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Catalytic Co-Pyrolysis of Biomass and Plastic Waste: A Comprehensive Review

Uchenna Ekene Okaforobah, Obiora Nnaemeka Ezenwa, John Chikaelo Okeke*, Chigozie Samuel Okaforobah

Department of Mechanical Engineering, Nnamdi Azikiwe University, Awka, Nigeria

ABSTRACT

Catalytic co-pyrolysis of biomass and plastic waste has gained significant attention as a strategically important thermochemical route for converting heterogeneous waste streams into high-value fuels and carbonaceous products. Recent advances demonstrate that the integration of suitable catalysts can substantially enhance product quality by promoting hydrogen transfer reactions, accelerating deoxygenation pathways, and facilitating the selective cracking of macromolecular intermediates. These catalytic effects not only enrich bio-oil with hydrocarbons and reduce oxygenated compounds but also improve syngas composition and tailor the structural properties of resultant chars for functional applications. This review synthesizes recent advancements in catalyst design, reaction mechanisms, synergistic effects, and reactor configurations. Special emphasis is placed on hydrogen donor interactions, deoxygenation mechanisms, and catalytic cracking behavior. Challenges related to catalyst stability, process scaleup, and technoeconomic feasibility are discussed, along with future research pathways.

Keywords: catalytic co-pyrolysis, biomass, plastic waste, hydrogen transfer, deoxygenation, waste valorization

1. INTRODUCTION

Biomass and plastic wastes constitute two of the largest and most problematic global waste streams, creating significant environmental, energy, and economic challenges. Biomass is abundant and renewable, but its thermal conversion typically generates oxygen-rich, chemically unstable bio-oils. In contrast, plastic wastes are hydrogen-rich but lack reactive functional groups, making their disposal and valorization increasingly difficult. These contrasting characteristics have driven interest in thermochemical processes that can convert both materials into valuable fuels and chemicals.

Pyrolysis has emerged as a flexible and effective route for converting solid waste into liquid, gaseous, and solid products. However, the standalone pyrolysis of biomass generally produces bio-oil with high oxygen content, poor stability, and considerable tar formation, all of which hinder downstream upgrading. To overcome these limitations, co-pyrolysis which involves processing biomass and plastics together has gained attention. The hydrogen-rich nature of plastics promotes hydrogen transfer and radical stabilization reactions that improve biomass decomposition, reduce tar formation, and enhance overall oil quality. Reported synergistic effects include hydrogen donation, suppressed polymerization, enhanced cracking, and more balanced product distributions (Seah et al, 2023).

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*Corresponding author: jc.okeke@unizik.edu.ng

The introduction of catalysts into co-pyrolysis further intensifies these beneficial interactions. Catalytic co-pyrolysis promotes deoxygenation, aromatization, controlled cracking, and improved gas composition, ultimately producing hydrocarbon-rich oils, cleaner syngas, and engineered chars with tailored properties. Recent studies highlight the importance of catalyst structure such as mesoporous frameworks and strong acid sites in facilitating improved diffusion, reducing deactivation, and enabling efficient aromatization pathways (Mo et al, 2023). Additionally, integrated systems that combine pyrolysis with partial gasification have been explored to increase hydrogen yield and minimize tar accumulation.

Given the rapid development of this field, a structured review is needed to consolidate current knowledge and highlight future opportunities. Therefore, this review aims to provide: (1) A classification of catalysts used in biomass–plastic co-pyrolysis, (2) Insights into the mechanistic pathways and synergistic interactions, (3) Assessment of the impacts on product quality, (4) Discussion of reactor configurations and process intensification strategies, and (5) Identification of key challenges and future research directions.

2. FEEDSTOCKS, CATALYSTS, AND REACTION MECHANISMS IN CATALYTIC CO-PYROLYSIS

2.1 Biomass Types

Lignocellulosic residues include agricultural by-products such as rice husks, corn stover, straw, and sawdust. They are composed of cellulose, hemicellulose, and lignin; the latter's aromatic structure can promote radical stabilization during co-pyrolysis, thereby influencing bio-oil and char yields (Mo et al, 2023; Chukwuneke et al, 2025).

Also, agricultural wastes such as stalks, husks, and fruit peels are attractive because of their low cost and regional abundance. Their properties including ash content, mineral composition, and moisture affect reactivity and catalytic performance. For example, inherent alkali metals in ash can serve as natural catalysts (Deng et al, 2025; Chukwuneke et al, 2025). Forestry biomass such as wood residues (bark, branches, logging waste) generally have lower ash but higher lignin content compared to agricultural residues. This compositional profile makes them particularly synergistic when co-pyrolyzed with hydrogen-rich plastics, promoting aromatic formation (Mo et al, 2023).

Energy crops, for example switchgrass, miscanthus, and short-rotation coppice are grown specifically for bioenergy. Because their composition can be engineered (e.g., lignin vs. cellulose content), they offer a controllable and sustainable feedstock for catalytic co-pyrolysis.

2.2 Plastics Used in Co-Pyrolysis

Polyethylene (PE) such as HDPE and LDPE are commonly used because they are abundant and rich in hydrogen. During co-pyrolysis, PE donates hydrogen radicals, helping stabilize biomass-derived radicals and improve bio-oil quality (Mo et al, 2023). Also, polypropylene (PP), another polyolefin, PP likewise acts as an in-situ hydrogen donor, improving the stability and hydrogen content of the pyrolysis products.

Polystyrene (PS) with its aromatic backbone, contributes to the formation of aromatic hydrocarbons in the co-pyrolysis products, particularly when catalyzed (Gonzalez-Aguilar et al, 2023).

