

Designing a hybrid activated carbon–kaolin catalyst for enhanced liquid fuel production from mixed plastic waste pyrolysis

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Abstract

The catalytic pyrolysis of mixed plastic waste has gained increasing attention as a promising pathway for liquid fuel production; however, the heterogeneous nature of municipal plastic feedstocks poses persistent challenges in achieving consistent yields and fuel quality. Recent studies indicate that single-function catalysts often struggle to simultaneously address adsorption, cracking, and upgrading requirements during pyrolysis. In response to this limitation, this paper presents a conceptual design framework for a hybrid activated carbon–kaolin catalyst intended to enhance diesel-range (C₁₃–C₂₀) liquid fuel production from mixed plastic waste pyrolysis. Drawing exclusively from recent, reputable literature, the study synthesizes current knowledge on polymer degradation mechanisms, carbon-based adsorption behavior, and clay-derived acidic catalytic functions to rationalize the proposed hybrid approach. Activated carbon is identified as an effective adsorption and secondary cracking medium, while kaolin offers thermally stable acidity capable of promoting hydrocarbon transformation. The integration of these complementary properties is conceptually expected to improve vapor–catalyst interactions and steer product distribution toward more fuel-relevant liquid fractions. Rather than reporting experimental results, this work focuses on design rationale, potential catalyst configurations, and anticipated synergistic effects under pyrolysis-relevant conditions. By explicitly addressing the lack of integrated hybrid catalyst frameworks for mixed plastic feedstocks, this study establishes a foundation for future experimental validation and supports the development of more controlled and scalable plastic waste-to-fuel conversion strategies.

Keywords

Hybrid catalyst, Plastic waste pyrolysis, Activated carbon, Kaolin clay, Liquid fuel production

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Introduction

Plastic waste accumulation is a pressing global environmental challenge that demands scalable valorization technologies to convert waste into valuable products and energy [1]. Pyrolysis the thermal decomposition of polymers in oxygen-free conditions has emerged as a versatile route to transform polymeric municipal solid waste into liquid fuels (pyrolysis oil), syngas, and solid char [2]. The product distribution (oil/gas/char) and chemical composition of the recovered oil are functions of feedstock type, reactor design, heating protocol, residence time, and importantly, catalytic formulation [3]. Empirical and review studies emphasize that process parameters such as heating rate and peak temperature critically control primary scission pathways and secondary reactions that ultimately determine yields and fuel quality [1].

From a mechanistic standpoint, different polymer classes behave distinctly under thermal stress due to their molecular architecture. Polyethylene (PE) and polypropylene (PP), as aliphatic polyolefins, undergo random homolytic C–C scission yielding alkyl radicals that propagate β -scission and radical transfer chains, producing a mix of alkanes and alkenes [4]. Polystyrene (PS), by contrast, preferentially depolymerizes via chain unzipping to monomeric styrene and its oligomers because of the stabilizing effect of the benzyl radical on the aromatic ring. Consequently, PS often delivers high liquid yields rich in aromatics under controlled thermal regimes [2]. These polymer-specific pathways set the stage for catalyst selection aimed at steering selectivity toward targeted hydrocarbon ranges.

Catalysts modulate both kinetics and selectivity: they lower activation energies, provide alternative reaction routes (e.g., acid-catalyzed β -scission, isomerization, aromatization), and can suppress undesirable secondary polymerization that leads to coke/char. Two catalyst families have attracted particular attention for plastic pyrolysis: carbonaceous catalysts (activated carbon and biochar) and acidic zeolites (e.g., HZSM-5, USY). Activated carbons typically prepared from biomass residues offer extremely high surface area and abundant microporosity with oxygenated surface groups that act as adsorption and radical-stabilizing sites; these properties have been linked to enhanced cracking of heavy tar fractions and improved oil quality via deoxygenation and redistribution of heavy aromatics [5] [6]. Because activated carbon operates largely via adsorption-mediated radical pathways rather than strong Brønsted acidity, it tends to favor liquid yields and reduce coke formation when applied at moderate loadings.

