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Pyrolysis of Mixed Plastic Waste (LDPE, HDPE, PP, and PS): A Critical Review of Fuel Oil Yield, Quality, and Process Performance

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Abstract: The rapid accumulation of plastic waste and the limitations of conventional recycling methods have intensified interest in thermochemical conversion technologies for resource recovery. Among these, pyrolysis has emerged as a promising chemical recycling route capable of converting plastic waste into valuable fuel products. However, existing literature is largely fragmented, with a strong emphasis on single-polymer systems or catalytic upgrading approaches, which obscures the intrinsic role of feedstock composition in determining process performance. This review critically examines the catalyst-free pyrolysis of mixed plastic waste composed of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS), focusing on fuel oil yield, quality, and overall process performance. A feedstock-centric framework is adopted to evaluate the thermal degradation behavior and synergistic interactions among polyolefins and polystyrene under non-catalytic conditions. The analysis reveals that hydrogen-rich polyolefins stabilize aromatic intermediates derived from PS, suppressing excessive gas formation and enhancing liquid oil yields, which typically range from 60 to 85 wt% under optimized conditions. The resulting pyrolysis oils exhibit high calorific values (41–46 MJ kg^{-1}) and physicochemical properties comparable to conventional fossil fuels, indicating strong potential for industrial heating and blending applications. Process performance is further assessed in terms of reactor configuration, heat transfer efficiency, and energy integration, highlighting the suitability of catalyst-free systems for scalable and decentralized waste-to-fuel applications. This review systematically evaluates mixed LDPE, HDPE, PP, and PS pyrolysis exclusively under catalyst-free conditions while simultaneously correlating feedstock composition with fuel oil yield, quality, and process performance. It demonstrates how improved oil yield and balanced hydrocarbon composition can be achieved without catalyst intervention. Furthermore, this work uniquely correlates feedstock composition with reactor performance parameters, including temperature optimization, vapor residence time, and condensation efficiency, providing insights directly relevant to pilot-scale and industrial implementation. Overall, this review establishes a new reference framework for catalyst-free mixed plastic pyrolysis, bridging laboratory findings with practical reactor design considerations. The outcomes support the development of low-cost, scalable, and industrially viable plastic-to-fuel systems, particularly suited for regions where catalyst availability, regeneration, and operational complexity pose significant challenges.

Keywords: *Plastic Waste Pyrolysis; Catalyst-Free Pyrolysis; Mixed Plastics; Fuel Oil Yield; Process Performance; LDPE; HDPE; PP; PS.*

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I. INTRODUCTION

The exponential growth in global plastic production has emerged as one of the most pressing environmental and resource management challenges of the twenty-first century. Annual plastic production has exceeded 400 million tonnes, with packaging, consumer goods, and short-life products accounting for a significant fraction of this volume, leading to rapid post-consumer waste generation (Geyer et al., 2020; OECD, 2022; Plastics Europe, 2023). Despite increased awareness and policy interventions, less than 10–15% of plastic waste is effectively recycled worldwide, while the remainder is landfilled, incinerated, or released into the environment, contributing to severe ecological and human health impacts (Borrelle et al., 2023; Lau et al., 2020; UNEP, 2023). These statistics underscore not only the scale of the plastic waste problem but also the inadequacy of existing waste management strategies to address it sustainably.

Mechanical recycling, the most widely implemented plastic recovery route, faces fundamental limitations related to polymer degradation, contamination, and feedstock heterogeneity. Repeated thermal and mechanical processing leads to deterioration of polymer properties, restricting recycled plastics to low-value applications and limiting closed-loop recycling potential (Ragaert et al., 2020; Al-Salem et al., 2021). In parallel, incineration and co-processing in cement kilns, although capable of volume reduction and energy recovery, raise concerns regarding greenhouse gas emissions, toxic by-product formation, and long-term environmental sustainability (Astrup et al., 2020; Jeswani et al., 2021). As a result, there is a growing consensus that alternative chemical recycling pathways are required to complement existing approaches and enable higher-value recovery from plastic waste streams (Vollmer et al., 2020; Garcia and Robertson, 2022).

Among chemical recycling technologies, pyrolysis has gained substantial attention due to its ability to convert plastic waste into liquid fuels, gases, and char under oxygen-free conditions. Pyrolysis offers flexibility in feedstock acceptance, compatibility with existing fuel infrastructure, and the potential for decentralized deployment, making it particularly attractive for regions lacking advanced waste sorting and recycling systems (Lopez et al., 2019; Miandad et al., 2019; Sharuddin et al., 2016). Recent advances in reactor design, process control, and product recovery have further strengthened the case for pyrolysis as a viable waste-to-fuel technology (Sogancioglu et al., 2021; Wong et al., 2023). However, despite this progress, significant gaps remain in understanding how real-world plastic mixtures behave under pyrolytic conditions.

Most municipal plastic waste streams are dominated by polyolefins, low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP), along with polystyrene (PS), which together account for over 70% of global plastic demand (Plastics Europe, 2023; Jambeck et al., 2020). Nevertheless, a substantial proportion of pyrolysis research continues to focus on single-polymer systems, which fail to capture the complexity and interactions inherent in mixed plastic waste (Zhang et al., 2020; Abbas-Abadi, 2021). This disconnect between laboratory-scale research and real waste composition has contributed to inconsistent performance metrics and limited industrial translation.

Catalytic pyrolysis has been widely explored as a means of improving oil quality and controlling product distribution. While catalysts can enhance aromatization and reduce wax formation, they introduce additional challenges related to catalyst cost, deactivation, fouling by contaminants, and regeneration requirements (Aguado et al., 2019; Alvarez et al., 2021; Chen et al., 2022). These issues are particularly critical in developing economies, where feedstock contamination is common and operational simplicity is essential. Consequently, catalyst-free pyrolysis remains highly relevant from an industrial and socio-economic perspective, yet it is often treated as a baseline rather than a subject of systematic investigation.

Recent studies have begun to indicate that mixed plastic systems may exhibit synergistic degradation behavior even in the absence of catalysts. In particular, hydrogen-rich polyolefins can donate hydrogen radicals that stabilize aromatic intermediates derived from PS, suppressing secondary cracking and promoting liquid oil formation (Aboulkas et al., 2020; Wu et al., 2021; Kumar et al., 2023). These intrinsic interactions suggest that feedstock composition itself can act as a functional parameter influencing yield, quality, and process efficiency, an aspect that remains underexplored in existing reviews.

Despite the practical importance of mixed plastic waste processing, existing reviews often treat mixed plastics superficially or group them into broad categories without detailed feedstock specificity. Moreover, very few reviews systematically isolate catalyst-free pyrolysis of mixed LDPE, HDPE, PP, and PS, while simultaneously correlating fuel oil yield, fuel quality, and process performance. As a result, the intrinsic role of feedstock composition in determining pyrolysis outcomes remains inadequately understood.

This review addresses this critical gap by providing a comprehensive and feedstock-centric evaluation of catalyst-free pyrolysis of mixed LDPE, HDPE, PP, and PS. Unlike previous reviews, this work deliberately excludes catalytic effects to isolate intrinsic polymer interactions and establish fair comparisons across studies. The review critically examines fuel oil yield trends, physicochemical properties of pyrolysis oils, and key process performance parameters, including temperature, heating rate, vapor residence time, and reactor configuration. Furthermore, the analysis explicitly

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links laboratory-scale findings to pilot-scale and industrial feasibility, emphasizing low-cost, scalable, and decentralized plastic-to-fuel systems.

II. CHARACTERISTICS OF LDPE, HDPE, PP, AND PS AS PYROLYSIS FEEDSTOCKS

The performance of plastic pyrolysis processes is fundamentally dependent on the physicochemical characteristics of the feedstock polymers. Low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) are the most prevalent plastics in municipal waste streams, collectively representing the most industrially relevant feedstock combination for waste-to-fuel applications (OECD, 2022; PlasticsEurope, 2023). Understanding their individual and collective thermal behaviors is crucial for interpreting the outcomes of mixed plastic pyrolysis.

➢ *Chemical Structure and Thermal Degradation Behavior*

The structural differences among LDPE, HDPE, PP, and PS directly influence their thermal stability and degradation mechanisms. As summarized in Table 1, LDPE and HDPE are aliphatic polyolefins composed entirely of saturated carbon–carbon and carbon–hydrogen bonds, but differ substantially in chain architecture. LDPE contains extensive short- and long-chain branching, which reduces crystallinity and lowers thermal stability, whereas HDPE is predominantly linear, resulting in stronger intermolecular forces and higher degradation temperatures (Zhang et al., 2020; Zhou et al., 2022).

Polypropylene differs from polyethylene due to the presence of methyl side groups attached to every other carbon atom along the polymer backbone. These tertiary carbon atoms weaken adjacent C–C bonds, facilitating β-scission reactions and lowering the activation energy for thermal degradation relative to HDPE (Zhou et al., 2022). Consequently, PP generally decomposes at slightly lower temperatures than HDPE, as reflected in the degradation ranges reported in Table 1.

Polystyrene is structurally distinct due to its aromatic phenyl substituent attached to the polymer backbone. This aromaticity promotes depolymerization reactions during pyrolysis, favoring monomer recovery rather than random chain scission. As a result, PS exhibits lower degradation activation energy and a narrower product distribution dominated by aromatic compounds (Qureshi et al., 2023).

Thermogravimetric studies consistently show that polyolefins degrade over a broad temperature range (350–500 °C), while PS undergoes rapid mass loss within a narrower window (350–450 °C). These differences underpin the synergistic behavior observed in mixed plastic systems. Thermal degradation of polyolefins primarily proceeds via random chain scission reactions, producing long-chain hydrocarbons that may further crack into shorter aliphatic fractions depending on temperature and vapor residence time. In contrast, PS undergoes depolymerization through an unzipping mechanism, yielding a narrow product distribution dominated by styrene and styrene derivatives (Singh & Ruj, 2016). These distinct degradation pathways strongly influence both product yield and fuel quality.

Table 1 Chemical and Structural Characteristics of Major Plastic Feedstocks (*Zhang et al. (2020); Zhou et al. (2022); Qureshi et al. (2023)).*

Polymer	Chemical Structure	Degree of Branching	Dominant Degradation Mechanism	Typical Degradation Temperature (°C)
LDPE	Aliphatic polyolefin	Highly branched	Random chain scission	350–450
HDPE	Aliphatic polyolefin	Linear	Random chain scission	400–500
PP	Aliphatic polyolefin	Moderately branched (methyl groups)	Chain scission with β-scission	380–480
PS	Aromatic polymer	Linear with phenyl rings	Depolymerization (unzipping)	350–450

➢ *Individual Pyrolysis Performance of LDPE, HDPE, PP, and PS*

The product yield distributions obtained from individual polymer pyrolysis under catalyst-free conditions are summarized in Table 2. LDPE typically produces liquid oil yields in the range of 55–70 wt%, but a significant fraction of the liquid may consist of waxy hydrocarbons due to incomplete cracking of long polymer chains (Ahmad et al., 2014). HDPE exhibits similar or slightly lower liquid yields (50–65 wt%), reflecting its higher crystallinity and resistance to thermal degradation (Demirbas, 2004).

PP generally yields higher liquid fractions (60–75 wt%) compared to polyethylene, owing to its branched structure, which promotes chain scission and formation of shorter hydrocarbons (Panda et al., 2018). PS consistently produces the highest liquid yields, often exceeding 70–85 wt%, due to its depolymerization-driven degradation mechanism (Singh & Ruj, 2016). However, PS-derived oils are highly aromatic, which may limit their direct applicability as fuels without blending or upgrading.