Plastics such as PET and PVC are less commonly used in catalytic copyrolysis. PET's ester linkages generate oxygenated intermediates, complicating downstream upgrading. PVC is problematic due to chlorine release (HCl) during pyrolysis, which can corrode equipment and poison catalysts (Deng et al, 2025).

In Nigeria, recent assessments indicate that the country's plastic waste stream is dominated by five major polymers, namely polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS). PET constitutes approximately 29% of the total annual plastic waste generated, followed by PE at about 22%, PVC at roughly 16%, PP at around 14%, and PS at close to 9%. Together, these polymers represent more than 80% of all discarded plastics nationwide. Their high prevalence in the waste stream provides a clear justification for selecting them as the primary feedstocks in co-pyrolysis studies and thermochemical conversion research carried out within the region (Ebere, 2019). The physicochemical properties of selected biomass and plastics were summarized in Table 1.

2.3 Feedstock Properties Influencing Catalysis

Lignin-Rich Biomass tends to yield more stable aromatics under catalytic cracking, as lignin-derived phenolic structures interact favorably with catalyst active sites (Mo et al, 2023). While Hydrogen Donor Plastics (Polyolefins) such as PE and PP are effective hydrogen donors, facilitating hydrogen transfer to biomass-derived radicals and improving deoxygenation (Mo et al, 2023). The inherent mineral matter (ash) in biomass—especially alkali and alkaline earth metals—can catalyze secondary reactions even without added catalysts. In some systems, these in-situ minerals enhance cracking and deoxygenation (Deng et al, 2025).

2.4. Catalysts for Co-Pyrolysis

Table 2 lists the advantages and limitations of common catalysts for co-pyrolysis.

2.4.1 Zeolite Catalysts

Zeolites remain the most widely used catalysts in co-pyrolysis because of their strong Brønsted acidity, shape-selective micropores, and thermal stability.

ZSM-5

ZSM-5 is the dominant catalyst due to its medium pore size (0.55 nm), which facilitates formation of mono-aromatic hydrocarbons from pyrolysis vapors. It enhances deoxygenation through dehydration, decarboxylation, and aromatization mechanisms, improving bio-oil stability (Dyer et al, 2021). Hydrogen-donor radicals derived from plastics such as polyethylene further strengthen its performance by suppressing coke formation (Deng et al, 2025).

Y Zeolite

Y zeolites especially when modified to increase their Si/Al ratio, can accommodate bulky biomass-derived oxygenates due to their relatively large pores (~0.6–0.8 nm). This promotes cracking of heavy oligomers and enhances aromatic production during copyrolysis. Indeed, hierarchical Sr-loaded Y-zeolite with an increased Si/Al ratio has been shown to elevate aromatics content in co-pyrolysis oil. Higher Si/Al ratios also contribute to improved acidity and thermal stability in such Y-zeolites (reviewed in recent catalysis literature) (Sudarsanam et al, 2019).

Beta Zeolite

Beta zeolite contains a three-dimensional interconnected pore network, making it suitable for isomerization, hydrocarbon rearrangement, and secondary cracking. It enhances hydrocarbon distribution uniformity and reduces tar formation in biomass–plastic co-pyrolysis (Yi et al, 2019).

Table 1: Physicochemical Properties of Typical Feedstocks

Feedstock Type	Typical Examples	Moisture Content (wt%)	Volatile Matter (wt%)	Fixed Carbon (wt%)	Ash Content (wt%)	Heating Value (HHV, MJ/kg)	Elemental Composition (wt%)	Remark
Biomass	Rice husk	8–12	70–75	12–15	15–20	14–16	C 45–48; H 6–7; O 41–45	High ash, silica-rich
	Corn stover	4–8	70–78	12–15	5–6	16–17	C 45–47; H 6–6.5; O 42–44	Low ash, good for co-pyrolysis
	Wheat straw	7–10	70–75	14–16	6–7	15–16	C 44–46; H 6–6.5; O 43–45	Lignocellulosic residue
	Wood chips	5–10	70–75	15–18	1–2	18–20	C 48–50; H 6–6.5; O 44–46	Low ash, high lignin content
Plastics	Polyethylene (PE)	0.00–0.25	94–99.8	0	0	44–46	C 85–86; H 14–15; O 0	Hydrogen-rich, good H donor
	Polypropylene (PP)	0.15–0.40	95–99	0	0	43–45	C 85–86; H 14–15; O 0	Hydrogen donor, easy cracking
	Polystyrene (PS)	0.25–0.30	98–99.8	0	0	41–43	C 91–92; H 8; O 0	Aromatic monomer, promotes aromatic formation
	PET	0.45–0.70	85–92	0	0	25–27	C 62; H 4; O 34	Generates oxygenates, may increase bio-oil oxygen content
	PVC	0.74–0.80	93–95	0	0	19–20	C 38; H 4; Cl 58	Produces HCl on pyrolysis, corrosive

