate flexibility but face energy penalties. Fast pyrolysis demonstrates the best balance between oil yield, scalability, and maturity, yet requires extensive feedstock pre-treatment and upgrading to be viable.

6. Methodology for analyzing composition

In addition to technical challenges at laboratory and pilot scale, several large-scale MSW pyrolysis projects have failed commercially. These failures provide valuable lessons on the limitations of the technology and the critical factors that must be addressed for future success. A summary of typical challenges and industrial case outcomes is provided in Table 11.

Front-end sorting and drying of MSW are indispensable to ensure stable operation. Tar fouling and insufficient gas cleaning were key reasons for operational shutdowns. Pyrolysis oils proved unstable and corrosive without proper upgrading. High CAPEX and OPEX made several stand-alone projects uneconomic. Integration with waste-to-energy (WtE) or refinery upgrading units is critical for future success.

Fast pyrolysis is widely considered a promising technology for renewable fuel production from municipal solid waste. However, optimizing pyrolysis conditions for efficient fuel production necessitates detailed compositional analysis of the resulting products. Among several analytical techniques available for studying thermal decomposition products, chromatography remains the most versatile method. However,

Table 11: Challenges and Lessons Learnt from Industrial MSW Pyrolysis.

Challenge / Case	Observed outcome	Lessons learnt	Ref.
Plant in Germany (1990s)	Frequent shutdowns due to tar fouling and corrosion	Insufficient gas cleaning and oil upgrading infrastructure led to operational failure	[130,131]
UK pyrolysis demo plant	Low oil quality, instability during storage, poor market acceptance	Product upgrading and stable end-use markets are essential before scale-up	[132]
Japan municipal project	High capital and operating costs, poor energy balance	Without integration into waste-to-energy systems, stand-alone pyrolysis is uneconomic	[135,136]
General technical barrier	Heterogeneous MSW feed causes variable yields and product composition	Pre-sorting and feed homogenization are critical for reliable operation	[135,136]

due to the complexity of bio-oils, which typically consist of hundreds of diverse organic compounds, interpreting chromatographic results poses significant analytical challenges.[58,158]

Beyond the reactor itself, integration of energy recovery systems is crucial for the overall performance of MSW pyrolysis facilities. Rebellón *et al*. reviewed the use of thermoelectric modules in building environments, demonstrating the potential to harvest low-grade heat from biomass and municipal waste conversion processes.[159] Aubakirov *et al*. carried out a comprehensive experimental study of coal-dust pyrolysis from Southern Kazakhstan, analysing how temperature and particle dispersion influence the distribution and composition of gaseous, liquid and solid products.[160] These findings complement the authors' previous techno-economic assessment of fast pyrolysis with a solid heat carrier for MSW,[161] collectively illustrating that successful industrial deployment requires co-optimisation of reactor design, heat-recovery systems and downstream utilisation of all product streams.

A variety of chromatographic methods have been employed to analyze pyrolysis products, including pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS),[162] two-dimensional gas chromatography (GC×GC),[163] two-dimensional liquid chromatography (LC×LC),[164] and initial fractionation of complex product mixtures. Additionally, researchers have highlighted the challenges associated with analyzing pyrolysis products from diverse reactor configurations and explored the potential of multivariate analysis techniques to handle this complexity.[83,163,165–167]

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is among the most commonly utilized methods for analyzing biomass behavior under rapid pyrolysis conditions. In Py-GC/MS, small samples (typically milligrams) are thermally decomposed in a microreactor with precise control over heating rates. The small sample mass allows heating rates reaching tens of thousands of °C per second, closely simulating conditions characteristic of fast pyrolysis reactors.[163,165] When catalytic or steam-assisted pyrolysis is conducted, the pyrolysis vapors pass through a catalyst bed before being temporarily trapped on an adsorption column maintained at low temperature (~30°C). The trapped compounds are subsequently desorbed by rapidly heating the column (approximately 300°C) and directed into the gas chromatograph coupled to a mass spectrometer.[123,140,168]

Due to the chemical complexity of bio-oils, chromatographic results typically produce intricate chromatograms with numerous overlapping peaks. Therefore, gas chromatographs are commonly interfaced with mass spectrometers, enabling identification of individual compounds via spectral matching against databases such as the NIST MS library. Despite this advantage, interpretation can remain difficult when low-abundance or structurally ambiguous compounds are present, leaving some chromatographic peaks unidentified.[136,158]

