

Review

Interface-Driven Carbon–Inorganic Hybrid Catalysts for Biodiesel Production from Low-Grade Lipid Feedstocks: Acid–Base Chemistry, Mass-Transfer Control, Heterogeneity, and Stability

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Abstract

Biodiesel production from waste cooking oils, non-edible oils and other low-grade lipid feedstocks is constrained by free fatty acids, water, salts, oxidation products, and the poor miscibility of triglycerides with short-chain alcohols. Carbon–inorganic hybrid catalysts are attractive because the inorganic phase can provide strong acid or base sites, while the carbon phase can alter dispersion, wettability, pore accessibility, microenvironment polarity, leaching, and recovery. Yet the term hybrid is often applied to materials for which the carbon component has not been shown to affect catalysis. This critical review therefore focuses on one defined reaction scenario: esterification and transesterification for biodiesel production from low-grade lipid feedstocks. The discussion is organized by the catalytic problem rather than by an unrestricted catalogue of materials. Carbon-supported CaO and MgO, carbon-coupled layered-double-hydroxide-derived mixed oxides, sulfonated carbon–inorganic acids, bifunctional acid–base systems, magnetically recoverable ferrite/carbon catalysts, and graphenic supports are compared through structure–activity relationships, reaction conditions, feedstock quality, FAME yield, heterogeneity, reusability, and post-reaction evidence. Particular attention is given to the distinction between a true interfacial effect and activity caused by leached Ca, K, Na or sulfonic species. A minimum evidence hierarchy is proposed, requiring carbon-only, inorganic-only, and physical-mixture controls, hot-filtration tests, elemental analysis of the liquid phase, recovered-mass accounting, and post-reaction structural characterization. The literature shows that high first-cycle yield is common, whereas water tolerance, low leaching, retained active-site density, and continuous operation remain uncommon. The most defensible future direction is therefore not greater compositional complexity, but simpler hybrid architectures designed around a specific failure mode and validated under realistic feedstock and reactor conditions.

Keywords: biodiesel; carbon–inorganic hybrids; biochar; CaO; layered double hydroxides; mixed metal oxides; sulfonated carbon; magnetic catalysts; waste cooking oil; esterification; transesterification; leaching



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1. Introduction

Biodiesel is produced by converting triglycerides and free fatty acids into fatty-acid alkyl esters, most commonly fatty-acid methyl esters (FAMEs). The chemistry is established, but the catalyst problem changes sharply when refined oils are replaced by waste cooking oils, rendered fats, acid oils, or non-edible seed oils. These feeds may contain several

weight percent free fatty acids (FFAs), variable water, salts, suspended solids, thermal-oxidation products, and polymerized lipids. Their viscosity and chemical heterogeneity create simultaneous demands on acid–base chemistry, interfacial transport, catalyst stability, and product separation [1–3].

Homogeneous NaOH or KOH remains difficult to beat for dry, low-FFA oils because methoxide is generated rapidly and transesterification can proceed near the boiling point of methanol. The same catalysts react with FFAs to form soaps, promote emulsions, and complicate glycerol separation. Homogeneous mineral acids tolerate FFAs but react more slowly with triglycerides, require corrosion-resistant equipment, and generate neutralization streams. Heterogeneous catalysts are therefore pursued less because they guarantee higher intrinsic activity and more because they may enable separation, reuse, lower wastewater production, feedstock tolerance, and continuous processing [1,4,5].

Carbon–inorganic hybrids occupy a distinct design space within heterogeneous catalysis. The inorganic component—CaO, MgO, mixed oxides, hydrotalcite-derived materials, ferrites, or acid oxides—normally supplies the dominant catalytic sites. The carbon phase can disperse those sites, change the local polarity experienced by methanol and oil, expose or shield basic centres, anchor magnetic particles, provide meso/microporosity, or facilitate shaping. In sulfonated materials, the carbon phase may also carry Brønsted acid groups directly. These roles are plausible, but they are not automatic. A powder containing carbon and an oxide is not necessarily an interface-driven catalyst.