Table 2: Advantages and Limitations of Common Catalysts

Catalyst Type	Examples	Advantages	Limitations
Zeolites	ZSM-5, Y zeolite, Beta zeolite	Strong acidity enhances cracking and aromatization (Dyer et al, 2021)	Prone to coke formation (Yi et al, 2019)
		High thermal stability and reusability	Micropores restrict diffusion of bulky biomass vapors
		Shape-selectivity improves aromatic yield	Requires periodic regeneration
Metal-Supported Catalysts	Ni, Fe, Co, Mo, Cu on Al_2O_3, SiO_2, ZSM-5, biochar	High activity for deoxygenation and reforming (Iisa et al, 2020)	Expensive (Ni, Co, Mo)
		Promote H_2 generation and improve syngas quality	Susceptible to poisoning by chlorine or sulfur compounds in plastics
		Metals allow tuning of product selectivity	Deactivation via sintering at high temperatures
Carbon-Based Catalysts	Biochar, activated carbon, metal-doped carbon	Low-cost, sustainable, and thermally stable	Lower intrinsic catalytic activity than zeolites
		Good metal-support interaction (Gin et al, 2021)	Ash impurities may affect reaction pathways
		Tunable porosity and functional groups	Properties depend strongly on preparation method
Natural & Waste-Derived Catalysts	CaO, dolomite, red mud, kaolin, biomass ash	Cost-effective and abundant	Variable composition leads to inconsistent performance
		Environmentally friendly waste-to-resource option	Lower surface area than engineered catalysts
		Basic/acidic minerals enhance cracking and deoxygenation (Zheng et al, 2019)	Possible contaminants (e.g., metals in red mud)

2.4.2 Metal-Supported Catalysts

Metal-supported catalysts are effective due to their redox activity and hydrogen transfer capabilities. They promote reforming reactions, reduce oxygen content, and generate hydrogen-rich gases.

Nickel-Based Catalysts

Ni catalysts exhibit strong catalytic cracking and steam-reforming activity, producing high H_2 and CO yields. Ni/Al_2O_3 and Ni/ZSM-5 significantly enhance deoxygenation and syngas quality during biomass–plastic co-pyrolysis (Iisa et al, 2020). Nickel also stabilizes radicals and suppresses char formation.

Iron-Based Catalysts

Fe-based catalysts are low-cost alternatives that improve aromatic hydrocarbon formation through dehydrogenation and cyclization reactions (Waziri et al, 2019). Fe/SiO_2 and Fe/biochar catalysts enhance product quality during co-pyrolysis by simultaneously improving tar cracking and promoting aromatic formation. The dispersed iron sites on silica and biochar provide active centers that facilitate the breakdown of heavy tar molecules into lighter volatile fragments, thereby reducing the formation of undesirable condensable species. Following cracking, these intermediates undergo deoxygenation and structural rearrangement on the catalyst surface, which favors the generation of monocyclic aromatic hydrocarbons such as benzene, toluene, and xylenes. As a result, Fe-supported catalysts contribute to higher-quality bio-oil with increased aromatic content and reduced oxygenated compounds.

Co, Mo, and Cu Catalysts

Cobalt-based catalysts significantly boost hydrogen production during the co-pyrolysis of plastics by catalyzing dehydrogenation reactions, where cobalt sites abstract hydrogen from volatile intermediates. This elevated hydrogen yield is beneficial for both upgrading syngas and stabilizing reactive fragments. In addition, cobalt facilitates the growth of carbon nanotubes from plastic-derived volatiles: the metal helps organize carbon radicals into graphitic structures, producing nanotubes while simultaneously driving hydrogen generation (Yao et al, 2017).

Molybdenum-based catalysts are highly effective in enhancing bio-oil stability through hydrodeoxygenation (HDO) and decarbonylation pathways. Mo active sites cleave C–O bonds in oxygenated pyrolysis vapors, leading to the removal of hydroxyl and carbonyl functionalities. This deoxygenation reduces polarity and improves thermal stability, while decarbonylation further lowers the oxygen content by releasing CO. The combined effect of these reactions results in a more stable, energy-dense liquid fuel (Ayala-Cortés et al, 2023).

Copper catalysts contribute to catalytic cracking during co-pyrolysis by facilitating C–C bond cleavage and fragmentation of long-chain intermediates. The presence of copper sites also encourages secondary rearrangement and hydrogen-transfer reactions, which tune the distribution of light hydrocarbons such as olefins and paraffins. Though less acidic than zeolites and less expensive than noble metals, Cu catalysts offer a practical and cost-effective way to influence product selectivity and improve yields of short-chain hydrocarbons (Dyer et al, 2021).

2.4.3 Carbon-Based Catalysts

Carbonaceous catalysts are valued for their cost-effectiveness, tunable surface chemistry, and high porosity.

Bio char Catalysts

Bio char acts as both catalyst and support due to mineral content and functional groups that promote cracking and deoxygenation. Modified biochar enhances tar reforming and increases aromatic content in co-pyrolysis vapors (Bisen et al, 2025).

Activated Carbon

Activated carbon is valued in pyrolysis and upgrading processes for its exceptionally high surface area and tunable porosity, which provide many active sites for secondary reactions. In particular, activated carbon pellets impregnated with basic species (such as NaOH) have been shown to catalyze cracking, reducing heavy oxygenated compounds and increasing the fraction of hydrocarbon-like products. For instance, Bernar et al, (2021) demonstrated that activated carbon pellets impregnated with NaOH can convert pyrolysis vapors into hydrocarbons, achieving up to 95% hydrocarbon selectivity in the biooil fraction.

Metal-Doped Carbons

Incorporation of metals (Ni, Fe, Co) onto carbon matrices generates bifunctional catalytic surfaces combining metal redox behavior and carbon cracking properties. This significantly increases H_2 yield and reduces coke formation (Gin et al, 2021).

2.4.4 Natural and Waste-Derived Catalysts

Low-cost catalysts from natural minerals and industrial residues have gained attention due to sustainability and availability.