Zeolites crystalline aluminosilicates such as HZSM-5 bring a contrasting catalytic functionality: well-defined microporous channels and tunable Brønsted/Lewis acidity that catalyze protolytic cracking, oligomerization, cyclization and aromatization [7]. Zeolites are particularly effective at converting long hydrocarbon fragments into gasoline-range aromatics (BTX) and olefins, improving fuel-like properties (e.g., octane index) but often at the cost of greater gas production and coke deposition under aggressive operating conditions. The strong acid sites of zeolites favor carbocation

mechanisms that differ fundamentally from the radical routes predominant on carbonaceous surfaces, leading to a complementary product spectrum [7].

Given the complementary action of activated carbon and zeolites, hybrid catalyst systems combining adsorption capability with acid-catalyzed molecular reorganization have been proposed to achieve both high liquid yields and improved liquid quality [8]. Recent experimental and review studies indicate that mixed or sequential catalyst configurations (e.g., layered beds, physical mixtures, or bifunctional supports) can exploit synergies: activated carbon limits tar polymerization and stabilizes radicals, reducing coke formation on zeolite surfaces; zeolite then restructures the resulting intermediates into desirable low-molecular-weight aromatics [9], [10]. Such hybridization is promising for waste streams with mixed polymer compositions where a single catalyst type cannot optimize both yield and selectivity simultaneously.

Heating rate interacts with catalyst performance in non-trivial ways. Higher heating rates raise the instantaneous availability of thermal energy, promoting rapid volatilization of primary fragments and often increasing secondary cracking if residence times in the hot zone are long; however, studies report divergent effects depending on reactor geometry and catalyst presence in some cases faster heating increased liquid yields, while in others it favored gas production due to intensified secondary reactions [1]. When catalysts are present, the effective residence time of vapors in contact with active sites and the diffusion limitations into micropores (especially in zeolites) determine whether higher heating rates will amplify desired catalytic transformations or instead favor over-cracking and coke [1]. These process-catalyst interactions highlight the need for systematic evaluation of heating profiles in tandem with catalyst composition and loading.

In summary, the existing body of literature highlights several conceptual foundations that motivate this preliminary study. First, the intrinsic decomposition pathways of polyolefins and polystyrene are governed by polymer chemistry, implying that any catalyst design for mixed plastic pyrolysis must accommodate heterogeneous cracking mechanisms. Second, activated carbon and aluminosilicate materials such as kaolin exhibit complementary catalytic roles activated carbon providing high surface area and adsorption capacity, while kaolin contributes acidity and structural stability suggesting potential synergy when combined into a hybrid catalyst system. Third, thermal parameters, including heating rate and operating temperature, are widely recognized as critical factors influencing pyrolysis behavior and product distribution, even prior to experimental optimization. Despite these insights, the literature remains limited in conceptual frameworks that explicitly integrate catalyst material design with mixed plastic feedstock characteristics under realistic pyrolysis conditions. Accordingly, this study is positioned as an initial design-oriented investigation that proposes a hybrid activated carbon–kaolin catalyst concept for enhanced liquid fuel production from mixed plastic waste pyrolysis, serving as a foundation for subsequent experimental validation.

Literature review and theoretical background

Mixed plastic waste pyrolysis fundamentals

Pyrolysis of mixed plastic waste is fundamentally governed by the thermal degradation behavior of its constituent polymers, primarily polyethylene (PE), polypropylene (PP), and polystyrene (PS), which exhibit distinct decomposition mechanisms due to differences in molecular structure and bond stability [11], [12]. PE and PP are polyolefins that predominantly undergo random chain scission and β -scission reactions at elevated temperatures, producing a broad range of hydrocarbons, mainly aliphatic compounds [13]. In contrast, PS decomposes primarily through depolymerization and side-chain scission, yielding aromatic-rich products such as styrene and its derivatives [14]. These differences in degradation pathways significantly influence product distribution during mixed plastic pyrolysis.