These trends demonstrate that while single-polymer pyrolysis provides valuable mechanistic insights, it produces oils with unbalanced compositions and operational challenges, particularly with respect to wax formation and aromatic excess.

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Table 2 Typical Product Yield Distribution from Individual Plastic Pyrolysis (Catalyst-Free)

Polymer	Liquid Oil Yield (wt%)	Gas Yield (wt%)	Char Yield (wt%)	Dominant Oil Components
LDPE	55–70	20–35	<5	Paraffins, olefins
HDPE	50–65	25–40	<5	Long-chain hydrocarbons
PP	60–75	15–30	<5	Branched aliphatics
PS	70–85	10–25	<3	Styrene, aromatics

➢ *Fuel Oil Quality from Single-Polymer Pyrolysis*

The physicochemical properties of oils derived from individual polymers are compared in Table 3. Polyolefin-derived oils exhibit high calorific values (42–46 MJ kg^{-1}) and low sulfur content, making them attractive from an energy perspective. However, their high wax content can result in poor cold-flow properties, increased viscosity, and operational difficulties during storage and transport (Lopez et al., 2017).

In contrast, PS-derived oils exhibit lower viscosity and excellent volatility due to their aromatic-rich composition. While these properties enhance ignition quality and octane number, excessive aromatic content can increase soot formation and emissions during combustion (Demirbas, 2004). These contrasting characteristics highlight the inherent limitations of single-polymer pyrolysis and reinforce the need for mixed feedstock approaches.

Table 3 Typical Fuel Properties of Pyrolysis Oils from Individual Plastics

Property	LDPE Oil	HDPE Oil	PP Oil	PS Oil	Diesel
Density (kg m^{-3})	780–820	800–840	770–810	900–980	820–850
Calorific Value (MJ kg^{-1})	42–45	43–46	44–46	40–42	42–45
Viscosity (cSt at 40°C)	2.5–4.5	3.0–5.0	2.0–4.0	1.5–3.0	2.0–4.5
Aromatic Content (%)	Low	Low	Low–Moderate	High	Moderate

➢ *Limitations of Single-Polymer Pyrolysis*

Despite extensive investigation, single-polymer pyrolysis suffers from inherent limitations when evaluated from an industrial and waste-management perspective. Municipal plastic waste streams are rarely homogeneous, and the segregation required to achieve single-polymer feedstocks significantly increases operational cost and complexity (Ragaert et al., 2017; Papari & Hawboldt, 2022).

Additionally, oils produced from single polymers often exhibit unbalanced compositions. Polyolefin-derived oils are prone to wax formation, while PS-derived oils are excessively aromatic. These limitations necessitate blending or upgrading steps, reducing overall process efficiency. Consequently, single-polymer studies, while mechanistically valuable, provide limited guidance for real-world plastic waste valorization.

These limitations highlight the importance of mixed plastic pyrolysis, where synergistic interactions between polymers, particularly hydrogen transfer from polyolefins to PS-derived radicals, can enhance oil yield and improve fuel quality under catalyst-free conditions.

Polystyrene exhibits a fundamentally distinct degradation mechanism due to its aromatic phenyl substituents. As illustrated schematically in Figure 1, PS predominantly undergoes depolymerization through an unzipping mechanism, producing styrene monomers and related aromatic compounds rather than undergoing random chain scission (Singh & Ruj, 2016; Qureshi et al., 2023). This mechanism results in a narrower degradation temperature window and a highly aromatic product spectrum.

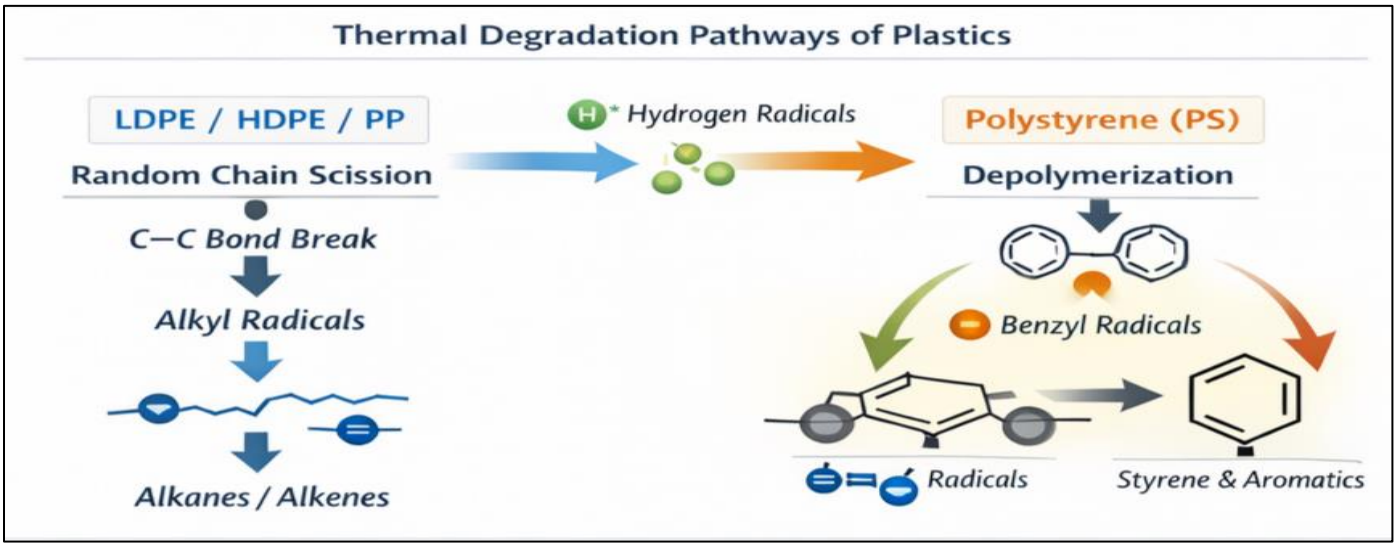

Fig 1 Schematic Representation of Thermal Degradation Pathways of LDPE, HDPE, PP, and PS

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- *Figure Description:* A comparative schematic illustrating random chain scission in polyolefins versus depolymerization in PS, highlighting hydrogen radical availability and aromatic stabilization.

III. CATALYST-FREE PYROLYSIS: RATIONALE AND INDUSTRIAL RELEVANCE

Pyrolysis can be broadly categorized into catalytic and non-catalytic (thermal) processes, depending on whether a catalyst is employed to influence reaction pathways and product selectivity. Catalyst-free pyrolysis operates solely through thermal energy input, allowing polymer decomposition pathways to be governed by intrinsic molecular structure rather than external catalytic influences. This is particularly advantageous for mixed plastic systems, where polymer–polymer interactions play a dominant role in determining product distribution (Al-Salem et al., 2020).

In non-catalytic systems, free-radical reactions dominate, including initiation via C–C bond cleavage, propagation through β-scission, and termination through hydrogen abstraction. The absence of catalysts ensures that observed synergistic effects arise exclusively from feedstock composition and operating conditions (Zhou et al., 2023). This section examines the fundamental rationale for catalyst-free pyrolysis, contrasts it with catalytic approaches, and discusses its suitability for large-scale and decentralized waste-to-fuel systems.

➢ *Scientific Basis for Catalyst-Free Pyrolysis*

Catalyst-free pyrolysis relies exclusively on thermal energy to induce polymer chain scission and depolymerization reactions. Under oxygen-free conditions, plastics undergo random chain cleavage, β-scission, and hydrogen abstraction reactions, producing volatile hydrocarbons that condense into liquid fuels (Kaminsky & Zorriqueta, 2007). In the absence of catalysts, reaction pathways are governed primarily by the intrinsic chemical structure of the polymers, allowing direct observation of feedstock-driven behavior.

For polyolefins such as LDPE, HDPE, and PP, thermal degradation is dominated by C–C bond cleavage, resulting in long-chain aliphatic hydrocarbons with high calorific value. In contrast, PS decomposes predominantly through depolymerization, yielding aromatic compounds such as styrene and ethylbenzene (Mastral et al., 2002; Zhou et al., 2023). In mixed plastic systems, these distinct degradation mechanisms interact, leading to synergistic effects that enhance liquid oil yield and suppress excessive gas formation. Such intrinsic interactions are most clearly observed under catalyst-free conditions, where external catalytic influences are absent (Breyer et al., 2017).

➢ *Economic and Operational Advantages of Catalyst-Free Systems*

From an economic standpoint, catalyst-free pyrolysis offers several advantages over catalytic systems. The elimination of catalysts reduces capital investment, as there is no requirement for catalyst procurement, handling, or replacement. Operational costs are also significantly lower due to the absence of catalyst regeneration, deactivation management, and coke removal processes (Lopez et al., 2017; Agyeman et al., 2022).

Operational simplicity is another key advantage. Catalyst-free reactors are less sensitive to feedstock contamination, such as food residues, fillers, or additives commonly present in municipal plastic waste. In catalytic systems, such contaminants can poison active sites and rapidly degrade performance, whereas thermal pyrolysis systems exhibit greater tolerance and robustness (Sharuddin et al., 2016). This makes catalyst-free pyrolysis particularly suitable for processing unsorted or minimally sorted plastic waste.

➢ *Comparison with Catalytic Pyrolysis*

Catalytic pyrolysis is often promoted for its ability to improve product selectivity, reduce wax formation, and increase aromatic content. However, these benefits are accompanied by trade-offs. Catalysts introduce additional complexity into reactor design, require precise temperature control, and are susceptible to deactivation due to coking and contamination (Miandad et al., 2016). Moreover, catalytic systems often favor gas production or highly aromatic oils, which may not be desirable for certain fuel applications. The comparative assessment in Table 4 clearly demonstrates the operational advantages of catalyst-free systems, including lower capital cost, higher feedstock tolerance, and reduced operational complexity relative to catalytic processes (Lopez et al., 2017; Agyeman et al., 2022). These attributes are especially important for processing heterogeneous municipal plastic waste, where contaminants and additives can rapidly deactivate catalysts. In contrast, catalyst-free pyrolysis produces a broader distribution of hydrocarbons, resulting in oils with balanced aliphatic and aromatic fractions. While these oils may require minimal downstream upgrading for specific applications, they are well-suited for industrial heating and blending with conventional fuels (Williams & Slaney, 2007; Papari & Hawboldt, 2022). Importantly, catalyst-free systems allow clearer attribution of product distribution to feedstock composition and operating conditions, enabling more rational process optimization.

Table 4 Comparison of Catalyst-Free and Catalytic Plastic Pyrolysis

Parameter	Catalyst-Free	Catalytic
Capital cost	Low	High
Feedstock tolerance	High	Low
Operational complexity	Low	High
Catalyst deactivation	None	Significant
Oil upgrading need	Moderate	Often required

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➢ *Industrial Relevance and Scalability*

Catalyst-free pyrolysis has demonstrated strong potential for pilot-scale and industrial implementation, particularly in continuous reactor configurations such as rotary kilns, auger reactors, and fluidized beds. These systems provide efficient heat transfer, stable operation, and high throughput without the need for catalyst management (Ali et al., 2021). Several pilot-scale studies have reported consistent oil yields and stable operation over extended periods using mixed plastic feedstocks, underscoring the practicality of non-catalytic approaches.