A significant limitation of Py-GC/MS is its inherently batch-wise operation, limiting its ability to simulate continuous industrial-scale pyrolysis processes. Nevertheless, studies have consistently demonstrated that Py-GC/MS results correlate closely with those obtained from bench-scale reactors, confirming the validity of this method for compositional investigations.[169,170] Additionally, since Py-GC/MS does not permit product collection and storage, mass balances are challenging to achieve directly from experimental data.[153]

Moreover, Py-GC/MS provides limited quantitative accuracy due to the large diversity of chemical species and the unavailability or prohibitive cost of analytical standards. Typically, the method is employed qualitatively or semi-quantitatively, based on the assumption of linearity between chromatographic peak intensities and compound concentrations when using consistent experimental conditions.[162,169,170] Nonetheless, focused quantitative analyses are achievable by applying external calibration for specific compounds of interest. For example, previous studies successfully quantified specific aromatic hydrocarbons and phenolic markers using external standards.[171,172] Similarly, Py-GC/MS has effectively determined the ratio of lignin-derived components such as sinapyl and coniferyl alcohols through targeted marker compounds.[173]

Due to the challenges associated with quantitative analysis, Py-GC/MS is primarily used to qualitatively describe bio-oil composition and compare relative distributions of major chemical groups. Typically, compounds identified from bio-oils are grouped into hydrocarbons, phenols, carboxylic acids, aldehydes, alcohols, and ketones.[174,175] More detailed analyses may further categorize additional compound classes, including carbohydrates, esters, and nitrogen-containing compounds. Unidentified compounds or those with complex structures are often categorized separately as "others".[176]

Nuclear magnetic resonance (NMR) spectroscopy represents another powerful analytical technique for characterizing bio-oils. NMR offers several distinct advantages: it can analyze non-volatile compounds, provide comprehensive information on functional groups, and quantitatively assess functional group distributions through chemical shift integrations.[56,177,178] Revised chemical shift ranges for interpreting 1H and 13C NMR spectra have improved accuracy and reliability, although uncertainties remain regarding assignments due to sample-specific conditions such as hydroxyl content and incomplete nuclear relaxation.[179,180]

However, NMR spectroscopy also has limitations. Due to its insensitivity relative to other analytical techniques and difficulty in online integration with pyrolysis reactors, NMR remains predominantly a laboratory-based research tool rather than an industrial diagnostic.[56,181] Furthermore, NMR is better suited for functional group analysis rather than identification of specific individual compounds, especially within highly complex mixtures. Thus, a multi-technique approach combining NMR with chromatographic methods remains essential for comprehensive bio-oil characterization.[81,181,182]

Two-dimensional NMR (2D-NMR), including heteronuclear single quantum correlation (HSQC) NMR, extends the analytical capability by resolving overlapping signals and providing more detailed structural information. The pioneering application of HSQC-NMR for bio-oils successfully identified numerous C–H bond environments within lignocellulosic-derived oils, highlighting major constituents such as levoglucosan, furfural, and phenolic derivatives.[56,177,181,183] Recent studies using HSQC-NMR further demonstrated clear compositional differences between oils from fast and slow pyrolysis, notably in aromatic hydrocarbon and polycyclic aromatic hydrocarbon (PAH) content.[184] Ultimately, while both chromatographic and spectroscopic methods offer valuable insights, integrating multiple analytical techniques remains essential for accurately determining the complex compositional characteristics of bio-oils derived from municipal solid waste.

These industrial outcomes demonstrate that technical feasibility does not guarantee economic viability. Failures were largely associated with inadequate feed preparation, lack of robust upgrading technologies, and poor alignment with existing energy markets. Future MSW pyrolysis deployment must therefore focus on integrated systems, coupling pyrolysis with energy recovery, advanced upgrading, and strict feedstock management.

Although laboratory- and pilot-scale studies demonstrate the technical feasibility of MSW pyrolysis, full-scale industrial implementation remains challenging. Past failures highlight recurring issues such as heterogeneous feed composition, high moisture and chlorine levels, tar formation, and instability of the produced bio-oil. Standalone pyrolysis plants have often struggled with economic viability. Lessons learned point to the need for (I) rigorous pre-treatment and sorting of MSW, (II) effective dechlorination and tar reduction strategies, (III) catalytic vapor and oil upgrading, and (IV) integration with existing waste-to-energy or refinery infrastructures. Embedding pyrolysis within broader resource recovery systems is considered more realistic for commercial deployment.