CaO, Dolomite, Red Mud

Alkaline-earth metal oxides such as CaO and dolomite ($CaMg(CO_3)_2$) are attractive as low-cost catalysts due to their basic nature, which promotes deoxygenation reactions and neutralization of acidic compounds. In a co-pyrolysis study, rice-husk biomass and high-density polyethylene (HDPE) were co-pyrolyzed in the presence of dolomite calcined at 900 °C. The calcined dolomite catalyst significantly improved bio-oil fuel properties and enhanced cracking, lowering oxygen content and increasing hydrocarbon yield (Bisen et al, 2025). Red mud, an alkaline industrial residue rich in Fe, Al, and Ti oxides, promotes cracking and increases gas yield in co-pyrolysis (Santosa et al, 2020).

Clay Minerals (Kaolin)

Kaolin provides moderate acidity and high thermal stability. Its layered structure enhances cracking of heavy volatiles and reduces the formation of polyaromatic tars (Luo et al, 2020).

Biomass Ash

Biomass ash contains alkaline and alkaline-earth metals (K, Mg, Ca) that catalyze cracking, water-gas shift reactions, and oxygenate removal. It is an environmentally friendly low-cost option for large-scale co-pyrolysis (Sun et al, 2020).

2.5. Reaction Mechanisms in Catalytic Co-pyrolysis

Catalytic co-pyrolysis of biomass and plastics involves complex chemical transformations where catalyst direct reaction pathways, stabilize intermediates, and improve product selectivity. The overall mechanism can be broadly divided into radical generation, cracking, and catalytic transformations that promote deoxygenation and aromatization (Figure 1).

2.5.1 Radical Generation and Cracking

The first stage involves thermal decomposition of biomass and plastics, producing free radicals such as alkyl, alkoxy, and acyl radicals. Plastics like polyethylene and polypropylene act as hydrogen donors, stabilizing biomass-derived oxygenated radicals (Deng et al, 2025).

Homolytic bond cleavage happens when at high temperatures, covalent bonds in biomass (C–C, C–O, C–H) and plastics break homolytically, forming reactive radicals. On the other hand, radical chain propagation is when radicals propagate chain reactions that lead to smaller volatile fragments.

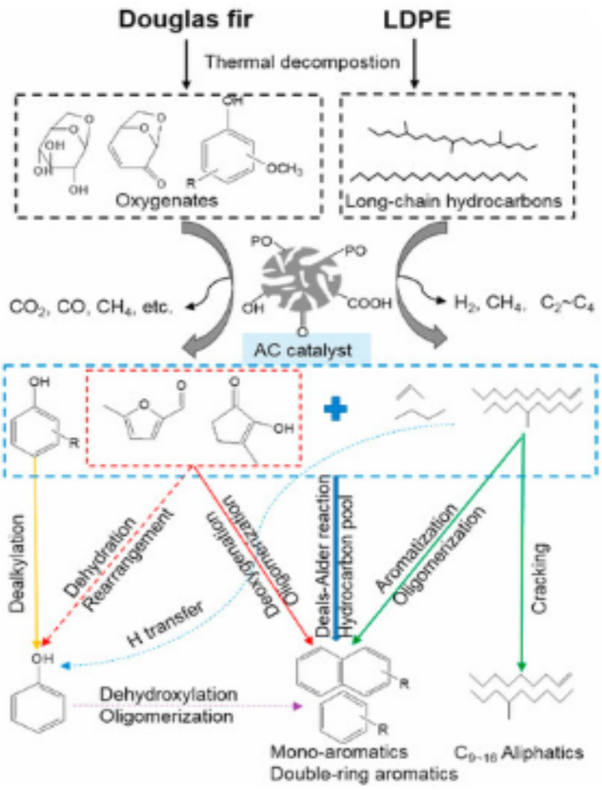

Figure 1: Proposed reaction mechanism for catalytic co-pyrolysis illustrating radical generation, hydrogen-transfer steps, intermediate stabilization, and catalyst-mediated deoxygenation pathways (Lin et al, 2023)

Synergistic stabilization occurs when plastics donate hydrogen atoms to biomass-derived radicals, thereby suppressing unwanted polymerization reactions and minimizing char formation (Gonzalez-Aguilar et al, 2023). This radical-quenching mechanism not only stabilizes reactive intermediates but also improves the selectivity of subsequent reactions. Overall, this process establishes a more controlled reaction environment that enables efficient catalytic transformations in the following stage.

2.5.2 Catalytic Cracking and Deoxygenation Pathways

Catalysts influence the intermediates through β-scission, aromatization, and hydrocarbon chain rearrangement, improving bio-oil and syngas quality.

β-Scission is when radicals cleave at the β-position relative to the reactive center, producing smaller hydrocarbons and olefins. Zeolites provide acidic sites that facilitate β-scission, enhancing gas formation and reducing oxygenated compounds (Dyer et al, 2021).

In aromatization, Zeolite catalysts, especially ZSM5, promote the conversion of light aliphatic intermediates into aromatic hydrocarbons via cyclization and dehydrogenation pathways. Metal-modified zeolites further enhance aromatic selectivity by facilitating dehydrogenation reactions, while their microporous structure restricts diffusion and suppresses secondary oligomerization (Iisa et al, 2020).

Hydrocarbon chain rearrangement occurs when hydrocarbon fragments generated during pyrolysis can undergo isomerization and skeletal rearrangement on the surface of bifunctional catalysts. For example, Ni-modified ZSM5 catalysts have been shown to balance acid catalyzed cracking with metal-catalyzed hydrogen transfer, improving the distribution of lighter, more stable hydrocarbons in the product mixture (Ding et al, 2020).