Heat integration further enhances the industrial viability of catalyst-free systems. Non-condensable gases generated during pyrolysis contain significant energy and can be recycled to supply process heat, reducing external energy demand and improving overall efficiency (Acomb et al., 2014). Such integration is particularly advantageous in decentralized waste-to-energy facilities, where access to external fuel sources may be limited.

➢ *Relevance to Developing and Resource-Constrained Regions*

Catalyst-free pyrolysis is especially attractive for developing economies and regions with limited technical infrastructure. The simplicity of operation, tolerance to feedstock variability, and reduced reliance on specialized materials make non-catalytic systems more accessible and resilient than catalytic alternatives (Agyeman et al., 2020). By enabling the conversion of locally generated plastic waste into usable fuel, catalyst-free pyrolysis supports energy security, waste reduction, and circular economy objectives.

➢ *Role of Catalyst-Free Pyrolysis in This Review*

In the context of this review, the exclusive focus on catalyst-free systems is a deliberate and central methodological choice. By eliminating catalytic influences, the review isolates the true impact of feedstock composition, particularly the interaction between LDPE, HDPE, PP, and PS, on fuel oil yield, quality, and process performance. This approach provides a clearer scientific basis for understanding mixed plastic pyrolysis and establishes a practical framework for designing low-cost, scalable systems that convert plastic waste into fuel.

IV. PYROLYSIS PROCESS DESCRIPTION FOR MIXED PLASTIC WASTE

Pyrolysis is a thermochemical conversion process involving the thermal decomposition of polymeric materials in the absence of oxygen, resulting in the formation of liquid hydrocarbons, non-condensable gases, and minor solid residues (Al-Salem et al., 2017). Unlike incineration, pyrolysis prevents complete oxidation of carbon, thereby enabling recovery of valuable hydrocarbon products rather than energy-only utilization.

Figure 2 summarizes the catalyst-free plastic pyrolysis process, in which mixed plastic waste, such as polyethylene (PE), polypropylene (PP), and polystyrene (PS), is thermally decomposed in an oxygen-free environment to produce valuable fuel products. Plastic feedstock is continuously introduced into a pyrolysis reactor, where it is heated to temperatures typically between 450 and 600 °C. Under these conditions, long polymer chains undergo thermal cracking via free-radical reactions, resulting in the formation of volatile hydrocarbons, solid char, and heavy residues (Williams, 2013; Al-Salem et al., 2017).

The volatile pyrolysis vapors exit the reactor and pass through a condensation unit, where condensable hydrocarbons are recovered as pyrolysis oil, a high-energy liquid fuel with properties comparable to conventional diesel. Heavier hydrocarbons that do not fully crack form wax or heavy oil, which can be recycled back into the reactor for further conversion (Lopez et al., 2017). Non-condensable gases, primarily light hydrocarbons and hydrogen, are cleaned in a gas scrubber and collected as fuel gas, which can be reused to supply process heat, thereby improving overall energy efficiency (Kaminsky & Zorriqueta, 2007).

A small fraction of char residue remains in the reactor and is removed as a solid by-product, consisting mainly of carbonaceous material and inorganic additives. Overall, Figure 2 highlights the simplicity, flexibility, and energy recovery potential of plastic pyrolysis, demonstrating its effectiveness as a sustainable technology for converting plastic waste into liquid fuels and gaseous energy carriers within a circular economy framework (Breyer et al., 2017; Papari & Hawboldt, 2022).

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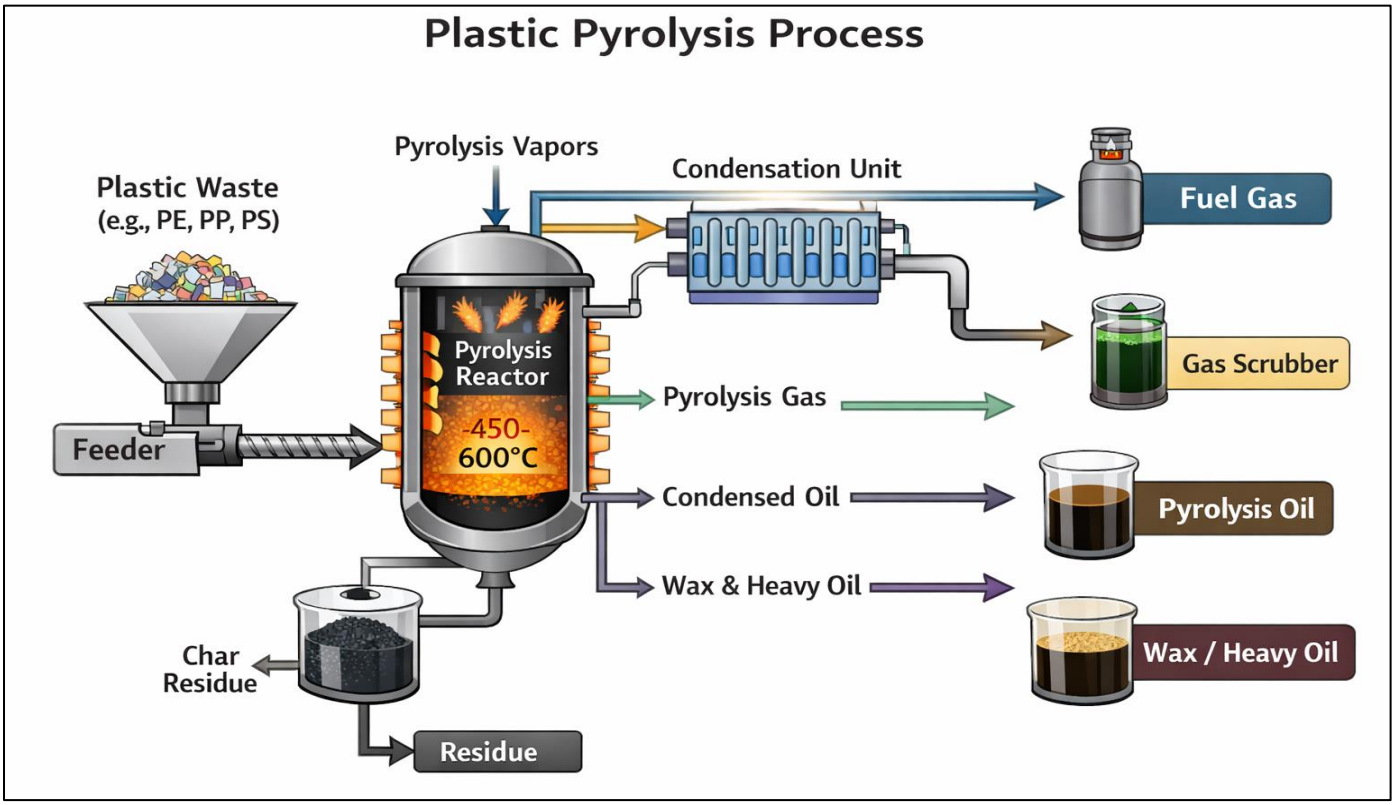

Fig 2 Schematic of the Catalyst-Free Plastic Pyrolysis Process Flow

➢ *Rationale for Mixed Feedstock Pyrolysis*

The primary motivation for mixed plastic pyrolysis lies in its ability to realistically represent municipal solid waste compositions. Mechanical sorting of plastics into single-polymer streams is costly, energy-intensive, and often impractical, particularly in developing economies. Mixed feedstock pyrolysis significantly reduces pretreatment requirements, enabling direct processing of heterogeneous plastic waste with minimal separation (Ragaert et al., 2017).

From a process perspective, mixed plastic pyrolysis also offers the potential for synergistic interactions between polymers with different degradation behaviors. Polyolefins (LDPE, HDPE, and PP) are hydrogen-rich materials that primarily generate aliphatic hydrocarbons, while PS produces aromatic compounds through depolymerization. When processed together, these polymers can interact at the radical level, influencing reaction pathways, product distribution, and fuel quality (Panda et al., 2018).

- *Influence of Contaminants and Additives in Mixed Plastic Pyrolysis*

Real municipal plastic waste streams differ fundamentally from virgin polymer feedstocks commonly used in laboratory pyrolysis studies due to the widespread presence of chemical additives, pigments, fillers, stabilizers, flame retardants, and residual packaging materials. These substances are intentionally incorporated during plastic manufacturing to enhance durability, flexibility, thermal stability, and aesthetic properties, and are therefore ubiquitous across commercial LDPE, HDPE, PP, and PS products. Comprehensive analyses have shown that such additives can migrate, degrade, or be released during waste handling and thermal recovery processes, potentially influencing degradation pathways, vapor composition, and the quality of resulting pyrolysis oils (Hahladakis et al., 2018). Consequently, catalyst-free pyrolysis systems must be evaluated under realistic feedstock conditions that account for additive-induced heterogeneity, as these non-polymeric constituents may alter reaction kinetics, promote secondary reactions, and affect downstream oil stability and emissions behavior.

In catalytic pyrolysis systems, feedstock contaminants such as chlorine, sulfur, and other heteroatoms can interact with active catalyst sites, leading to catalyst poisoning, coke formation, and accelerated deactivation, which ultimately reduce process efficiency and operational lifespan (Miandad et al., 2016). In contrast, catalyst-free (thermal) pyrolysis operates without active catalytic surfaces, making its thermal degradation pathways inherently more tolerant to the presence of impurities, additives, and mixed polymer fractions. This tolerance improves the feasibility of processing unsorted or minimally sorted municipal plastic waste without extensive pretreatment. Although additives, fillers, and residual contaminants can influence secondary gas and char formation, evidence from comparative studies of mixed plastic pyrolysis suggests that overall liquid fuel yield is more strongly dependent on feedstock composition and key operating conditions such as temperature, residence time, and heating rate than on minor additive effects (Williams & Slaney, 2007). Consequently, a feedstock-centric optimization approach remains a viable strategy for industrial-scale deployment of catalyst-free pyrolysis systems.

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➢ *Thermal Degradation Behavior of Mixed Plastics*

The thermal degradation of mixed plastics does not simply represent the weighted average of individual polymer behaviors. Instead, experimental studies have demonstrated shifts in degradation temperatures, altered product distributions, and enhanced liquid yields due to interactions between polymer fragments (Ahmad et al., 2014).

Thermogravimetric analysis (TGA) of mixed LDPE/HDPE/PP/PS blends typically shows overlapping degradation peaks, indicating simultaneous decomposition over a broad temperature range of approximately 350–500 °C. As shown in Table 5, mixed LDPE/HDPE/PP/PS feedstocks exhibit overlapping degradation ranges, indicating simultaneous decomposition of multiple polymers. The presence of PS often lowers the onset degradation temperature of the mixture due to its depolymerization behavior, while polyolefins contribute to sustained liquid production at higher temperatures. This overlap facilitates interaction between degradation intermediates, which does not occur in isolated single-polymer systems (Singh & Ruj, 2016).

Table 5 Thermal Degradation Characteristics of Individual and Mixed Plastic Feedstocks

Feedstock	Onset Degradation Temp (°C)	Peak Degradation Temp (°C)	Degradation Range (°C)
LDPE	380–420	450	350–480
HDPE	400–440	470	380–500
PP	370–410	440	350–470
PS	350–380	420	330–450
LDPE/HDPE/PP/PS (Mixed)	360–390	440–460	350–500

➢ *Synergistic Effects in Catalyst-Free Mixed Plastic Pyrolysis*

One of the most significant advantages of mixed plastic pyrolysis is the occurrence of synergistic effects that enhance liquid oil yield and improve product quality without the need for catalysts. These effects are particularly pronounced in catalyst-free systems, where intrinsic polymer interactions dominate reaction pathways.