The heterogeneity of mixed plastic feedstocks presents a major challenge in achieving controlled and efficient liquid fuel production [10]. Variations in polymer composition, melting behavior, and degradation temperature windows in mixed PE/PP/PS streams can create non-uniform vapor generation and overlapping reaction pathways inside the reactor, which complicates heat and mass transfer control in practical pyrolysis systems [15], [16], [17], [18]. Consequently, non-catalytic pyrolysis of mixed plastics is frequently associated with broad and unstable product distributions, where liquid oils may show inconsistent composition and fuel-relevant properties, while heavier fractions (e.g., wax-like products) and permanent gases can increase depending on operating conditions and feedstock variability [15], [17], [18], [19]. These limitations motivate catalyst systems that can accommodate multiple degradation mechanisms (polyolefin cracking and aromatic-rich PS pathways) and steer the vapor-phase upgrading reactions toward more consistent liquid products [16], [17].

Catalytic pyrolysis: Roles of carbon-based and clay catalysts

Carbon-based catalysts, including activated carbon, remain attractive for plastic pyrolysis/upcycling because their high surface area and porosity provide adsorption sites for pyrolysis vapors, which can intensify secondary cracking and alter product selectivity via vapor–surface interactions [16], [20]. Recent studies and reviews emphasize that activated carbon particularly when engineered or metal-incorporated can promote further cracking of heavier hydrocarbons and contribute to improved liquid fractions by enhancing contact between volatile intermediates and active surfaces [20]. However, activated carbon alone is often limited by relatively weak intrinsic acidity compared with conventional acidic catalysts, which can constrain its ability to selectively generate fuel-range hydrocarbons via acid-catalyzed cracking/isomerization routes [16], [17].

Clay-based catalysts such as kaolin offer complementary functionality due to their aluminosilicate nature, accessible acidity, and thermal robustness, while remaining comparatively inexpensive and scalable for waste-to-fuels applications [16]. Empirical

comparisons of natural clays (including kaolin) in plastic pyrolysis show that kaolin can enhance liquid hydrocarbon yields and support cracking reactions relative to purely thermal conversion, consistent with its catalytic contribution through acid sites and mineral surface effects [21]. More broadly, recent literature on additives/fillers in plastic pyrolysis also identifies kaolin among inorganic materials that can promote cracking behavior during plastic thermal decomposition, reinforcing its relevance as a low-cost catalytic component under pyrolysis conditions [22]. These complementary roles support the design rationale for hybrid systems where carbon-based adsorption/secondary cracking and clay-derived acidity/thermal stability can be combined to target improved liquid quality and process consistency [16], [17], [21].

Catalyst polymer interaction at elevated temperatures

At elevated temperatures, catalyst–polymer (and more precisely catalyst–vapor) interactions are governed by physicochemical phenomena such as adsorption/desorption, surface-mediated radical reactions, catalytic cracking on acid sites, and secondary transformations of pyrolysis intermediates [16], [17], [23]. Reviews of catalytic plastic pyrolysis highlight that hybrid or multi-functional catalysts can exhibit synergy when adsorption-driven confinement and extended residence of intermediates on porous surfaces increase the probability of transformation on acidic or otherwise active sites, thereby reshaping reaction pathways and product distributions [16], [17]. Importantly, these interactions remain sensitive to thermal severity (temperature profile and heating rate), because operating conditions regulate the residence time, intermediate concentration, and the extent of secondary vapor-phase reactions that ultimately control the balance between liquids, wax-like fractions, and gases [15], [16], [17]. While experimental verification is required to quantify such effects for a specific activated carbon–kaolin configuration, recent high-quality literature supports the plausibility of synergistic adsorption–acidity coupling in hybrid catalyst concepts for improving liquid fuel production from mixed plastic waste pyrolysis [16], [21].