2.6. Role of Acid–Base Catalytic Sites

In co-pyrolysis, acid–base sites on catalysts crucially influence cracking, deoxygenation, and product composition. Acidic and basic functionalities act in a complementary manner: acid sites drive dehydration and aromatization, while base sites promote deoxygenation and stabilize reactive intermediates, thereby minimizing coke formation (Sun et al, 2025).

Acidic Sites (Brønsted / Lewis)

Brønsted acid sites in zeolites such as ZSM5 facilitate dehydration of oxygen-rich biomass fragments and drive cyclization, yielding aromatic hydrocarbons (Asadieraghi et al**,** 2015). Lewis acid sites (or more moderate acid sites) can mediate skeletal rearrangement and isomerization of intermediate hydrocarbons, which helps produce more stable, uniform fuel molecules (Ding et al, 2020).

Basic Sites (Alkaline-Earth Oxides)

Basic oxides such as CaO contribute through decarboxylation, removing acid functionalities (e.g., –COOH) from pyrolysis intermediates, thus reducing acidity and oxygen content in the bio-oil (Yi et al, 2019). In addition, base sites neutralize acidic compounds, suppressing polymerization and condensation that can lead to coke buildup (Sun et al, 2025).

Synergistic Acid–Base Catalysis

When both acid and base sites are present, their synergy enhances performance: acid sites crack and form aromatics, while base sites deoxygenate and buffer the reaction environment. For example, a dual CaO / ZSM5 catalyst system was shown to improve the yield of aromatics and reduce coke by combining the deoxygenation capacity of CaO with the acid-driven aromatization of ZSM-5 (Yi et al, 2019).

2.7. Summary of Mechanistic Role of Catalysts

Catalysts play a central role in guiding the co-pyrolysis of biomass and plastics, influencing product distribution, stability, and energy content. Their mechanistic contributions can be summarized under three main functions; radical stabilization, cracking enhancement, and product upgrading (Figure 2).

2.7.1 Radical Stabilization

During co-pyrolysis, hydrogen-rich plastics such as polyethylene and polypropylene donate hydrogen atoms to oxygenated biomass radicals. This transfer stabilizes reactive intermediates, preventing condensation and polymerization that would otherwise lead to excessive char formation. Supported metals and noble metal catalysts enhance this hydrogen transfer, promoting more efficient radical stabilization and increasing the yield of lighter hydrocarbons (Mo et al, 2023). In the study by Ding *et al.* (2018), co-pyrolysis of corn stover and LDPE over CeO_2 + HZSM-5 nearly eliminated oxygenates from the product oil, producing predominantly hydrocarbons.

2.7.2 Cracking Enhancement

Catalysts accelerate the fragmentation of long-chain hydrocarbons through β-scission and other cracking mechanisms. Acidic sites on zeolites, for example, promote selective scission of C–C bonds, generating shorter-chain hydrocarbons suitable for liquid fuels, while metal oxides such as CaO or MgO tend to facilitate secondary reforming reactions thus enhancing gas composition. This cracking not only increases bio-oil yield but also reduces the formation of heavy tars and coke (Sun et al, 2025).

2.7.3 Product Upgrading

Zeolite and metal-supported catalysts guide key upgrading reactions such as aromatization, cyclization, and hydrocarbon chain rearrangement. Brønsted acid sites in zeolites promote formation of mono-aromatic and poly-aromatic hydrocarbons, while metal sites (e.g., Ni, Co, Mo) enable hydrodeoxygenation, decarbonylation, and hydrogenation reactions. The combined effect is improved bio-oil quality, enhanced syngas composition, and more uniform hydrocarbon distribution (Sun et al, 2025). Overall, the synergistic action of radical stabilization, cracking enhancement, and product upgrading illustrates the mechanistic versatility of catalysts in biomass–plastic co-pyrolysis. These mechanisms are critical for optimizing product yield, improving energy content, and reducing undesirable by-products such as char and coke.