A key synergistic mechanism is hydrogen transfer from polyolefins to PS-derived radicals. Polyolefins are hydrogen-rich and readily donate hydrogen atoms during thermal cracking, stabilizing aromatic radicals produced from PS depolymerization. This stabilization suppresses secondary polymerization and coke formation, thereby increasing liquid oil yield (Panda et al., 2018; Zhang et al., 2020; Qureshi et al., 2023). These synergistic mechanisms governing mixed plastic pyrolysis are summarized in Table 6 and illustrated in Figure 3. When processed together, hydrogen transfer from polyolefin-derived radicals stabilizes aromatic intermediates formed from PS, suppressing secondary cracking and excessive gas formation. This interaction promotes the formation of stable liquid hydrocarbons and enhances overall oil yield (Ahmad et al., 2014; Zhou et al., 2022).

In addition to hydrogen transfer, PS plays a critical role in mitigating wax formation. Long-chain waxes produced during polyolefin pyrolysis can be partially cracked in the presence of PS-derived aromatic radicals, resulting in shorter-chain hydrocarbons that remain in the liquid phase (Santella et al., 2023).

Table 6 Synergistic Effects Observed in Catalyst-Free Mixed Plastic Pyrolysis

Synergistic Interaction	Dominant Polymer	Observed Effect	Impact on Process
Hydrogen transfer	LDPE, HDPE, PP, PS	Radical stabilization	Increased liquid yield
Aromatic–aliphatic interaction	PS + polyolefins	Suppressed wax formation	Improved oil flow properties
Overlapping degradation	All polymers	Broader reaction window	Stable operation
Reduced coke formation	Polyolefins + PS	Lower char yield	Improved reactor performance

Fig 3 Synergistic Interaction Mechanisms in Catalyst-Free Mixed Plastic Pyrolysis

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- Figure Description: A conceptual schematic illustrating hydrogen transfer from polyolefins to PS-derived aromatic radicals, wax suppression pathways, and enhanced liquid oil formation.

➢ *Oil Yield Trends from Mixed Plastic Pyrolysis*

Experimental studies consistently report higher or comparable liquid oil yields from mixed plastic pyrolysis compared to single-polymer systems. Oil yield data in Table 7 confirm that mixed plastic pyrolysis consistently achieves higher or comparable liquid yields (65–80 wt%) relative to single-polymer systems (Singh & Ruj, 2016).

Blends containing moderate proportions of PS (20–40 wt%) often achieve optimal oil yields due to enhanced depolymerization and reduced secondary cracking. Excessive PS content, however, can increase aromatic concentration and gas formation at elevated temperatures (Demirbas, 2004).

Table 7 Comparison of Liquid Oil Yield from Individual and Mixed Plastic Pyrolysis
(*Zhou et al. (2022); Qureshi et al. (2023); Santella et al. (2023)*)

Feedstock	Liquid Yield (wt%)	Gas Yield (wt%)	Char Yield (wt%)
LDPE	55–70	20–35	<5
HDPE	50–65	25–40	<5
PP	60–75	15–30	<5
PS	70–85	10–25	<3
Mixed LDPE/HDPE/PP/PS	65–80	15–30	<3

➢ *Effect of Feedstock Ratio on Pyrolysis Performance*

The relative proportions of LDPE, HDPE, PP, and PS significantly influence pyrolysis outcomes. Studies examining varying blend ratios in Table 8 demonstrate that feedstock composition critically influences performance, with blends containing 20–40 wt% PS achieving optimal yield and oil quality due to a balanced aliphatic–aromatic composition. Also, that increasing PS content generally enhances liquid yield up to an optimal threshold, beyond which excessive aromaticity may negatively impact oil stability (Zhang et al., 2020). Conversely, polyolefin-rich blends favor higher aliphatic content but may suffer from increased wax formation if PS content is insufficient. Balanced mixtures leverage the strengths of each polymer, achieving improved oil yield and quality (Panda et al., 2018).

Optimal performance is typically observed in blends containing 20–40 wt% PS, where hydrogen transfer and wax suppression effects are maximized without excessive aromatic enrichment (Zhou et al., 2022). These findings highlight the importance of feedstock characterization and controlled blending in industrial applications.

Table 8 Effect of Feedstock Composition on Catalyst-Free Mixed Plastic Pyrolysis

Blend Composition	Dominant Products	Observed Challenges	Overall Performance
High polyolefin (>70%)	Paraffinic oils	Wax formation	Moderate
Moderate PS (20–40%)	Balanced hydrocarbons	Minimal	High
High PS (>50%)	Aromatic-rich oils	Gas formation	Moderate

➢ *Comparison with Single-Polymer Pyrolysis*

Compared to single-polymer systems, mixed plastic pyrolysis offers superior operational stability, reduced wax formation, and improved liquid yield consistency. These advantages are particularly relevant for catalyst-free systems, where feedstock-driven interactions replace catalyst-mediated upgrading (Sharuddin et al., 2016).

➢ *Influence of Operating Conditions on Mixed Plastic Pyrolysis*

Temperature remains the most influential operating parameter in mixed plastic pyrolysis. Liquid yields generally increase with temperature up to approximately 500–550 °C, beyond which secondary cracking reactions favor gas production (Papari et al., 2023). Heating rate and vapor residence time also play critical roles; moderate heating rates and sufficient residence times promote wax cracking and liquid stabilization.

Importantly, mixed plastic systems exhibit broader optimal operating windows than single-polymer systems, reflecting their enhanced thermal stability and synergistic degradation behavior (Santella et al., 2023). This characteristic improves process robustness and reduces sensitivity to operational fluctuations.

➢ *Industrial Implications of Mixed Plastic Pyrolysis*

The demonstrated synergistic benefits of mixed plastic pyrolysis have significant implications for industrial deployment. By enabling higher liquid yields, reduced gas formation, and improved oil quality without catalysts, mixed feedstock pyrolysis supports the development of simpler, more cost-effective systems. These advantages are particularly relevant for decentralized waste-to-fuel facilities, where feedstock variability and operational simplicity are critical (Agyeman et al., 2022; Santella et al., 2023).

V. FUEL OIL YIELD FROM CATALYST-FREE MIXED PLASTIC PYROLYSIS

Fuel oil yield is a critical performance indicator in plastic waste pyrolysis, as it directly determines process economics and energy recovery efficiency. In catalyst-free pyrolysis of mixed LDPE, HDPE, PP, and PS, oil yield is governed by the intrinsic thermal degradation behavior of the polymers, synergistic interactions among degradation

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intermediates, and operational parameters such as temperature, heating rate, and residence time. (Papari et al., 2023; Zhou et al., 2023).

During pyrolysis, polymer chains undergo random chain scission, β-scission, and hydrogen abstraction reactions, producing volatile hydrocarbons that subsequently condense into liquid oil (Kaminsky & Zorriqueta, 2007). Polyolefins such as LDPE, HDPE, and PP degrade primarily through random scission of C–C bonds, yielding long-chain aliphatic hydrocarbons, while PS decomposes predominantly via depolymerization, producing aromatic compounds such as styrene monomers (Mastral et al., 2002).

In mixed plastic systems, synergistic interactions occur when hydrogen-rich polyolefins donate hydrogen radicals to stabilize aromatic fragments from PS, reducing secondary cracking and enhancing liquid oil yield (Breyer et al., 2017). This intrinsic synergy is particularly significant under catalyst-free conditions, where polymer–polymer interactions dominate reaction pathways.

➢ *Liquid Fuel Yield Trends*

Studies on mixed plastic pyrolysis consistently report liquid oil yields between 60 and 82 wt% under catalyst-free conditions, depending on feedstock composition and operating parameters (Williams & Slaney, 2007; Breyer et al., 2017). The inclusion of PS in polyolefin-rich mixtures has been shown to significantly enhance liquid yield due to its depolymerization-driven degradation pathway, which favors condensable aromatic products. (Santella et al., 2023; Zhou et al., 2023).

The influence of operating conditions on yield is illustrated in Figure 4, which shows that optimal oil production occurs at intermediate temperatures and moderate vapor residence times. Kinetic studies indicate reduced activation energies for mixed plastics, attributed to radical stabilization and hydrogen transfer effects (Zhang et al., 2020; Qureshi et al., 2023). The influence of temperature and residence time on oil yield is illustrated in Figure 4, which shows that intermediate temperatures favor liquid production, while excessive temperatures promote gas formation due to secondary cracking. Optimal liquid production generally occurs within the temperature range of 400–460 °C. Below this range, incomplete polymer breakdown results in higher solid residues, while temperatures exceeding 500 °C promote secondary cracking reactions that convert condensable vapors into permanent gases (Adrados et al., 2012; Papari et al., 2023). Heating rate also plays a crucial role; moderate heating rates facilitate uniform heat penetration and controlled volatilization, whereas excessively rapid heating increases gas formation and reduces oil yield.

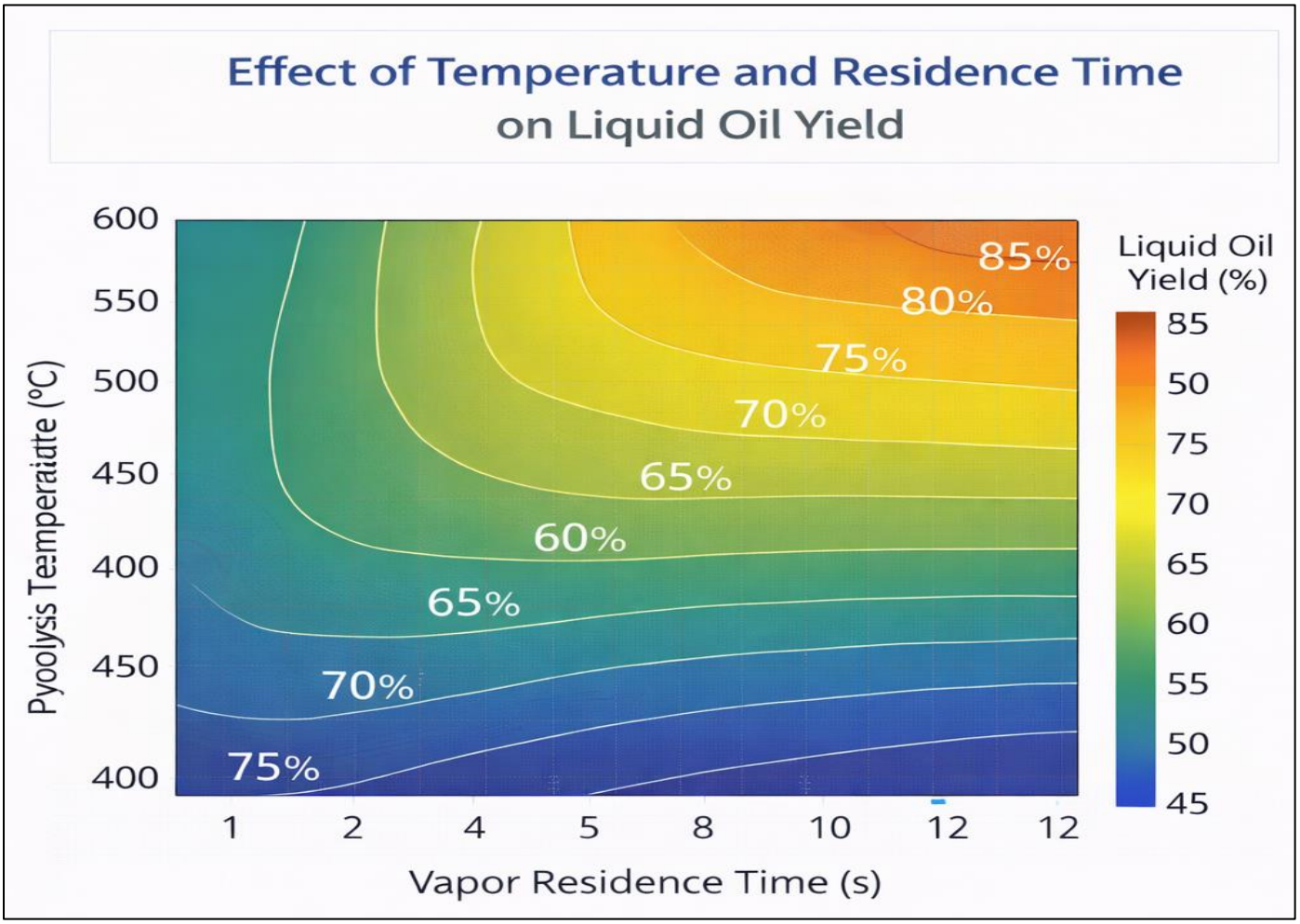

Fig 4 Effect of Temperature and Residence Time on Liquid Oil Yield

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- Figure Description: A contour plot showing liquid oil yield as a function of pyrolysis temperature and vapor residence time for mixed LDPE/HDPE/PP/PS under catalyst-free conditions.