The broad literature on carbonaceous and inorganic catalysts often places biodiesel synthesis alongside pyrolysis, hydrodeoxygenation, reforming, photocatalysis, and wastewater treatment. Such breadth obscures the fact that each reaction family is controlled by different active structures and performance metrics. The present review deliberately narrows the scope to biodiesel production from lipid feedstocks. The esterification of FFAs and transesterification of triglycerides are treated as linked reactions within the same process window, especially for feeds that cannot be converted reliably by a single homogeneous base step.

The central question is therefore practical: when does the carbon–inorganic interface solve a problem that the corresponding inorganic catalyst, carbon catalyst, or physical mixture does not solve? The answer requires more than a high FAME yield. Feedstock acid value and water content, methanol-to-oil ratio, catalyst loading, mixing, temperature, time, leaching, recovered mass, filtrate activity, and post-reaction structure must be considered together. The review develops this argument through reaction chemistry, material classes, evidence standards, benchmark studies, deactivation, and scale-up.

2. Scope and Critical Review Approach

This article is a critical narrative review rather than a formal meta-analysis. Research was selected from the literature when it addressed at least one of the following: (i) carbon-supported or carbon-coupled inorganic catalysts for esterification or transesterification; (ii) biochar-derived acidic, basic, or bifunctional solids containing a defined inorganic contribution; (iii) LDH-derived mixed oxides relevant to carbon-coupled catalyst design; (iv) magnetic carbon–inorganic systems whose recovery function was tested during biodiesel synthesis; or (v) graphenic supports used with oxide catalysts. Reviews were used to frame established chemistry [1,6]. Representative primary studies were retained for numerical benchmarking.

Studies were not considered evidence of an interfacial effect merely because the terms “hybrid,” “nanocomposite,” or “supported catalyst” appeared in the title. The discussion distinguishes four material states: physical mixture, supported catalyst, composite, and interface-driven hybrid. A true hybrid claim requires a measurable difference relative

to relevant single-component and physical-mixture controls. Where the literature lacks those controls, the material is discussed as a promising composite rather than as proven synergistic catalysis.

Numerical comparisons are restricted to studies whose operating conditions are sufficiently reported, so that unlike reaction systems are not ranked as though they were directly comparable.

3. Reaction Chemistry and Feedstock Constraints

3.1. Base-Catalyzed Transesterification

Transesterification converts one triglyceride molecule into three FAME molecules and glycerol through consecutive triglyceride–diglyceride–monoglyceride steps. On basic solids, methanol is activated at basic oxygen centres or ion pairs to form surface methoxide-like species. Nucleophilic attack on the ester carbonyl produces a tetrahedral intermediate, followed by alkoxy-group exchange and the stepwise release of FAME. Strong basicity accelerates methanol activation, but catalytic performance also depends on the accessibility of sites to large triglyceride molecules and on the ability of methanol and oil to contact the same surface [4,7,8].

CaO is attractive because it is inexpensive and strongly basic, but its active surface is sensitive to H₂O and CO₂. Hydration forms Ca(OH)₂, carbonation forms CaCO₃, and both processes alter the number and strength of available basic sites. In methanol, soluble calcium species may contribute to the observed rate. MgO is less basic but can be more stable; mixed oxides and LDH-derived materials allow basicity and dispersion to be tuned. The role of carbon is therefore potentially valuable only when it preserves accessible basic sites, changes phase contact, or limits material loss.

3.2. Acid-Catalyzed Esterification and High-FFA Feeds

Esterification converts an FFA and methanol into FAME and water. Brønsted acids protonate the fatty-acid carbonyl, increasing its susceptibility to methanol attack. The reaction is equilibrium-limited, and water is both a product and an inhibitor, so hydrophobic microenvironments and efficient water management can matter as much as nominal acid density [5,9–11]. Sulfonated carbons, carbon-supported acid oxides, and acid–base bifunctional catalysts are therefore most relevant when the feedstock acid value is high enough to make direct base transesterification impractical.

A solid acid may also catalyze triglyceride transesterification, but generally at a higher temperature, longer time, or larger alcohol excess than a strong base catalyst. For this reason, many low-grade-feed processes use a two-step strategy: Acid esterification lowers the FFA content. This is followed by base transesterification. A genuinely bifunctional hybrid would enable both transformations without mutual neutralization, uncontrolled leaching, or severe diffusion penalties.