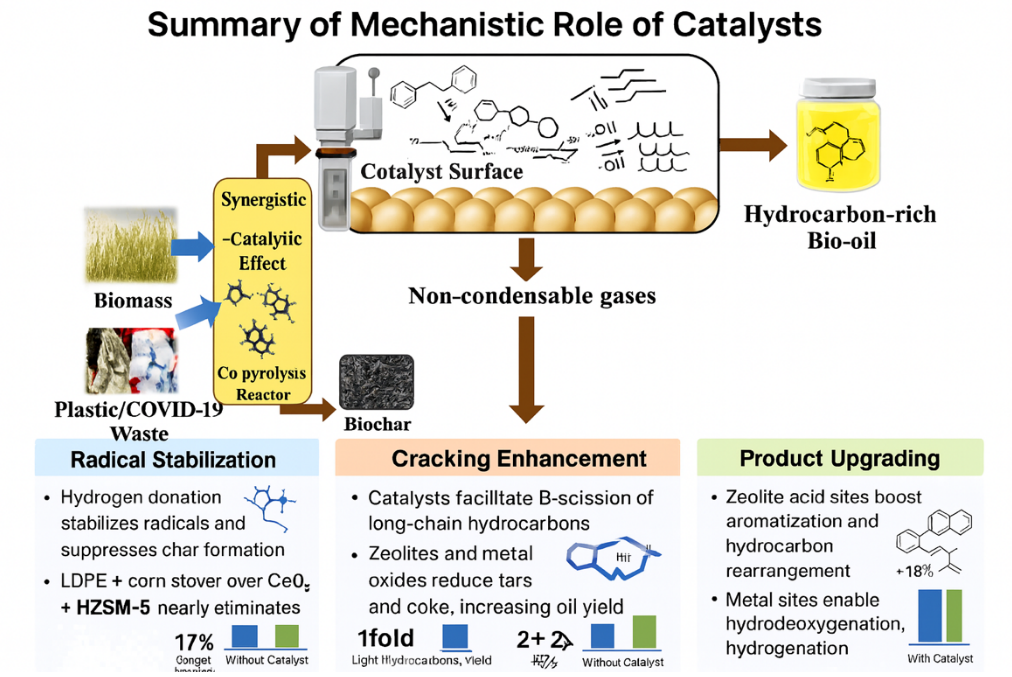

Figure 2: Catalytic roles in biomass–plastic co-pyrolysis: radical stabilization, cracking enhancement, and product upgrading leading to improved bio-oil and syngas quality.

2.8. Reactor Configurations for Catalytic Co-Pyrolysis

Various reactor configurations have been employed for catalytic co-pyrolysis of biomass and plastics. The choice of reactor influences heat and mass transfer, catalyst contact efficiency, and product distribution. Table 3 summarizes the main reactor types, their operating principles, advantages, and limitations.

Table 3: Principle, Advantages and Limitation of Various Reactor Types Used in Catalytic Co-Pyrolysis

Reactor Type	Principle / Description	Advantages	Limitations	References
Fixed-Bed Reactor	Biomass and plastic feedstock is pyrolyzed over a stationary bed of catalyst.	Simple design; easy to operate and scale; good for screening catalysts.	Poor heat/mass transfer; potential hot spots; limited mixing; char buildup.	Sun et al., 2025; Seah et al, 2023
Fluidized-Bed Reactor	Feedstock and catalyst are fluidized by gas flow, promoting uniform heat transfer.	Excellent heat/mass transfer; uniform temperature; suitable for continuous operation; high contact efficiency.	Catalyst attrition; complex design; higher operational costs.	Mo et al., 2023; Yi et al, 2019
Auger / Screw Reactor	Feedstock is conveyed mechanically through a heated reactor with catalyst.	Continuous operation; controlled residence time; less catalyst attrition than fluidized bed.	Limited scale; potential mechanical wear; uneven heat distribution.	Sun et al, 2025
Microwave-Assisted Reactor	Uses microwave heating to rapidly pyrolyze feedstock in presence of catalyst.	Fast, selective heating; energy efficient; can enhance product yield and selectivity.	Limited scale; uneven heating for larger batches; high equipment cost.	Ding et al., 2020; Sun et al, 2025
Rotary Kiln Reactor	Feedstock moves through a rotating drum in contact with catalyst.	Good heat transfer; continuous operation; suitable for large-scale biomass-plastic mixtures.	Lower heat transfer efficiency than fluidized beds; slower reaction kinetics; higher maintenance.	Asadieraghi et al**,** 2015; Seah et al., 2023

3. ADVANCES, PERFORMANCE TRENDS, AND PROCESS INSIGHTS IN CATALYTIC CO-PYROLYSIS

3.1 Synergistic Interactions in Catalytic Co-Pyrolysis

3.1.1 Hydrogen Transfer Mechanisms

During catalytic co-pyrolysis, radicals generated from hydrogen-rich plastics such as polyethylene (PE) and polypropylene (PP) can donate hydrogen atoms to oxygenated intermediates derived from biomass (Seah et al, 2023; Mo et al, 2023). This hydrogen transfer stabilizes reactive biomass fragments, preventing condensation and polymerization reactions that could otherwise form tars or heavy oligomers. The process effectively increases the yield of lighter, more valuable hydrocarbons in the bio-oil fraction while simultaneously reducing oxygen content, improving energy density, and enhancing product quality (Li et al, 2022). Recent studies have shown that the efficiency of hydrogen transfer can be influenced by catalyst type, feedstock ratio, and reactor configuration, highlighting opportunities to optimize this synergy for higher hydrocarbon yield (Deng et al, 2025).

3.1.2 Reduction of Oxygenated Compounds

Catalysts play a critical role in accelerating deoxygenation reactions, including decarboxylation (removal of CO_2), decarbonylation (removal of CO), and dehydration (removal of H_2O) collectively lowering bio-oil oxygen content, increasing calorific value, and reducing acidity (Deng et al, 2025). Acid-treated or metal-doped zeolites enhance the breakdown of oxygen-rich intermediates such as furans, ketones, and aldehydes, facilitating conversion to hydrocarbons

(Cheng et al, 2024). Emerging work indicates that specific catalyst structures can preferentially target certain oxygenates, which remains a topic of active investigation due to variable results across different biomass–plastic blends. The catalytic pathway is often more selective than non-catalytic pyrolysis, minimizing coke formation and promoting the formation of stable liquid products suitable for downstream refining.