➢ *Kinetic Considerations in Mixed Plastic Pyrolysis*

Kinetic studies provide insight into the enhanced oil yields observed in mixed plastic systems. Apparent activation energies for mixed LDPE/HDPE/PP/PS pyrolysis are consistently reported to be lower than those of individual polymers, indicating facilitated degradation pathways (Zhang et al., 2020; Zhou et al., 2022). This reduction in activation energy is attributed to hydrogen transfer reactions and radical stabilization mechanisms occurring between polyolefins and PS.

Polyolefin-derived radicals act as hydrogen donors, stabilizing aromatic radicals generated during PS depolymerization. This interaction suppresses recombination and gas-phase cracking reactions, favoring the formation of stable liquid hydrocarbons (Qureshi et al., 2023). As a result, mixed plastic systems exhibit smoother mass loss profiles and higher liquid selectivity under equivalent thermal conditions.

➢ *Gas and Char Formation*

Gas formation in catalyst-free mixed plastic pyrolysis is primarily associated with secondary cracking reactions at elevated temperatures. The presence of PS has been shown to suppress excessive gas formation by stabilizing intermediate radicals, particularly when PS content is maintained within optimal ranges (William,2013; Zhou et al., 2022). Non-condensable gases typically consist of light hydrocarbons (C_1–C_4), hydrogen, and small amounts of CO and CO_2. Fuel oil yield is the primary economic driver of plastic pyrolysis. As summarized in Table 9, catalyst-free mixed plastic systems typically produce 60–82 wt% liquid oil, with minimal char formation (<3 wt%) across most operating conditions due to the low aromatic crosslinking tendency of polyolefins. Unlike biomass pyrolysis, plastic pyrolysis does not favor char formation, making it particularly attractive for liquid fuel production (Jung et al.,2010; Santella et al., 2023).

Table 9 Fuel Yield Distribution in Catalyst-Free Mixed Plastic Pyrolysis

Product	Typical Yield (wt%)	Key Influencing Factors
Liquid oil	60–82	Temperature, PS content
Gas	15–30	Heating rate, residence time
Char	<3	Temperature uniformity

➢ *Comparison with Catalytic Systems*

While catalytic pyrolysis can enhance selectivity toward specific hydrocarbon fractions, comparative studies in Table 10 indicate that catalyst-free systems often achieve comparable or higher liquid yields when processing mixed plastics, particularly at pilot scale, without the penalties of catalyst deactivation or coke formation (Papari & Hawboldt, 2022; Zhou et al., 2023). Moreover, catalyst-free systems avoid yield losses associated with coke formation and catalyst deactivation.

Table 10 Comparison of Liquid Yield: Catalyst-Free vs Catalytic Pyrolysis

System Type	Liquid Yield (wt%)	Operational Stability	Feedstock Sensitivity
Catalyst-free	**70–85**	High	Low
Catalytic	60–80	Moderate	High

VI. FUEL OIL QUALITY FROM CATALYST-FREE MIXED PLASTIC PYROLYSIS

Beyond yield, the quality of pyrolysis-derived fuel oil is a decisive factor in determining its suitability for direct utilization or blending with conventional fuels. In catalyst-free pyrolysis of mixed LDPE, HDPE, PP, and PS, fuel quality is governed by the balance between aliphatic hydrocarbons derived from polyolefins and aromatic compounds originating from polystyrene degradation. Recent studies emphasize that mixed plastic systems produce oils with more favorable compositional balance than oils derived from single polymers (Alaba et al., 2021; Jung et al., 2010).

➢ *Physical Fuel Properties*

Catalyst-free mixed plastic pyrolysis oils as show in Table 11 exhibit densities in the range of 0.78–0.92 g cm^{-3}, viscosities between 2.0 and 6.5 mm^2 s^{-1} at 40 °C, and higher heating values (HHV) of 41–46 MJ kg^{-1}, which are comparable to diesel and light fuel oils (Alaba et al., 2021; Lopez-Urionabarrenechea et al., 2023). These properties indicate strong potential for use in industrial boilers, furnaces, and stationary engines. Compared to oils derived from pure PS, mixed plastic oils demonstrate reduced aromatic concentration and improved stability, while polyolefin-rich oils benefit from the presence of PS-derived aromatics that enhance volatility and reduce wax precipitation (Jung et al., 2010).

Table 11 Typical Physical Properties of Catalyst-Free Mixed Plastic Pyrolysis Oils

Property	Mixed Plastic Oil	Diesel (Typical)
Density (g cm^{-3})	0.78–0.92	0.82–0.85
Viscosity (mm^2 s^{-1})	2.0–6.5	2.0–4.5
HHV (MJ kg^{-1})	41–46	43–46
Flash point (°C)	30–55	>52

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➢ *Chemical Composition and Hydrocarbon Distribution*

Gas chromatography mass spectrometry (GC–MS) analyses in Figure 5 reveal that mixed plastic pyrolysis oils consist predominantly of C_5–C_{20} hydrocarbons, including paraffins, olefins, naphthenes, and aromatics. Polyolefins contribute long-chain aliphatic hydrocarbons, while PS contributes mono-aromatic compounds such as styrene, ethylbenzene, and toluene (Artetxe et al., 2015; Lopez-Urionabarrenechea et al., 2023; Shah et al., 2021).

The coexistence of these fractions improves combustion behavior and reduces the instability associated with highly unsaturated PS oils. Importantly, catalyst-free systems avoid excessive aromatization, often observed in catalytic pyrolysis, which can negatively affect fuel emissions and regulatory compliance (Alaba et al., 2021).

➢ *Fuel Compatibility and End-Use Applications*

Recent combustion and blending studies indicate that mixed plastic pyrolysis oils can be blended with diesel at ratios of up to 20–30 vol% without significant engine performance penalties in stationary applications (Frigo et al., 2014; Shah et al., 2021; Jung et al., 2010). While further upgrading may be required for transportation fuels, direct use in industrial heating and power generation applications is technically feasible.

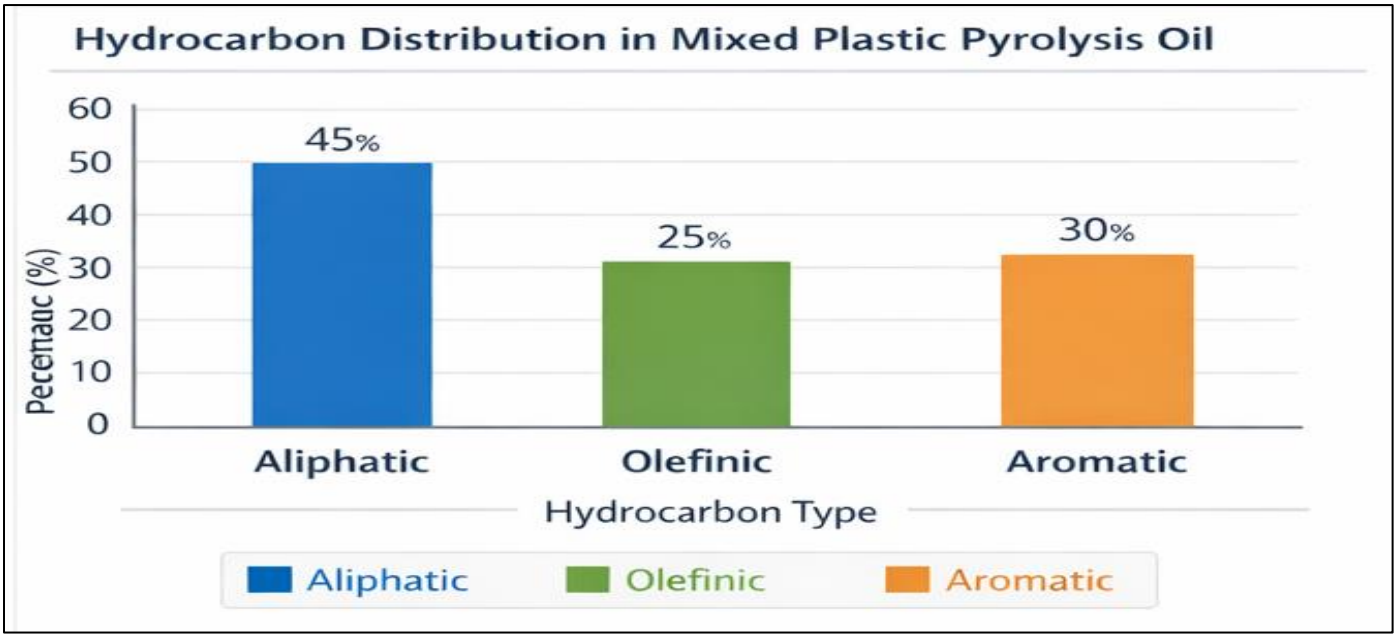

Fig 5 Hydrocarbon Distribution in Mixed Plastic Pyrolysis Oil

- Figure Description: Bar chart showing relative proportions of aliphatic, olefinic, and aromatic hydrocarbons in catalyst-free mixed plastic pyrolysis oil.