Table 1 synthesizes representative recent studies on clay- and carbon-based catalysts applied in plastic waste pyrolysis, highlighting reported liquid yields and selected fuel-related properties under varying feedstocks and operating conditions. Collectively, these studies demonstrate that kaolin and other clay minerals can contribute acidity and thermal stability conducive to cracking reactions, while activated carbon can enhance liquid yields through adsorption-driven secondary cracking and vapor–surface interactions. However, the findings are largely reported in isolation, with individual studies focusing on either clay-based or carbon-based catalysts under specific conditions. Systematic investigations that integrate both functionalities within a single hybrid catalyst framework particularly for mixed plastic feedstocks representative of municipal waste remain limited in the recent literature. This gap underscores the need for a design-oriented exploration of hybrid activated carbon–kaolin catalysts that intentionally combine adsorption capacity and acidic catalytic sites to address the heterogeneous degradation mechanisms inherent to mixed plastic pyrolysis.

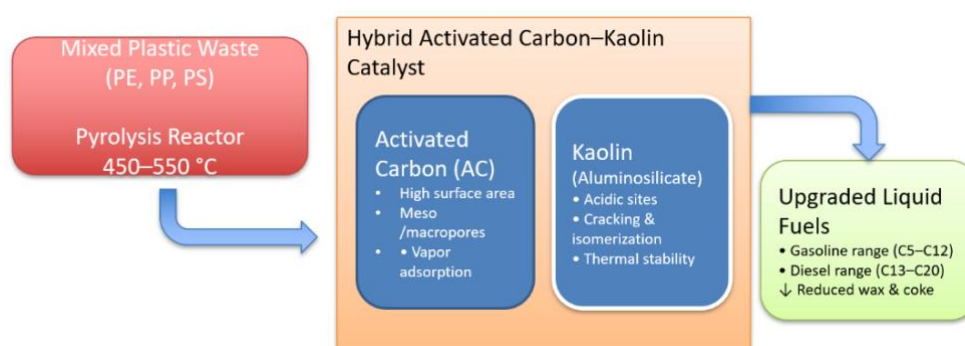
Table 1. Summary of recent studies on clay- and carbon-based catalysts for plastic waste pyrolysis

Study / Catalyst / Feedstock / Conditions	Liquid Yield	Calorific Value	Cetane Number / Diesel Comparison	Ref.
kaolin-clay catalyst, mixed plastic waste (HDPE, LDPE, PS, PP), reactor 425 °C, 5.3 L CSTR	~63% (oil)	Improved vs thermal pyrolysis	Improved fuel stability and heating value	[24]
mesoporous kaolin catalyst, waste plastics	High selectivity toward liquid hydrocarbons	Not specified	Improved liquid yield vs non-catalytic	[25]
using natural (low-cost) mineral catalysts including kaolin; waste PP pyrolysis	High gas fraction; liquid fuel useable as conventional fuel	High calorific value (gas fraction)	Liquid hydrocarbons usable in place of conventional fuels	[26]
activated carbon catalyst + PP waste)	70.03% (at 400°C, 7% catalyst)	~44.7 MJ/kg (heating value)	Fits within diesel fuel standard (SNI 7390:2008)	[27]
clays / minerals, co-pyrolysis of plastic + biomass	42–61 MJ/kg (high heating value range)	42–61 MJ/kg	Liquid products comparable to some fuels	[28]

Result and discussion

Design rationale of activated carbon–kaolin hybrid catalyst

Figure 1 shows the proposed hybrid activated carbon–kaolin catalyst, which is motivated by a functionality-complementarity logic: plastic pyrolysis vapors comprise a wide spectrum of intermediates (heavy wax-like fragments, olefins, and aromatics), and improving liquid fuel production requires both (i) efficient capture and contact of these intermediates and (ii) controlled catalytic transformation toward fuel-range molecules rather than uncontrolled over cracking to gaseous products [29], [30]. Activated carbon (AC) is selected primarily for its high surface area and porous architecture, which can intensify vapor adsorption and increase vapor–solid contact time, thereby promoting secondary cracking and suppressing the persistence of heavy fractions in the liquid stream [31], [32]. In contrast, kaolin is selected as an inexpensive aluminosilicate with thermally stable structure and accessible acidity capable of supporting catalytic cracking/isomerization-like reactions that can shift product distribution toward lighter hydrocarbons and more usable fuel fractions [33], [34].