3.1.3 Catalyst-Enhanced Synergy

Catalysts, such as microporous zeolites (e.g., HZSM-5), metal oxides, and supported noble metals, enhance the intrinsic synergy of biomass–plastic co-pyrolysis by modifying reaction pathways to improve product quality. HZSM-5, with its high surface area and strong acidity, promotes deoxygenation and aromatization, converting oxygen-rich biomass intermediates into stable hydrocarbons. Metal oxides provide acidic or basic sites that facilitate decarboxylation, decarbonylation, and dehydration, reducing char formation and stabilizing reactive species. Supported noble metals catalyze hydrogen transfer and hydrocracking, effectively using hydrogen from plastics to stabilize biomass-derived intermediates. Together, these catalysts enhance hydrogen utilization, suppress unwanted polymerization, and increase the yield of high-quality bio-oil, thereby amplifying the synergistic interaction between biomass and plastics (Gonzalez-Aguilar et al, 2023). Key functions include:

- **Cracking of Heavy Compounds**: Catalysts break down long-chain oxygenated and hydrocarbon molecules into smaller, more volatile compounds, increasing bio-oil yield and reducing char formation.
- **Aromatization**: Acidic sites on zeolites promote cyclization and dehydrogenation reactions, converting aliphatic fragments into aromatic hydrocarbons that are valuable fuel components.
- **Isomerization**: Catalysts can rearrange molecular structures, thereby, improving volatility and stability of pyrolysis products, and facilitating downstream refining.
- **Reduction of Acid and Phenolic Content**: Catalytic reactions reduce phenolic and carboxylic functional groups, decreasing acidity, corrosion potential, and viscosity of bio-oils. This is particularly important for producing oils compatible with conventional fuels (Li et al, 2022; Mo et al, 2023).

Recent developments and ongoing debates highlight that advanced catalysts, including biochar-derived and activated-carbon-based materials, follow alternative mechanistic pathways compared with traditional zeolites and metal oxides, influencing the distribution of oil, gas, and char (Seah et al, 2023). The observed synergistic outcomes are highly dependent on feedstock ratio, catalyst type, and reactor conditions, with some studies reporting reduced oil yield or catalyst deactivation when biomass-rich blends, halogenated or oxygenated plastics (such as PVC, PET, or PU), slow-pyrolysis conditions, or heterogeneous mixed-waste feedstocks alter reaction pathways or promote char formation (Deng et al, 2025). Emerging research further emphasizes that catalytic co-pyrolysis can be tailored not only for fuel production but also for the generation of high-value carbon materials and specialty hydrocarbons, reflecting a shift toward multifunctional process design.

Overall, the use of suitable catalysts not only enhances the synergistic effect between biomass and plastics but also tailors the product distribution toward higher-value hydrocarbons, cleaner syngas, and engineered chars with desirable properties for applications in energy and material sectors.

3.2. Product Distribution and Catalytic Effects

The inclusion of catalysts in biomass–plastic co-pyrolysis significantly alters product distribution thus promoting liquid upgradation, enhancing syngas yield, and improving char characteristics and these effects are discussed below.

3.2.1 Catalytic Bio Oil Upgrading

Catalysts can markedly improve the quality of bio-oil by reducing the concentration of undesirable oxygenated species, such as acids and phenols, while increasing the fraction of more stable hydrocarbons (Sun et al, 2025). For instance, activated carbon derived from industrial organic waste promotes aromatization of polyolefins during pyrolysis, and the acid sites introduced during activation using H_3PO_4 facilitate the formation benzene, toluene, and ethylbenzene from plastic precursors. Co-pyrolysis of biomass and plastics in the presence of such activated carbon catalysts also decreases oxygen content in the liquid product and increases the formation of aliphatics and aromatics, leading to higher energy density and improved chemical stability in the bio-oil fraction.

3.2.2 Syngas Enhancement

Metal catalysts, especially nickel and iron-based systems, are powerful promoters of syngas generation during co-pyrolysis. A recent study reported that the addition of Ni–Fe bimetallic catalysts during co-pyrolysis generated syngas with a high H_2 content while also achieving effective tar reduction. Under gasification like conditions, H_2 constituted the largest fraction of the gas, indicating enhanced water-gas shift activity (Mbeugang et al, 2025). In other systems, Ni–Co/Ca catalysts (with boron promoters) significantly boosted hydrogen and CO yield during rice-straw pyrolysis, highlighting how tailored metal compositions can optimize gas composition (Wang et al, 2024).

3.2.3 Char Quality Improvement

Catalysts can also enhance the quality of the residual char produced during co-pyrolysis. Chemical activation of pyrolysis char (e.g., with KOH) can transform low-surface-area materials into highly microporous structures. Hwang et al, (2017) reported that the BET surface area of fast-pyrolysis char increased from approximately 9 m^2/g to over 1,900 m^2/g. The high–surface-area char has potential applications in adsorption, catalysis, or as a support material. Additionally, catalytically activated systems often yield char with a higher fixed-carbon content, improving its value for use as a carbon material or fuel, rather than low-grade residue.

Overall, the presence of catalysts shifts the collective product distribution by directing biomass–plastic co-pyrolysis toward higher-quality bio-oils, richer syngas, and engineered chars, demonstrating their integral role in tuning product yields and properties.

3.3. Techno Economic and Environmental Analysis

3.3.1 Economic Feasibility

Economic viability is a major challenge for catalytic co-pyrolysis. According to Yadav et al. (2023), the minimum selling price (MSP) of a BTX (benzene, toluene, xylene) mixture from a conceptual catalytic fast pyrolysis (CFP) facility processing 240 tons per day of mixed plastic waste is about US$ 1.07/kg, assuming co-products fetch average market prices (Yadav et al, 2023). At this price point, achieving competitiveness with virgin BTX (~US$ 0.68/kg) depends heavily on low-cost feedstock (<US$ 0.10/kg) or high crude oil prices (Yadav et al, 2023). Catalyst costs, separation units, and operating expenditures (e.g., utilities) emerged among the strongest cost drivers in

their sensitivity analysis, indicating that catalyst cost remains a key economic limitation (Yadav et al, 2023). On the other hand, co-pyrolysis helps reduce certain operational costs: combining plastic with biomass can lower pre-treatment or feedstock logistics costs, since biomass residues may be locally available and cheaper than pure plastic feedstock (Deng et al, 2025). In some technoeconomic models for mixed waste pyrolysis, the integration of biomass reduces reliance on pure polymer waste streams, improving process economics (Yadav et al, 2023).