3.3. Water, Soaps and Multiphase Transport

Figure 1 summarizes the coupled reaction network. Water promotes triglyceride hydrolysis and shifts esterification backwards. FFAs neutralize basic sites and generate soaps. Soaps stabilize emulsions, retain glycerol and methanol in the ester phase, and make separation difficult. These side reactions explain why a catalyst that performs well with refined oil may fail with waste cooking oil even when nominal FAME yield is high in an optimized laboratory batch.

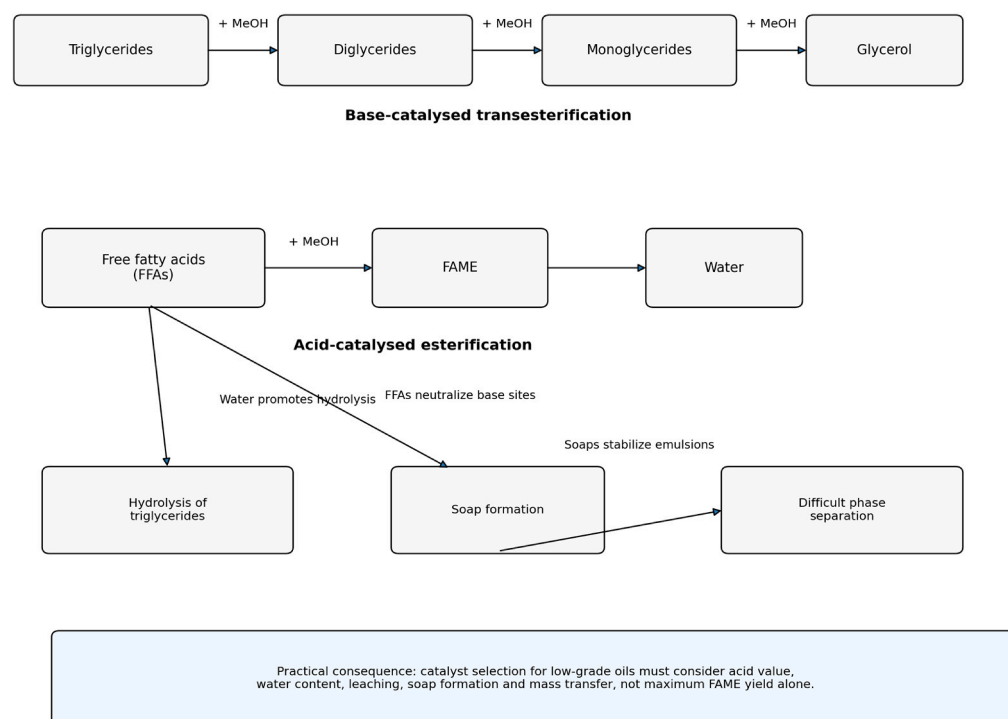


Figure 1. Reaction network governing esterification and transesterification of low-grade lipid feedstocks. Water and free fatty acids couple catalyst chemistry to hydrolysis, soap formation, and separation. Original schematic prepared for this review.

The oil–alcohol–solid system is initially multiphase. Apparent catalytic rates may therefore be controlled by mixing, droplet size, viscosity, and surface wetting rather than by intrinsic site chemistry. A carbon phase can increase mesoporosity and alter polarity, but hydrophobicity is not universally beneficial: excessive affinity for oil can limit methanol access, whereas a highly oxygenated carbon can bind water and deactivate basic sites. The useful design target is a balanced interfacial microenvironment, not maximum hydrophobicity in isolation [1,4].

The feedstock-dependent requirements in Table 1 provide the basis for comparing catalyst families. A single maximum-yield value is inadequate unless the acid value, water content, alcohol ratio, and separation protocol are also reported.

Table 1. Feedstock-dependent catalyst requirements for biodiesel production.