**Figure 1.** Hybrid activated carbon–kaolin catalyst framework for plastic pyrolysis

Within the hybrid concept, AC is positioned as the “adsorption/contact enhancer” and secondary-cracking facilitator, while kaolin is positioned as the “acidic transformation platform” that provides mineral stability and acid-site-driven upgrading [32], [33]. This design aims to address a recurring limitation highlighted in recent plastic pyrolysis literature: single-function catalysts often trade-off between yield and quality, whereas multi-functional or hybrid catalyst strategies are increasingly explored to better control vapor upgrading pathways [29] [30].

Proposed catalyst configuration and structure

Because the present work is a pre-experimental, design-oriented study, the catalyst is proposed in a small set of practical, scalable configurations that can be realized with commonly available processing routes. First, physical blending (powder mixing) is the simplest configuration: AC and kaolin powders are co-mixed and introduced as a bed (fixed-bed insert) or dispersed additive, enabling parallel adsorption (AC) and acidic upgrading (kaolin) without requiring complex fabrication [30], [35]. Second, coating/impregnation-inspired architectures are conceptually proposed, where kaolin particles are coated with a thin carbonaceous layer or AC is immobilized on kaolin surfaces to increase the probability that adsorbed vapors encounter acid sites before desorption, which is a common logic in multi-functional catalyst design for vapor upgrading [32]. Third, composite granules/pellets are proposed for reactor operability (pressure drop, handling, catalyst recovery), aligning with recent reactor-oriented studies that emphasize practical constraints in catalytic plastic pyrolysis deployments [31], [8].

Regarding material ratio, this framework does not prescribe a single “optimal” composition because the literature indicates that catalyst loading and composition are strongly dependent on reactor type, residence time, and target selectivity (liquid vs gas, gasoline-range vs diesel-range) [29]. Instead, the framework defines a design space: (i) AC-dominant blends for maximizing adsorption-driven secondary cracking and reducing heavy fractions, and (ii) kaolin-dominant blends for strengthening acid-site upgrading and shifting liquid composition toward lighter hydrocarbons. Screening studies on kaolin modification also suggest that acidity tuning (e.g., acid-treated or activated kaolin) can materially influence condensable yields and reaction time, reinforcing that “ratio” and “site density” should be treated as coupled design variables rather than fixed constants [33].

Expected catalytic functions and synergistic effects

Figure 2 represent the mechanism of synergetic effect of activated carbon and kaolin as catalyst. The expected performance mechanism is framed as an adsorption–acid site coupling. In this coupling, activated carbon concentrates pyrolysis intermediates within pores and on surfaces (adsorption/confinement), increasing local intermediate concentration and effective residence time, which can intensify secondary cracking and rearrangement reactions [32], [31]. Simultaneously, kaolin provides acid sites that can promote cracking and transformation reactions that help reduce molecular weight and shift the vapor composition toward more fuel-relevant hydrocarbons, while maintaining

mineral thermal stability under pyrolysis conditions [34], [33]. The synergy is expected when adsorption-driven enrichment on AC increases the probability that intermediates undergo acid-site upgrading on kaolin rather than simply condense as heavy oils/waxes or over crack into gases [29].