3.3.2 Lifecycle Assessment

From an environmental perspective, life-cycle assessment (LCA) of catalytic pyrolysis is critical to understanding its climate impact and sustainability. Yadav et al. (2023) also conducted an LCA of their CFP system and found that while total supply-chain energy use could be reduced by 24%, the greenhouse gas (GHG) emissions per kg of BTX produced increased by 2.4 times compared to conventional petrochemical routes (Yadav et al, 2023). This suggests a trade-off: energy savings are achieved, but carbon emissions may be higher unless process improvements are made.

Valorization of plastic waste through copyrolysis can also mitigate CO_2 emissions by diverting plastics from landfills or incineration, and by displacing fossil-derived chemicals (Deng et al, 2025). Furthermore, feasibility studies of integrated pyrolysis plants show that carbon credits (or other policy incentives) can significantly improve economic and environmental performance.

3.4 Industrial Challenges

Despite promising modeling and lab-scale results, there are significant industrial-scale barriers to deploying catalytic co-pyrolysis:

Catalyst Deactivation: Catalysts suffer coking and poisoning during pyrolysis, which degrades performance and raises regeneration costs. Frequent regeneration or replacement of catalysts increases operating costs and reduces overall process efficiency (Wang et al, 2022).

Scaling Reactor Systems: Translating small-scale reactors to large throughput (e.g., 240 t/day as in modeling studies) involves scaling challenges. Capital expenditure for large reactors, regeneration systems, and separation units can be prohibitively high (Yadav et al, 2023). In particular, capital cost for product separation (e.g., BTX recovery) is a major contributor to the total investment (Yadav et al, 2023).

Feedstock Variability: Plastic waste streams are highly heterogeneous (different polymers, contamination, additives). Similarly, biomass sources vary in composition and moisture content. This variability complicates reactor control, catalyst selection, and process optimization (Wang et al, 2022; Deng et al, 2025).

3.5. Future Prospects

3.5.1 AI-Driven Modeling and Optimization

The integration of artificial intelligence (AI) and machine learning (ML) is poised to significantly advance catalytic co-pyrolysis. Recent work demonstrates that ML models can predict co-pyrolysis yields, optimize operating parameters such as temperature, catalyst-to-feed ratios, and feed composition, and help interpret complex data. For example, an XGBoost-based model achieved $R^2 \approx 0.96$ in predicting co-pyrolysis yields and identified key features like polymer ratio and catalyst acidity (Paavani et al, 2025). In a related study, evolutionary ML (e.g., Gaussian process regression tuned by particle swarm optimization) was used to predict product distributions and optimize operating conditions for co-pyrolysis systems (Shahbeik et al, 2023).

These AI-driven approaches can significantly reduce experimental costs, accelerate catalyst screening, and guide scale-up design.

3.5.2 Novel Catalysts

Emerging catalyst designs are expected to play a pivotal role in advancing co-pyrolysis. Multifunctional catalysts that integrate acidity, redox activity, and hydrogen-transfer capabilities can more effectively manage the complex reactions of biomass–plastic mixtures. These innovations also enhance catalyst stability and facilitate recovery or regeneration, improving process efficiency and supporting scalability for industrial applications.

Bifunctional Metal–Zeolite Hybrids: Metal-modified zeolites (e.g., Zn/ZSM-5) have demonstrated improved aromatics production by combining the strong acidity of zeolite frameworks with the dehydrogenation and hydrogen-transfer capabilities of metals. Such hybrids help promote deoxygenation and reduce coke formation during pyrolysis (Stanton et al, 2018).

Magnetic Catalysts for Easy Recovery: Magnetic catalyst such as Fe_3O_4 supported on carbon can be separated easily by a magnet and reused, reducing regeneration costs. Fe- or Co-based magnetic catalysts have been explored in biofuel production, offering both catalytic activity and recyclability. Some designs such as FeCo embeded magnetic nanoparticles in a stable carbon shell for high-temperature magnetic catalysis, which could be adapted for pyrolysis systems (Martínez-Prieto et al, 2020).

3.5.3 Reactor Innovations

Technological innovation in reactor design will be critical for the commercialization of catalytic co-pyrolysis. Modular, containerized pyrolysis units can be deployed near waste-generation sites, reducing transport costs, increasing feedstock flexibility, and enabling scalable operation in both urban and rural areas. Additionally, integrated pyrolysis–refining systems that combine pyrolysis with downstream upgrading, such as catalytic upgrading, distillation, or hydrogenation, within a single modular platform, can enhance overall process efficiency, lower capital expenditure, and simplify product purification.

4. CONCLUSION

Catalytic co-pyrolysis presents a highly promising pathway for transforming biomass and plastic wastes into cleaner, more valuable fuels and chemicals. By enhancing cracking, deoxygenation, and hydrogen-transfer reactions, catalysts enable stronger synergistic interactions between feedstocks and produce liquids with lower oxygen content, higher stability, and improved energy quality. Despite these advantages, large-scale implementation remains constrained by challenges such as catalyst deactivation, reactor complexity, operational variability, and overall economic feasibility. Continued progress in catalyst design, data-driven process optimization, and the development of efficient continuous reactor systems will be essential for overcoming these barriers. With these advancements, catalytic co-pyrolysis has strong potential to become a central technology in sustainable waste valorization and circular economy frameworks.

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