Feedstock Class	Dominant Challenge	Required Catalyst Function	Minimum Reporting
Refined, dry oil	Low FFA and low H ₂ O; mass transfer dominates early stage	Strong, accessible base sites; moderate mesoporosity	FAME yield, initial rate, alcohol/oil ratio, catalyst loading
Waste cooking oil	Variable FFA, H ₂ O, oxidation products and solids	Water/FFA tolerance, robust base or staged acid–base route	Acid value, H ₂ O, pretreatment, hot filtration, cycles
High-FFA non-edible oil	Direct base route causes saponification	Stable Brønsted acid or spatially separated acid–base sites	FFA conversion, FAME yield, water sensitivity, S/metal leaching
Rendered fats/high viscosity oils	High viscosity and transport resistance	Hierarchical pores, wetting control, process intensification	Mixing, viscosity, kinetics, recovered mass
Feed containing salts or metals	Possible poisoning and ash interactions	Chemically stable sites and defined inorganic composition	ICP of feed and leachate, post-reaction XPS/XRD

4. What Constitutes an Interface-Driven Carbon–Inorganic Catalyst?

The phrase carbon–inorganic hybrid should be reserved for a material in which the interface changes a catalytic or process descriptor. Four increasingly demanding levels can be distinguished. A physical mixture simply contains both phases. A supported catalyst places an inorganic phase on carbon, but the carbon may function only as an inert carrier. A composite combines functions such as catalysis and magnetic recovery without proving that the interface changes the active site. An interface-driven hybrid shows that carbon modifies dispersion, acid/base character, wetting, leaching, reaction rate, or stability relative to matched controls. The corresponding evidence matrix is summarized in Table 2.

Figure 2 maps the principal functions and the measurements needed to support them. In basic oxide systems, TEM or STEM-EDS can establish particle dispersion, CO₂-TPD can probe basic-site density and strength, and ICP analysis can reveal whether Ca, K, Na, Mg, or transition metals enter the liquid phase. In acidic systems, sulfur content, acid-site titration, NH₃-TPD or pyridine-FTIR should be measured before and after reaction. Contact angle or water-uptake measurements can support microenvironment claims, but they must be connected to kinetics or feedstock tolerance.

Carbon-inorganic interfacial functions in biodiesel catalysis

Claimed interfacial function	Minimum descriptor to measure	Why it matters in biodiesel
Oxide dispersion / site exposure	TEM or STEM-EDS; XRD; BET surface area	Higher accessibility of CaO or mixed-oxide sites can increase apparent rate and reduce agglomeration.
Acid or base strength / density	CO ₂ -TPD, NH ₃ -TPD, pyridine-FTIR, titration	Determines whether the material is suited to transesterification, esterification, or both.
Hydrophobic microenvironment	Contact angle, water uptake, kinetic comparison	Can improve contact with oil-rich feeds and reduce deactivation by water.
Resistance to leaching	ICP of filtrate; hot filtration; post-reaction phase analysis	Distinguishes true heterogeneous catalysis from dissolved Ca, K, Na, Mg or S species.
Recovery / structural stability	Recovered mass, magnetic saturation, post-cycle XRD or Raman	Shows whether the hybrid improves catalyst handling and reuse.

Figure 2. Interfacial functions and corresponding evidence for carbon–inorganic biodiesel catalysts. Each claimed function should be tied to a measurable descriptor. Original schematic prepared for this review.

The physical-mixture control is decisive. If a prepared CaO/biochar hybrid and a hand-mixed CaO + biochar sample give the same conversion, leaching and reuse behaviour, the synthetic interface has not demonstrated added value. Conversely, a lower first-cycle rate may still be worthwhile if the hybrid sharply reduces leaching and retains activity over time. Interface value is therefore multi-metric rather than synonymous with the highest level of conversion.

Table 2. Evidence matrix for common claims in carbon–inorganic biodiesel catalyst studies.

Claim	Minimum Control	Methods	Evidence Required
Carbon alters inorganic dispersion	Inorganic-only catalyst; same loading and thermal history	TEM/EDS, XRD crystallite size, chemisorption where applicable	Smaller/more stable particles and retained dispersion after reaction
Carbon changes acid/base sites	Carbon-only, inorganic-only and physical mixture	CO ₂ /NH ₃ -TPD, pyridine-FTIR, titration before/after use	Different site density/strength consistent with kinetics
Carbon improves oil/alcohol contact	Matched surface area and mixing conditions	Contact angle, water uptake, interfacial-tension or kinetic tests	Lower transport limitation without loss of methanol access
Catalyst is truly heterogeneous	Hot-filtration and leachate reaction test	ICP-OES/MS, pH/conductivity, recovered mass	Low dissolved active species and inactive filtrate
Magnetic recovery is durable	Non-magnetic analogue and repeated separations	VSM, recovery time, mass recovery, ICP	Retained magnetization and catalytic function