➢ *Effect of Temperature on Product Distribution in Catalyst-Free Plastic Pyrolysis*

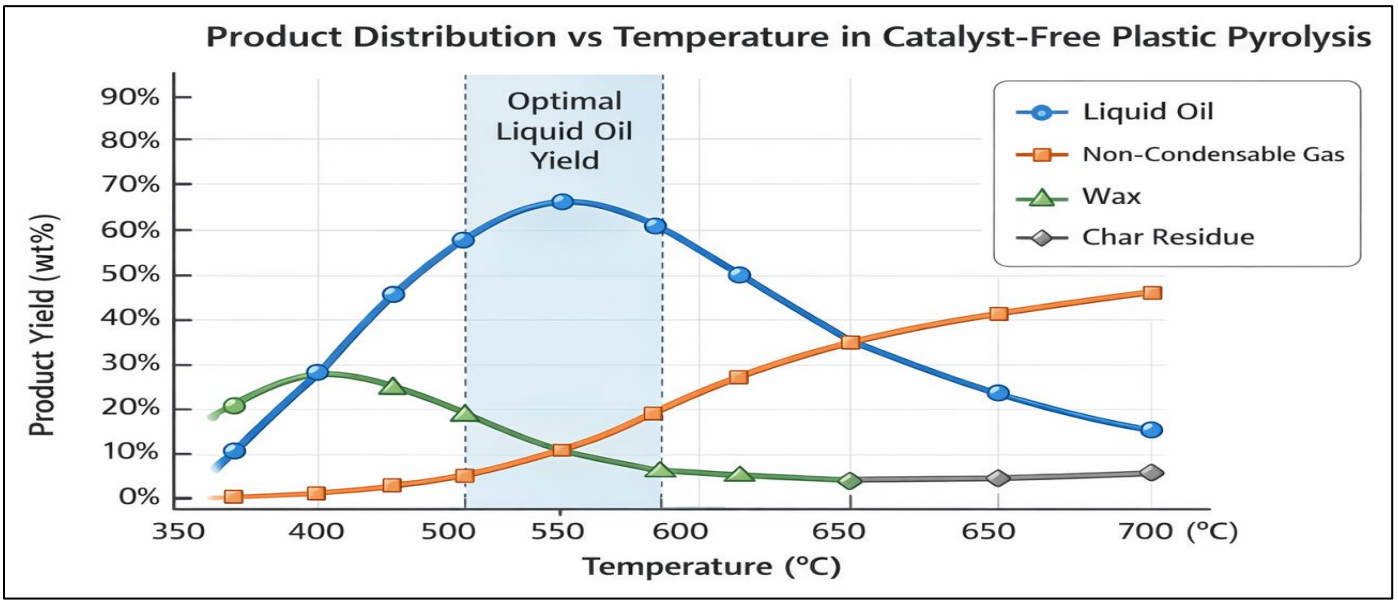

Fig 6 Effect of Temperature on Product Distribution in Catalyst-Free Plastic Pyrolysis

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Figure 6 illustrates the influence of reaction temperature on product distribution during catalyst-free plastic pyrolysis, highlighting the relative yields of liquid oil, non-condensable gas, wax, and char residue. Temperature is a critical operational parameter in pyrolysis, as it governs polymer chain scission, secondary cracking reactions, and phase transformation of intermediates (Williams, 2013).

At lower temperatures (≈350–400 °C), wax formation is dominant, accounting for, in the range of 20–28 wt%. This behavior is attributed to incomplete thermal cracking of long polymer chains, resulting in heavy hydrocarbons that condense as waxy products (Al-Salem et al., 2017). Liquid oil yield remains relatively low in this range, indicating insufficient energy to promote extensive depolymerization.

As the temperature increases to the intermediate range of approximately 500–600 °C, liquid oil yield rises sharply and reaches a maximum of around 65–67 wt%, indicating an optimal thermal cracking regime. In this temperature window, polymer chains undergo efficient β-scission, producing condensable hydrocarbons with molecular weights suitable for liquid fuels (Lopez et al., 2017). The shaded region in the figure highlights this optimal operating range, where liquid oil production is maximized while gas formation remains moderate.

Beyond 600 °C, a noticeable decline in liquid oil yield is observed, accompanied by a significant increase in non-condensable gas production, which reaches approximately 45 wt% at 700 °C. This trend is associated with secondary cracking reactions, where liquid-range hydrocarbons are further decomposed into lighter gaseous compounds such as hydrogen, methane, and C_2–C_4 hydrocarbons (Aguado et al., 2008). Concurrently, wax yield diminishes to negligible levels, indicating near-complete cracking of heavy hydrocarbons at elevated temperatures.

Char residue remains minimal across the entire temperature range, typically below 6 wt%, reflecting the low fixed-carbon content of most commodity plastics and the dominance of volatilization reactions over solid-phase carbonization (Al-Salem et al., 2017).

Overall, the figure demonstrates that catalyst-free plastic pyrolysis exhibits a clear temperature-dependent shift in product distribution, with intermediate temperatures favoring liquid oil production and higher temperatures promoting gaseous products. These findings underscore the importance of temperature optimization in designing pyrolysis systems aimed at maximizing liquid fuel yield.

- *Environmental Considerations of Catalyst-Free Mixed Plastic Pyrolysis:*

Environmental performance, as illustrated in Figure 7, is a critical criterion in evaluating plastic waste management technologies, particularly in comparison to conventional disposal routes such as landfilling and incineration. Catalyst-free pyrolysis of mixed plastic waste offers several potential environmental advantages by enabling material recovery while avoiding direct combustion and associated emissions. Unlike incineration, which results in complete oxidation of carbon and the formation of flue gases containing CO_2, NO_x, SO_x, dioxins, and particulate matter, pyrolysis operates under oxygen-free conditions, thereby limiting the formation of combustion-related pollutants and enabling recovery of hydrocarbon-rich products (Al-Salem et al., 2009; Williams, 2013).

One of the primary environmental benefits of catalyst-free pyrolysis lies in its avoidance of catalyst-related impacts. Catalytic systems often require metal- or zeolite-based catalysts that are energy-intensive to manufacture, susceptible to deactivation, and associated with disposal or regeneration challenges, which can increase both environmental burden and operational complexity (Miandad et al., 2016). In contrast, non-catalytic systems eliminate these material inputs and reduce secondary waste streams, thereby simplifying lifecycle considerations and improving overall environmental robustness.

Emissions associated with catalyst-free pyrolysis are primarily linked to non-condensable gases and trace contaminants released during thermal degradation. However, these gases, composed mainly of light hydrocarbons and hydrogen, can be effectively recovered and utilized as internal process fuel, reducing net external energy demand and lowering indirect greenhouse gas emissions (Acomb et al., 2014). This internal heat integration contributes to improved energy efficiency and supports more favorable energy balances compared to disposal-only waste treatment methods.

The presence of additives and heteroatoms in mixed plastic waste can influence emission profiles, particularly with respect to acid gases or trace pollutants. Nevertheless, studies indicate that under controlled operating conditions, catalyst-free systems can maintain stable operation with minimal char formation and manageable emissions, especially when compared to uncontrolled open burning or poorly regulated incineration practices (Hahladakis et al., 2018). Importantly, the absence of catalysts reduces sensitivity to feedstock impurities, which is advantageous for processing heterogeneous municipal plastic waste without extensive pretreatment.

From a broader sustainability perspective, catalyst-free mixed plastic pyrolysis supports circular economy objectives by diverting plastic waste from landfills and recovering its embedded chemical energy in the form of liquid fuels. While pyrolysis-derived fuels are ultimately combusted and therefore not carbon-neutral, their utilization can offset fossil fuel consumption and reduce the environmental footprint associated with virgin fuel production (Breyer et al., 2017). Consequently, when integrated with appropriate emission controls and energy recovery strategies, catalyst-free pyrolysis represents a transitional waste-to-energy solution with measurable environmental benefits relative to conventional disposal pathways.

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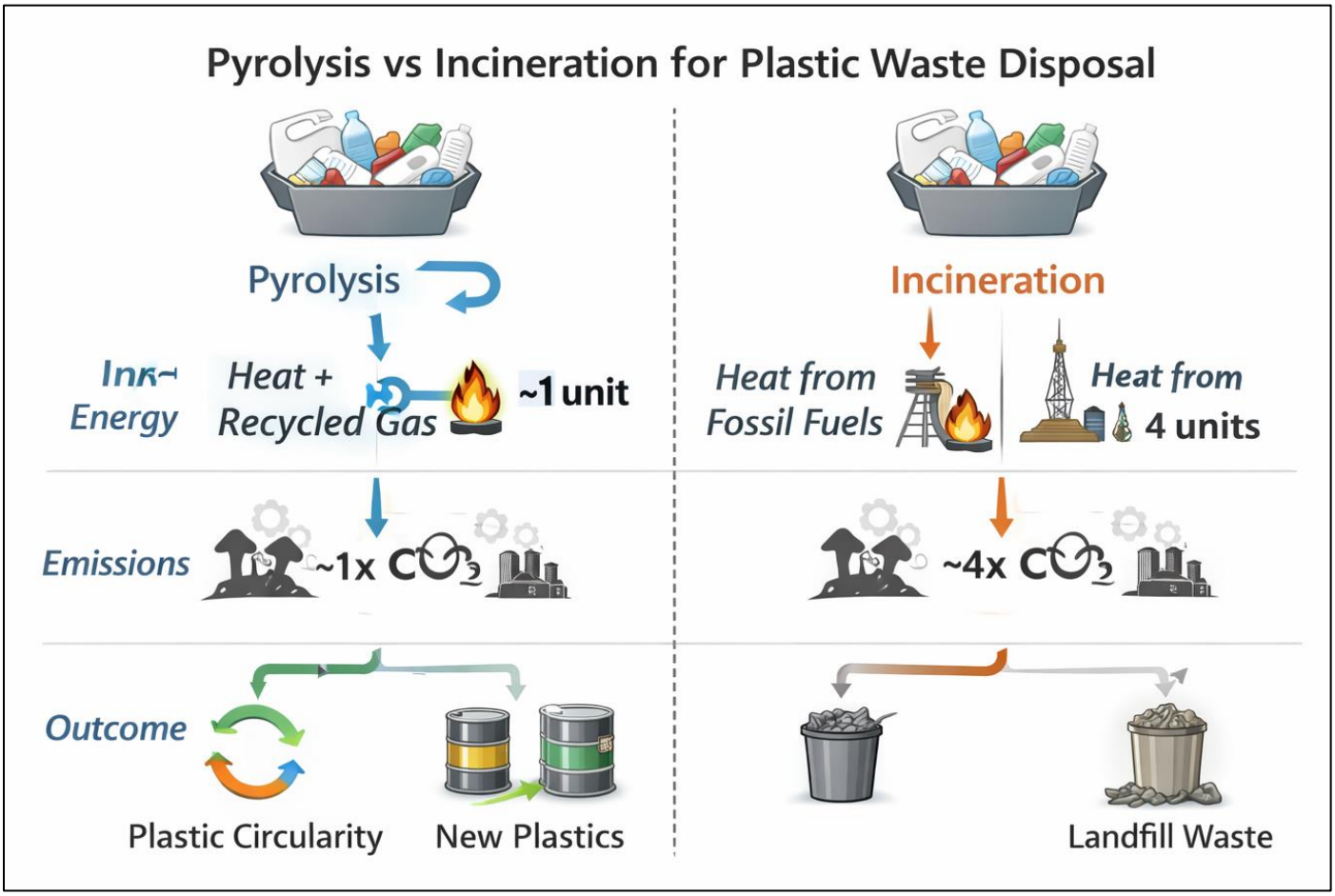

Fig 7 Pyrolysis Vs Incineration for Plastic Waste Disposal

VII. ENERGY EFFICIENCY AND HEAT INTEGRATION

Process performance in catalyst-free pyrolysis is strongly influenced by energy efficiency and heat recovery strategies. Recent energy balance studies in Table 12 demonstrate that up to 60–70% of the thermal energy input can be recovered through combustion of non-condensable pyrolysis gases, significantly reducing net energy demand (Kaminsky & Zorriqueta, 2007; Mastellone et al., 2020; Arena et al., 2023).

Continuous reactor configurations, such as auger and rotary kiln systems, exhibit superior heat transfer characteristics and operational stability compared to batch reactors, particularly when processing mixed plastic feedstocks (Arena et al., 2023).