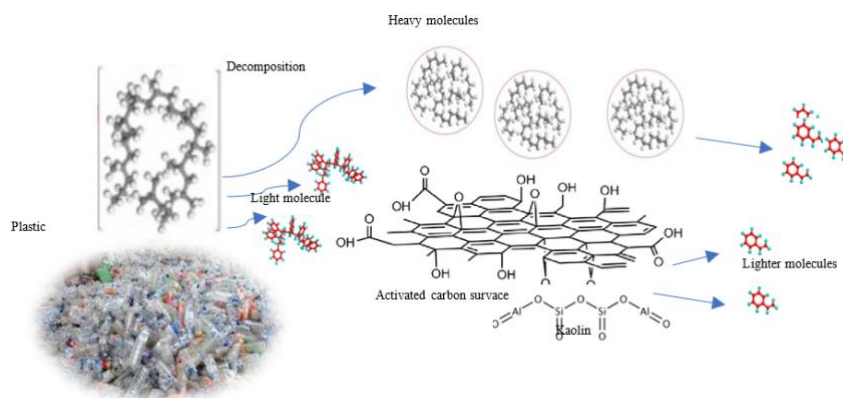


Figure 2. Expected catalytic functions and synergistic effects

Conceptually, the pathway toward enhanced liquid fuel production from mixed plastics proceeds through: (i) primary polymer scission producing a wide distribution of radicals and oligomers, (ii) rapid volatilization generating heavy and light vapors, (iii) AC-mediated adsorption and secondary cracking that reduces wax-like fractions, and (iv) kaolin-mediated acid-site transformations that shift the condensable pool toward more stable, lighter hydrocarbons. Recent work on activated-carbon-based catalysts for mixed plastic pyrolysis underscores that tailoring carbon catalysts (including metal-incorporation) can significantly affect product selectivity and upgrading behavior, supporting the broader premise that AC is a tunable component within a hybrid architecture [31]. Complementarily, recent kaolin-focused studies indicate that kaolin activation/modification alters catalytic performance, suggesting that kaolin is not merely an inert filler but a design-active phase that can be engineered for targeted upgrading [33].

Conclusions

This paper presents a conceptual, design-oriented framework for a hybrid activated carbon–kaolin catalyst aimed at enhancing liquid fuel production from mixed plastic waste pyrolysis. Drawing exclusively from recent, reputable literature, the study synthesizes current understanding of polymer degradation behavior, catalyst functionality, and vapor-phase upgrading mechanisms to rationalize the integration of carbon-based adsorption capacity with clay-derived acidic catalytic sites. The analysis highlights that activated carbon and kaolin individually address different limitations of non-catalytic and single-catalyst pyrolysis systems namely, uncontrolled formation of heavy fractions, inconsistent liquid quality, and excessive gas production when processing heterogeneous plastic feedstocks.

Rather than proposing a finalized catalyst formulation, this work contributes a structured conceptual framework that defines catalyst roles, plausible configurations, and expected synergistic interactions under pyrolysis-relevant thermal conditions. By explicitly addressing the heterogeneity of mixed plastic waste and the need for multi-functional catalytic behavior, the proposed hybrid design responds to a clear gap in recent literature, where clay-based and carbon-based catalysts are predominantly studied in isolation. As such, this paper establishes a theoretically grounded basis for future experimental investigations and supports the broader transition toward more controlled and scalable catalytic plastic waste valorization strategies.

Future work

Future research should focus on experimental validation of the proposed hybrid activated carbon–kaolin catalyst concept across multiple scales. Initial studies should include systematic catalyst synthesis and characterization, emphasizing surface area, pore structure, acidity distribution, and thermal stability to verify whether the intended adsorption–acid site coupling can be achieved in practice. Bench-scale pyrolysis experiments using representative mixed plastic feedstocks (e.g., PE/PP/PS mixtures) are necessary to quantify liquid yield, product composition, and fuel-relevant properties under controlled heating rates and residence times.

Further work should also investigate the influence of catalyst configuration (blended powders, coated structures, or composite pellets) and material ratios on vapor upgrading behavior and catalyst durability, including deactivation and coke formation tendencies. Advanced analytical techniques, such as gas chromatography–mass spectrometry (GC–MS) and thermogravimetric analysis coupled with evolved gas analysis, would enable deeper insight into reaction pathways and synergistic mechanisms. Ultimately, reactor-level studies and techno-economic assessments will be required to evaluate the scalability, cost-effectiveness, and environmental implications of hybrid catalyst deployment within practical plastic waste-to-fuel systems.

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