5. Carbon Phases: Functional Support, Hidden Catalyst, or Source of Variability?

5.1. Biochar and Ash-Derived Activity

Biochar is not a chemically uniform support. Feedstock, pyrolysis temperature, residence time, atmosphere, activation and washing determine aromaticity, oxygen functionality, surface area, pore structure and ash composition [12–16]. Alkali and alkaline-earth species in ash can dominate transesterification. A banana-peel-derived carbon may contain catalytically active K compounds, whereas an acid-washed lignocellulosic biochar may behave primarily as a porous support. Consequently, the label biochar cannot substitute for proximate/ultimate analysis, ash quantification and elemental characterization.

Lower pyrolysis temperatures generally preserve oxygen-containing groups that can anchor inorganic precursors or be converted into acidic sites. Higher temperatures increase aromatic condensation and may improve hydrophobicity and mechanical stability, but can reduce functional-group density. Activation can create useful mesoporosity while introducing residual K or other inorganic species. Because these same species may leach into methanol, hot-filtration and ICP tests are essential whenever high activity is associated with alkali-rich biochar.

5.2. Activated Carbon, Graphenic Carbon and Doped Carbon

Activated carbon provides higher and more reproducible surface area than many raw biochars, but its surface chemistry still depends on oxidation, activation and washing. Graphene oxide (GO), reduced graphene oxide (rGO) and N-doped graphene provide large interfacial area and strong anchoring interactions, yet they introduce cost, aggregation and characterization burdens. In liquid-phase transesterification, electrical conductivity is rarely the rate-limiting property. The relevant benefits are instead oxide dispersion, pore accessibility, adsorption and surface polarity.

N-doping can change acid–base behaviour and metal–support interactions, but pyridinic, pyrrolic and graphitic nitrogen should be distinguished by XPS. A statement that N-doped graphene increases catalytic activity is not mechanistic unless the improvement is separated from changes in oxide loading, particle size, surface area and reaction severity.

5.3. Minimum Materials Passport

Table 3 lists the minimum information needed to compare carbon-containing biodiesel catalysts. These descriptors should be reported before reaction and, for the most relevant variables, after reuse. The table is intentionally more demanding for waste-derived carbons because batch-to-batch variability can be large.

Table 3. Minimum materials passport for carbon–inorganic biodiesel catalysts.

Variable	Recommended Reporting	Why It Matters
Carbon source	Feedstock/specification, ash content, batch identity	Hidden K, Ca, Mg, Fe or P may be catalytic
Thermal history	Heating rate, peak temperature, dwell, atmosphere, yield	Controls aromaticity, functionality and mineral phases
Surface chemistry	C/O ratio, $-\text{SO}_3\text{H}$ or dopant content, acidity/basicity	Defines anchoring and catalytic contribution
Texture and morphology	BET area, pore-size distribution, SEM/TEM	Separates site chemistry from accessible surface area
Inorganic phase	Loading, phase identity, particle size, distribution	Required to compare supported and physical-mixture controls
Wetting behaviour	Contact angle or water/alcohol uptake	Tests microenvironment claims
Stability	Recovered mass, leached elements, post-reaction structure	Distinguishes reuse from material loss

6. Basic Oxide–Carbon Hybrids

6.1. CaO/Carbon Systems

CaO remains the reference strong solid base for triglyceride transesterification [7]. Supporting CaO on carbon can reduce agglomeration, increase accessible interfacial area and improve separation. The benefit is most credible when CaO loading and thermal history are matched, because calcination can simultaneously form active CaO, burn carbon, create CaCO_3 or redistribute ash species. A nominal CaO/biochar catalyst may therefore contain a complex mixture of CaO, $\text{Ca}(\text{OH})_2$, CaCO_3 and potassium salts.