Table 12 Process Performance Metrics for Catalyst-Free Mixed Plastic Pyrolysis

Parameter	Typical Range	Industrial Relevance
Energy efficiency (%)	65–80	High
Operating temperature (°C)	400–460	Moderate
Feedstock tolerance	High	Very high
Operational complexity	Low	Favorable

➢ *Reactor Design and Operational Stability*

Reactor configuration strongly influences process stability. Fixed-bed reactors are suitable for laboratory studies, while rotary kiln, screw, and fluidized-bed reactors offer better heat transfer and throughput for pilot-scale operations (Mastral et al., 2002; Lopez et al., 2021).

Efficient heat transfer is a critical requirement for maximizing liquid oil yield in catalyst-free pyrolysis systems. Uniform temperature distribution prevents localized overheating, which can promote excessive gas formation and reduce oil yield (Adrados et al., 2012). Common reactor configurations include batch, semi-batch, and continuous reactors, with continuous systems such as rotary kilns, auger reactors, and fluidized beds offering superior scalability and process stability (Ali et al., 2021). Reactor comparisons in Figure 8 and energy flow pathways illustrated in Figure 9 emphasize the importance of reactor design and heat integration in achieving stable, scalable operation. Catalyst-free systems offer distinct advantages, including: Elimination of catalyst deactivation and regeneration, reduced fouling and coke formation, and lower capital and operating costs.

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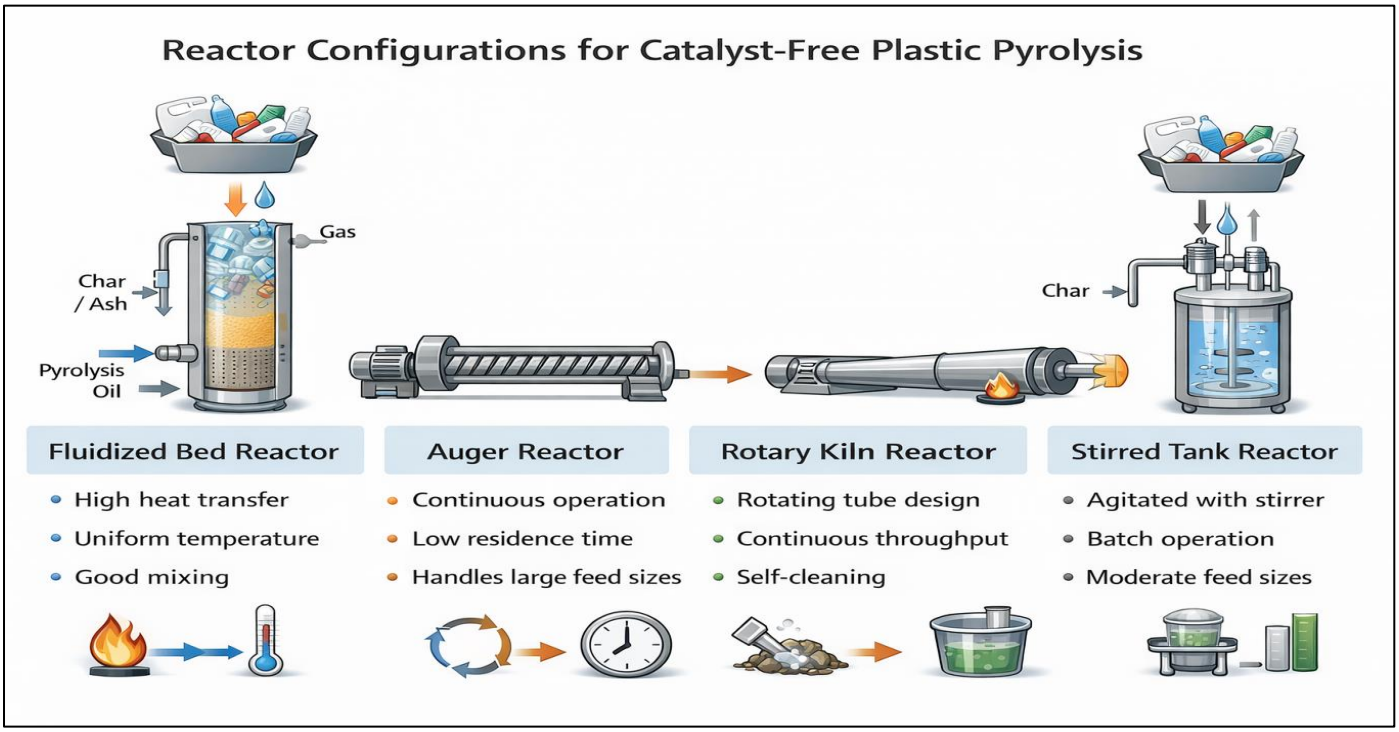

Fig 8 Comparison of Reactor Types for Catalyst-Free Plastic Pyrolysis

➢ *Scale-Up Challenges and Industrial Feasibility*

Key challenges in scaling up catalyst-free mixed plastic pyrolysis include controlling wax deposition, ensuring uniform temperature distribution, and optimizing vapor condensation systems. Nonetheless, several pilot-scale demonstrations have confirmed the technical feasibility of processing mixed plastic waste without catalysts, particularly for decentralized waste-to-energy applications (Acomb et al., 2014; Lopez et al., 2017; Arena et al., 2023).

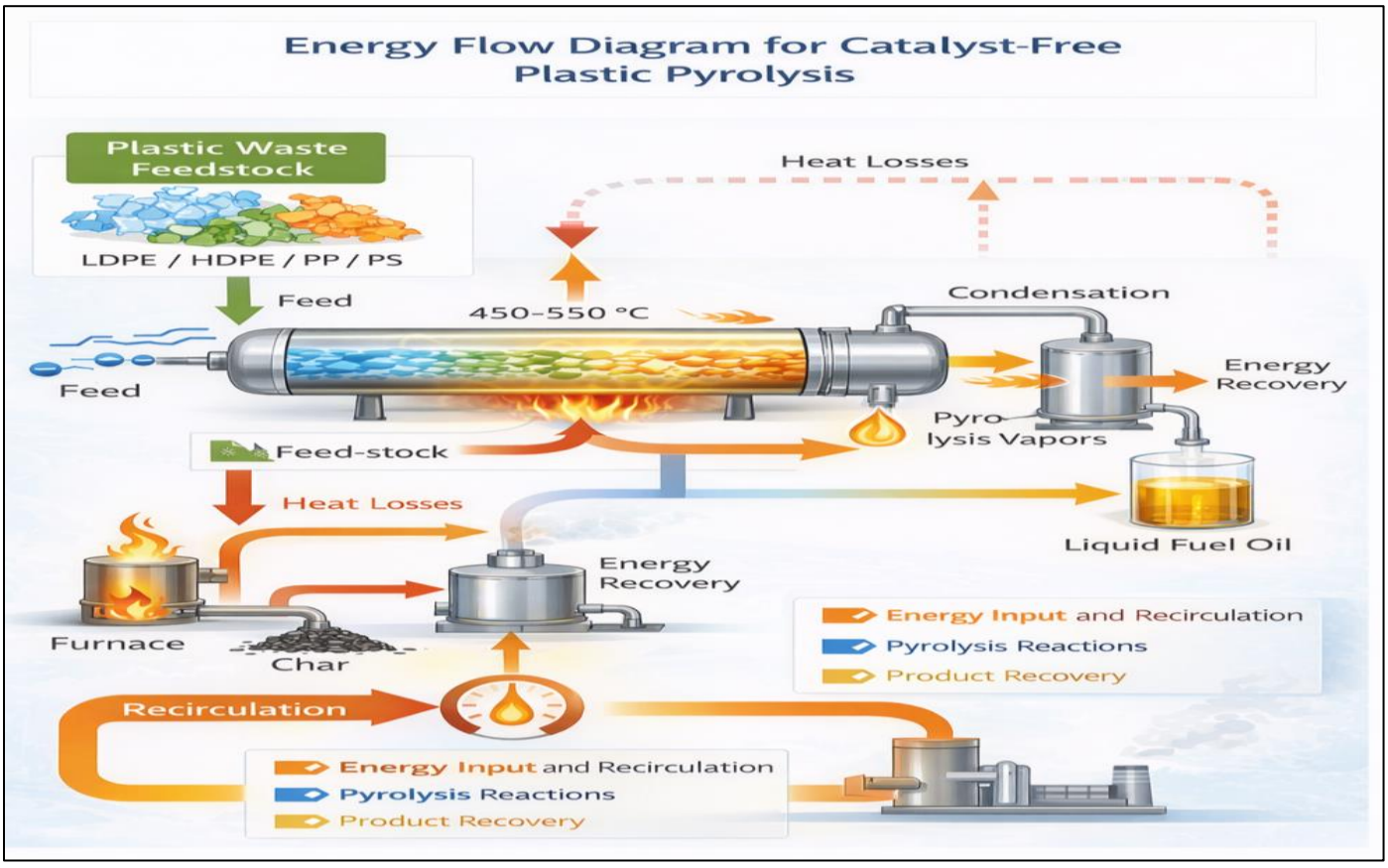

Fig 9 Energy Flow Diagram for Catalyst-Free Plastic Pyrolysis

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- Figure Description: Diagram showing energy input, pyrolysis reactions, gas recirculation, oil recovery, and heat losses.

VIII. NOVELTY OF THIS REVIEW AND COMPARATIVE ASSESSMENT WITH EXISTING LITERATURE

➢ *Limitations of Existing Plastic Pyrolysis Reviews*

Over the past two decades, numerous review studies have examined plastic waste pyrolysis as a route for fuel and chemical recovery. However, the majority of these reviews adopt broad, non-specific frameworks that obscure critical feedstock process relationships. For instance, several widely cited reviews categorize plastics simply as *polyolefins*, *polystyrenics*, or *mixed plastics*, without differentiating the intrinsic thermal and chemical behavior of individual polymers within mixed systems (Al-Salem et al., 2009; Sharuddin et al., 2016; Alaba et al., 2021; Jung et al., 2010).

Additionally, a dominant trend in the literature is the emphasis on catalytic pyrolysis, often portraying catalysts as indispensable for achieving acceptable oil quality or yield (Miandad et al., 2016; Lopez et al., 2017). While catalytic systems can enhance aromatization and reduce wax formation, they introduce significant operational challenges, including catalyst deactivation, coke formation, regeneration requirements, and increased capital and operating costs (Kaminsky & Zorriqueta, 2007). As a result, existing reviews tend to conflate feedstock effects with catalytic influences, making it difficult to isolate the true role of polymer composition in determining pyrolysis outcomes.

Furthermore, many reviews focus on single-polymer pyrolysis, particularly polyethylene or polypropylene, even though real municipal plastic waste streams are inherently heterogeneous (Williams, 2013). This disconnects between laboratory-scale studies and real-world waste composition limits the industrial relevance of such reviews.

➢ *Comparative Analysis of Existing Reviews*

Table 13 summarizes the focus and limitations of six representative review studies frequently cited in the plastic pyrolysis literature and contrasts them with the approach adopted in this work.

Table 13 Comparison of Existing Review Studies with the Present Review

Author(s)	Feedstock Focus	Catalyst Use	Mixed Plastics Treated Systematically	Yield–Quality–Process Linked	Industrial Relevance
Al-Salem et al. (2020)	Broad plastic waste	Mixed	No	No	Moderate
Sharuddin et al. (2016)	General plastic waste	Emphasized	Limited	Partial	Moderate
Miandad et al. (2016)	Plastic waste	Strong focus	No	No	Low–Moderate
Lopez et al. (2017)	Polyolefins	Catalytic	No	Partial	Moderate
Panda et al. (2018)	Global plastic waste	Mixed	No	No	Moderate
This review	LDPE, HDPE, PP, PS	Catalyst-free only	Yes	Yes	High

The comparative assessment summarized in Table 13 reinforces this distinction by demonstrating that no prior review simultaneously focuses on LDPE, HDPE, PP, and PS, restricts analysis to catalyst-free systems, and explicitly links feedstock behavior to industrially relevant process performance metrics. While earlier reviews offer breadth, the present work offers depth and specificity, enabling meaningful comparison and practical interpretation.