7. Conclusion

This review analysed MSW pyrolysis in four aspects: global trends in MSW generation and composition; comparison of slow, intermediate and fast pyrolysis technologies; the influence of feedstock and process variables on product quality; and lessons from laboratory, pilot and industrial deployment. The main conclusions are as follows.

MSW composition and variability are decisive for process design. Mixed MSW strongly differs between regions in moisture content, plastic share, biogenic fraction and inorganic contaminants. High moisture and chlorine contents, together with inert materials, impose strict requirements on pre-treatment, operating temperatures and gas cleaning. Any realistic MSW pyrolysis scheme must therefore start from systematic feedstock characterisation and pre-segregation, especially of chlorine-bearing plastics, fines and metals.

Slow, intermediate and fast pyrolysis concepts occupy different niches. Slow pyrolysis in fixed-bed units is mechanically simple and tolerant to heterogeneous feeds, but primarily produces char and is most suitable for decentralised, char-oriented applications. Rotary-kiln and microwave-assisted intermediate pyrolysis offer a compromise between throughput and selectivity; rotary kilns are attractive for heterogeneous MSW and RDF, whereas microwave systems can deliver higher-quality liquids at higher capital cost and with scale-up challenges. Fast pyrolysis in fluidised- and spouted-bed reactors provides the highest liquid yields and is technically attractive for large-scale MSW-to-liquid-fuel conversion, provided that adequate pre-sorting, drying and size reduction are implemented.

Product upgrading is central for fuel applications. Bio-oil from real MSW is typically oxygen-rich, acidic and thermally unstable, while solid residues may contain inorganic species limiting their direct use. Catalytic upgrading, co-pyrolysis with selected biomass or plastic fractions, and integration with hydrotreating, steam-cracking or gas-engine systems are required to obtain products that meet fuel and emission standards. Recent catalytic fast-pyrolysis studies on agricultural residues, plastics and other MSW-related feedstocks confirm that catalyst type, loading and reactor configuration strongly affect liquid and gas composition and must be matched to the specific MSW-derived fraction.

System-level integration is essential for successful deployment. Experience from pilot and industrial MSW pyrolysis plants shows that failures were often caused by inadequate feed preparation, tar and gas-cleaning issues, unstable outlets for liquids and char, and high specific CAPEX and OPEX rather than by fundamental technical limits. The critical scoring matrix developed in this work indicates that fast pyrolysis with a solid heat carrier can provide a balanced pathway for MSW-to-fuel conversion when combined with robust pre-treatment, reliable gas cleaning and well-defined utilisation routes for all product streams. Kazakhstan is used here as a representative case, but these conclusions are applicable to many countries with similar regulatory, infrastructural and economic constraints.

Future work on MSW pyrolysis should focus on several directions. First, standardised methodologies are needed for characterising mixed MSW and RDF, including moisture, ash chemistry and chlorine-bearing components. Second, robust, low-cost and regenerable catalysts should be developed for specific MSW fractions and tested under realistic impurity levels. Third, pyrolysis units need closer integration with heat-recovery, power generation and flue-gas cleaning systems, supported by advanced monitoring and control. Fourth, demonstration projects should cover the full chain from pre-treatment to final fuel use under realistic MSW compositions and operating conditions. Such integrated demonstrations are required to translate laboratory and pilot advances into reliable industrial projects in Kazakhstan and other regions facing similar MSW management challenges.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supporting Information

Not applicable.

CRediT Statement

Eldar Kopishev: Conceptualization, Supervision, Writing – Original draft. **Gartzen Lopez:** Writing – Review & editing, Writing – Original draft. **Ruslan Safarov:** Data curation, Formal analysis, Writing – Original draft. **Yelaman Aibuldinov:** Conceptualization, Supervision, Writing – Original draft. **Ruslan Muratov:** Investigation, Methodology, Writing – Original draft. **Zharas Berdenov:** Resources, Visualization, Writing – Original draft. **Nurken Nuragaliyev:** Validation, Resources, Writing – Original draft. **Ayat Sabitov:** Project administration, Writing – Review & editing, Writing – Original draft.

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