The 2024 banana-peel biochar study by Dias and co-workers is instructive because the best catalyst was not the most heavily alkali-modified material. Biochar carbonized at $350\text{ }^\circ\text{C}$ produced 97.5% FAME from waste frying oil with an acidity of 1.2 mg KOH g^{-1} [17]. The result shows that a waste-derived carbon can function as a catalyst under mild feed acidity, but it also illustrates why ash composition and leaching must be considered before attributing activity to carbon functionality.

More complex waste-derived hybrids can combine carbon, CaO and a magnetic phase. Xia et al. prepared a CoFe/biochar/CaO material from sargassum and river-snail-shell waste and reported a maximum biodiesel yield of 99.21% from waste cooking oil [18]. The architecture is attractive because acid/base function and magnetic recovery are integrated, but the mechanistic burden is high: Ca, Fe and Co leaching, the activity of the filtrate, retained magnetization and the role of the carbon scaffold must all be established over repeated cycles.

Mansooramaei et al. used banana-peel-derived biochar containing $\text{Fe}_2\text{O}_3/\text{Fe}_2\text{K}_6\text{O}_5$ phases for waste-cooking-oil conversion [19]. Such materials can be highly active because K-containing phases promote methoxide formation and Fe-containing phases facilitate magnetic separation. The same K species can also dissolve, producing apparent heterogeneous activity. The correct interpretation therefore depends on liquid-phase elemental analysis and hot-filtration experiments, not only on magnetic reuse.

6.2. Mixed Oxides and Graphenic Supports

Mixed oxides can moderate the extremes of CaO by combining strong base sites with more stable phases. MgO, ZnO, CuO and mixed Ca–Mg or Zn–Cu systems have been examined as biodiesel catalysts, either as standalone solids or on porous supports [20–23]. Carbon can increase dispersion and reduce diffusion length, but it should not be assumed to change intrinsic basicity unless TPD or spectroscopic data show it.

The ZnCuO/N-doped-graphene nanocomposite reported by Kuniyil et al. produced 97.1% biodiesel from waste cooking oil at 180 °C using 10 wt% catalyst, a 15:1 methanol/oil ratio and an 8 h reaction time [24]. The high yield demonstrates catalytic capability, but the severe conditions also show why yield alone cannot establish superiority. A useful follow-up comparison would hold ZnCuO loading, surface area and particle size constant while replacing N-doped graphene with activated carbon and biochar. Representative basic and magnetic systems are compared in Table 4.

Table 4. Representative basic and magnetic carbon–inorganic systems for biodiesel production. Values should be interpreted only with the associated reaction conditions.

Catalyst	Feedstock	Key Conditions/Design	Reported Performance	Critical Interpretation
Banana-peel biochar [17]	Waste frying oil; acid value 1.2 mg KOH g ^{−1}	Carbonization at 350 °C; no alkali modifier in best sample	97.5% FAME	Ash identity and leaching needed for mechanistic attribution
CoFe/biochar/CaO [18]	Waste cooking oil	Waste-derived magnetic acid–base hybrid	99.21% maximum yield	Ca/Fe/Co leaching and retained magnetization are decisive
Banana-peel biochar–Fe ₂ O ₃ /Fe ₂ K ₆ O ₅ [19]	Waste cooking oil	Magnetic K/Fe-containing biochar	High optimized yield reported	K-mediated homogeneous contribution must be excluded
ZnCuO/N-doped graphene [24]	Waste cooking oil	10 wt% catalyst; 15:1 methanol/oil; 180 °C; 8 h	97.1% biodiesel yield	High severity; graphenic advantage versus simpler carbon not isolated
Diatomite-supported CaO/MgO [20]	Waste cooking oil	Porous mineral support with mixed basic oxides	High conversion under optimized conditions	Useful non-carbon baseline for dispersion and pore-access effects
Citrus-peel biochar process [25]	Food-waste-derived oil	RSM optimization with economic/environmental analysis	Mid-90% optimized yield	Catalyst lifetime and batch variability control process value

7. Layered-Double-Hydroxide-Derived Mixed Oxides and Carbon Coupling

Layered double hydroxides (LDHs) provide a chemically controlled route to mixed metal oxides. Their general composition permits the Mg/Al, Ca/Al, Zn/Al, Mg/Fe or Ni/Mg/Al ratio to be varied before calcination. Thermal treatment collapses the layered structure and produces mixed oxides with tunable basic sites, high dispersion and, in some cases, a memory effect upon contact with water [26–28]. These characteristics make LDH-derived materials a stronger inorganic foundation for catalyst design than an arbitrary blend of commercial oxides.