➢ *Core Novelty: Feedstock-Centric, Catalyst-Free Performance Framework*

The central novelty of this review lies in the introduction of a feedstock-centric, catalyst-free performance framework for the pyrolysis of mixed plastics. Rather than treating mixed plastics as a statistical average of individual polymers, this work conceptualizes LDPE, HDPE, PP, and PS as a functional pyrolysis system with complementary degradation pathways. The intrinsic polymer interaction model illustrated in Figure 10 highlights the central novelty of this work: the demonstration that hydrogen transfer and radical stabilization mechanisms inherent to mixed plastics can substitute for catalytic upgrading under optimized conditions (Breyer et al., 2017).

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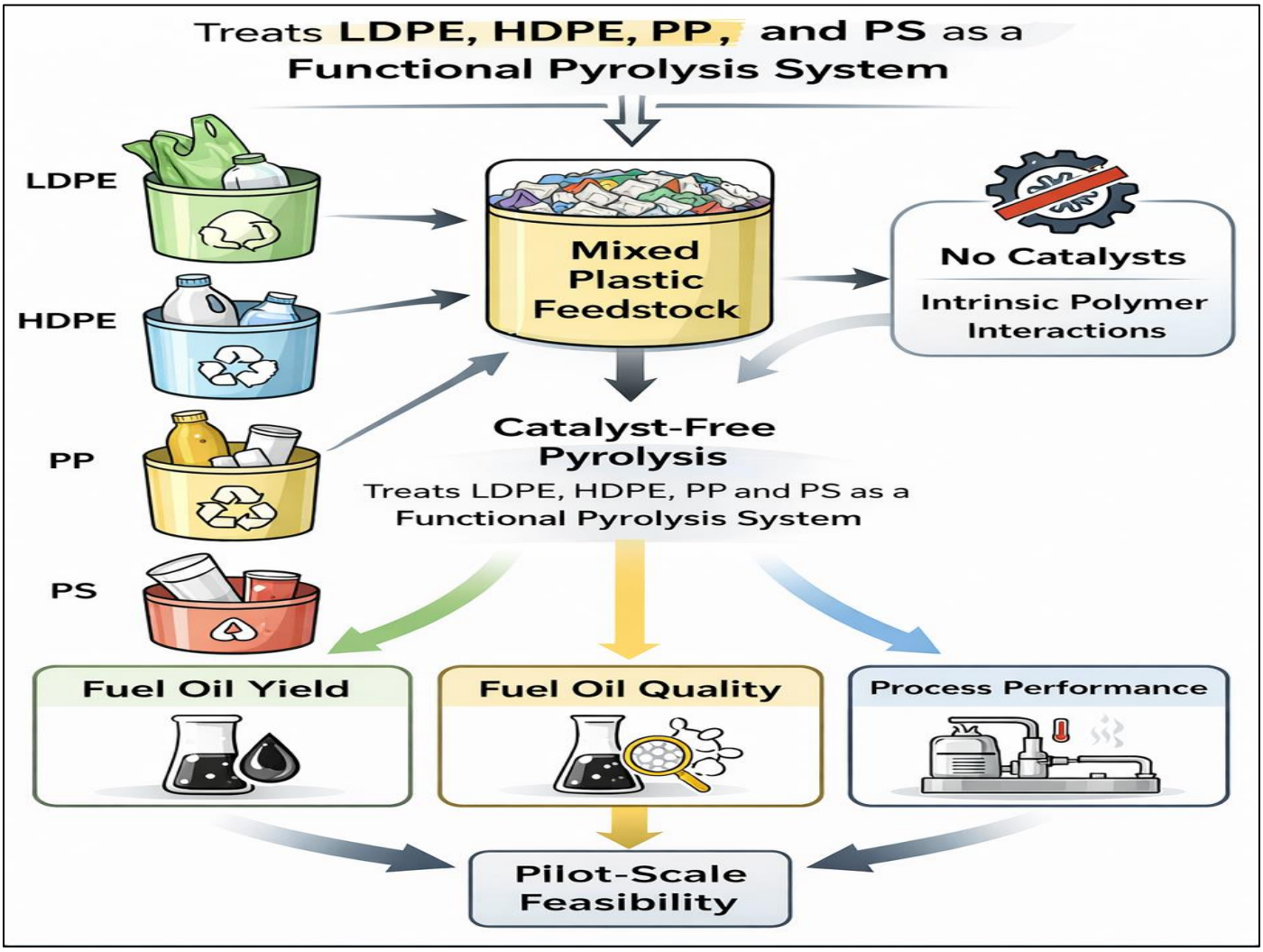

Fig 10 Catalyst-Free Polymer Intrinsic Interactions for a Mixed Plastics Pyrolysis

Polyolefins (LDPE, HDPE, and PP) are hydrogen-rich and predominantly yield long-chain aliphatic hydrocarbons, while PS undergoes depolymerization to produce aromatic compounds such as styrene (Mastral et al., 2002; Ahmad et al., 2014). Under catalyst-free conditions, hydrogen transfer from polyolefins stabilizes aromatic radicals derived from PS, suppressing excessive secondary cracking and gas formation (Breyer et al., 2017). This intrinsic synergistic behavior is often masked or overridden in catalytic systems, where catalyst acidity dictates product distribution. By excluding catalysts, this review isolates polymer–polymer interactions, allowing a clearer understanding of how feedstock composition alone governs oil yield and quality.

➢ *Novel Contribution to Yield and Quality Normalization*

Another major contribution of this review is the normalization of oil yield and quality trends under catalyst-free conditions. Existing reviews frequently compare yields obtained under vastly different catalytic systems, temperatures, and reactor configurations, leading to inconsistent conclusions (Sharuddin et al., 2016). In contrast, this review systematically compares: Liquid yield ranges (typically 60–85 wt%), Gas and char formation trends, Physical fuel properties (density, viscosity, calorific value), Chemical composition (aliphatic vs aromatic fractions) across studies employing non-catalytic pyrolysis of LDPE/HDPE/PP/PS mixtures, enabling fair and meaningful comparison (Williams & Slaney, 2007; Jung et al., 2010).

➢ *Bridging Laboratory Studies with Pilot-Scale Design*

A further novelty of this work is the explicit linkage between feedstock behavior and reactor design requirements, a connection largely absent in previous reviews. While many studies report laboratory-scale results, few translate these findings into implications for heat transfer, vapor residence time, wax management, and condensation efficiency at larger scales (Ali et al., 2021). By correlating polymer composition with operational challenges, such as wax formation in polyolefin-rich feeds and gas evolution in PS-rich blends, this review provides actionable insights for pilot-scale and industrial system design, particularly for low-cost, decentralized applications.

➢ *Practical and Socio-Economic Novelty*

Finally, this review uniquely positions catalyst-free mixed plastic pyrolysis as a technically and economically appropriate solution for developing economies, where catalyst procurement, regeneration infrastructure, and skilled operation may be limited (Agyeman et al., 2020). By demonstrating that acceptable fuel oil yield and quality can

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be achieved without catalysts, this work challenges the prevailing assumption that catalytic upgrading is essential for plastic-to-fuel systems.

IX. RESEARCH GAPS AND FUTURE DIRECTIONS

Despite significant progress in plastic waste pyrolysis research, several critical gaps remain that limit the widespread deployment of catalyst-free systems for mixed plastic waste conversion. One of the most prominent gaps is the lack of standardized feedstock composition in experimental studies. While many authors acknowledge that municipal plastic waste is dominated by LDPE, HDPE, PP, and PS, the ratios of these polymers vary widely across studies, making direct comparison of results difficult (Williams, 2013; Breyer et al., 2017). Future research should prioritize the development of standardized or representative feedstock blends that reflect regional waste compositions, enabling more meaningful benchmarking of process performance.

Another major gap lies in the limited availability of pilot-scale data for catalyst-free mixed plastic pyrolysis. The majority of studies remain confined to laboratory-scale batch or semi-batch reactors, which do not adequately capture challenges associated with heat transfer, vapor residence time, wax management, and continuous operation (Ali et al., 2021). Scaling up catalyst-free systems requires systematic investigation into reactor hydrodynamics, thermal efficiency, and long-term operational stability under realistic feedstock variability.

Fuel oil quality and stability also represent underexplored areas. While numerous studies report basic physicochemical properties such as calorific value and density, long-term storage stability, aging behavior, and compatibility with existing fuel infrastructure are rarely evaluated (Butler et al., 2011). Given the presence of unsaturated and aromatic compounds in pyrolysis oils, future work should focus on oxidation stability, sediment formation, and emission characteristics during combustion.

From a process integration perspective, there is a need for deeper analysis of energy integration and life-cycle performance. Although non-condensable gases are frequently cited as a potential internal energy source, few studies quantify the net energy balance or greenhouse gas reduction potential of catalyst-free mixed plastic pyrolysis systems (Acomb et al., 2014). Comprehensive techno-economic and life-cycle assessments are essential to validate the environmental and economic viability of these systems relative to incineration, landfilling, and mechanical recycling.

Finally, future research should explore the regulatory and fuel standardization challenges associated with pyrolysis-derived oils. The absence of universally accepted standards for plastic-derived fuels limits their commercial adoption. Collaborative efforts between researchers, industry stakeholders, and regulatory bodies are required to define acceptable fuel specifications and facilitate market integration (Hopewell et al., 2009).

X. CONCLUSIONS

This review has systematically examined the catalyst-free pyrolysis of mixed plastic waste composed of LDPE, HDPE, PP, and PS, with a specific focus on fuel oil yield, quality, and overall process performance. By adopting a feedstock-centric and non-catalytic perspective, the review isolates the intrinsic thermal and chemical interactions among polymers, providing a clearer understanding of mixed plastic pyrolysis behavior than existing catalyst-dominated frameworks.

The analysis demonstrates that catalyst-free pyrolysis of realistic mixed plastic feedstocks can achieve high liquid fuel yields (typically 60–85 wt%), minimal char formation, and fuel oils with calorific values comparable to conventional fossil fuels. The presence of PS in polyolefin-rich mixtures enhances liquid yield and aromatic content through synergistic hydrogen transfer mechanisms, while polyolefins contribute to high energy density and reduced coke formation. These intrinsic synergies enable efficient fuel production without the complexity and cost associated with catalytic upgrading.

Importantly, the review highlights that catalyst-free systems offer significant advantages in terms of operational simplicity, feedstock tolerance, and scalability, making them particularly suitable for decentralized and resource-constrained waste management contexts. By explicitly linking feedstock composition to reactor design considerations and process performance, this work bridges the gap between laboratory-scale studies and industrial implementation.

In conclusion, catalyst-free pyrolysis of mixed LDPE, HDPE, PP, and PS represents a technically viable and economically attractive pathway for converting plastic waste into valuable fuel oil. This review establishes a novel reference framework that integrates feedstock behavior, product characteristics, and process performance, thereby providing a foundation for future research, pilot-scale development, and industrial deployment of sustainable plastic waste-to-fuel technologies.

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