The 2022 study by Gabriel et al. systematically examined mixed metal oxides derived from LDHs for biodiesel production [26]. The value of this family lies in the relation between cation composition, calcination, textural properties and base-site distribution. Ma et al. showed that calcined Mg/Al hydrotalcite could catalyze waste-cooking-oil transes-

terification with mixed methanol/ethanol, while also revealing that alcohol composition affects phase behaviour and product separation [27]. Such studies establish the baseline that a carbon-coupled LDH must surpass.

Carbon can be introduced during co-precipitation, after calcination by deposition, or as a structured support for the LDH precursor. The plausible benefits are smaller mixed-oxide domains, improved access for viscous oils, reduced particle aggregation and easier shaping. The risk is that carbon changes the local carbonate and water environment, thereby reconstructing or poisoning basic sites. For this reason, XRD before and after reaction, CO₂-TPD, cation leaching and water-exposure tests are more important than nominal surface area.

Direct evidence for carbon–LDH synergy in biodiesel remains less mature than the literature on stand-alone LDH-derived mixed oxides. This gap should be stated rather than filled by analogy. Future studies should compare carbon-coupled and carbon-free LDHs prepared with the same cation ratio, calcination history and particle size; otherwise improved activity may reflect only increased dispersion or altered catalyst loading.

8. Sulfonated Carbon–Inorganic Acid Catalysts and Bifunctional Systems

8.1. Sulfonated Carbons for FFA Esterification

Sulfonated carbon catalysts emerged as a route to strong, recoverable Brønsted acidity on a hydrophobic or amphiphilic framework. The sugar-derived carbon reported by Toda et al. established that incompletely carbonized saccharides could be functionalized with –SO₃H groups and used as solid acids [29]. Dehkhoda et al. subsequently developed sulfonated biochar catalysts active in both esterification and transesterification [30], while Yu et al. examined biochar-based catalysts for canola-oil conversion [31].

The relevant variable is not total sulfur alone. Sulfonic groups must remain accessible and covalently retained during contact with hot methanol, water and FFAs. Carboxylic and phenolic groups can contribute weaker acidity and affect wettability. Acid density should therefore be measured after reaction, and sulfur in the liquid phase should be quantified. If the filtered liquid remains active, the material cannot be described as a purely heterogeneous acid catalyst.

Chellappan et al. demonstrated a biochar-based Brønsted acid catalyst for simultaneous esterification and transesterification of a high-FFA non-edible oil [32]. Lim et al. prepared a sulfonated catalyst from oil-palm empty-fruit-bunch biochar using 4-benzenediazonium sulfonate [33]. Saidi et al. combined sulfonated biochar with a magnetic phase for oleic-acid esterification and process optimization [34]. These studies show the appeal of coupling acid function, waste-derived carbon and recoverability, but they also emphasize the need to separate surface acidity from dissolved sulfur species.

8.2. Spatially Organized Acid–Base Hybrids

High-FFA oils motivate acid–base bifunctionality because esterification and transesterification must occur within one process. Simply mixing a sulfonated carbon with CaO is rarely sufficient: strong acid and base sites can neutralize each other, water formed during esterification can deactivate the basic phase, and soluble species may dominate both steps. Useful architectures therefore require spatial separation, controlled sequence or different accessibility for FFAs and triglycerides.

Core–shell particles, hierarchical pores, physically separated domains in a shaped body and magnetically recoverable composite particles are plausible solutions. The design should be tested with feedstocks spanning low, intermediate and high acid values. A catalyst that performs only after an unreported pretreatment is not a one-pot bifunctional

system. The minimum evidence includes FFA conversion, FAME yield, water balance, acid/base-site density before and after use, and leaching of both acidic and basic species. Representative acidic and bifunctional systems are summarized in Table 5.

Table 5. Representative acidic and bifunctional carbon-based systems relevant to high-FFA biodiesel feedstocks.

System	Architecture	Target Reaction	Evidence Still Required
Sulfonated biochar [30]	Biochar + covalent/adsorbed acid groups	Esterification and transesterification	Acid density and S retention after reaction
Biochar Brønsted acid [32]	Waste-derived carbon with strong acid functionality	Simultaneous conversion of high-FFA oil	Matched non-sulfonated carbon and filtrate test
EFB-biochar/4-BDS [33]	Diazonium-derived sulfonic functionality	FFA-rich feed/biodiesel synthesis	S leaching, water tolerance and reuse
Magnetic sulfonated biochar [34]	Rice-husk biochar + magnetic phase + $-\text{SO}_3\text{H}$	Oleic-acid esterification	VSM, sulfur balance and retained acid density
Dual-waste acidic biochar [35]	Surface-modified bamboo/coconut carbon	Oleic-acid esterification	Role of each waste-derived phase and water inhibition

9. Magnetically Recoverable Carbon–Inorganic Catalysts

Magnetic recovery is a genuine process function in viscous oil–methanol–glycerol mixtures. Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and spinel ferrites such as CoFe_2O_4 or CuFe_2O_4 can be incorporated into carbon supports or combined with CaO and acidic domains. The material can then be removed without fine filtration or high-speed centrifugation. However, magnetic attraction in a photograph is not evidence of durable recovery.

A credible magnetic catalyst study should report saturation magnetization, recovery time, recovered mass and magnetization after cycling. It should also quantify Fe and any catalytically active metals in the product phase. Ferrite oxidation, aggregation and coating by glycerol or organic residues can reduce both magnetic and catalytic performance. Acidic media can dissolve ferrites, while repeated calcination can change phase composition or destroy the carbon support.

The CoFe/biochar/CaO and banana-peel biochar–Fe/K systems illustrate both the potential and the ambiguity of magnetic hybrids [18,19]. Magnetic separation can simplify handling, yet the strongest base species may be the most soluble. Xia et al. also reported magnetic Co-doped Fe_2O_3 –CaO nanocatalysts for biodiesel production without a carbon scaffold [22], providing a useful baseline for judging whether carbon improves more than physical recovery.

10. Graphenic Supports: Functional Interface or Decorative Complexity?

Graphene-related materials can stabilize oxide nanoparticles and expose large interfacial areas, but biodiesel transesterification is not an electrochemical reaction. Conductivity should therefore not be invoked as a primary advantage unless the catalyst is integrated into a microwave, electrochemical or externally heated process where transport of charge or heat is demonstrably relevant. In conventional batch methanolysis, dispersion, wetting, pore accessibility and oxide stability are the more plausible functions.

The ZnCuO/N-doped-graphene study [24] shows that a graphenic mixed-oxide catalyst can achieve high yield, but it does not by itself prove that graphene is the optimal support. The correct control set includes ZnCuO alone, N-doped graphene alone, a physical mixture, and ZnCuO supported on activated carbon or biochar at matched loading and particle size. Without this hierarchy, graphenic complexity may increase synthesis cost without delivering a process-level advantage.

GO and rGO also require strict material definition: oxidation level, lateral size, defect density, residual metal impurities, reduction route and aggregation state can alter catalyst behaviour. Raman I_D/I_G values should be interpreted with XPS, microscopy and surface-area data rather than as standalone activity descriptors.

11. Benchmarking, Heterogeneity and Deactivation

11.1. Why Maximum Yield Is Not a Sufficient Benchmark

A large fraction of the literature reports FAME yields above 90%, but operating conditions vary over a range that prevents simple ranking. High catalyst loadings, methanol/oil ratios of 15:1 or greater, temperatures far above methanol reflux and reaction times of several hours can compensate for limited intrinsic activity. A catalyst used with refined oil should not be ranked above one used with wet, high-FFA waste oil without accounting for feed quality.

The most useful benchmark is a matrix rather than a single number. At minimum, studies should report feedstock acid value and water content, alcohol/oil ratio, catalyst loading, temperature, time, mixing, FAME analytical method, recovered mass, number of cycles, leached elements and post-reaction phase. Tables 4 and 5 illustrate how performance and evidence gaps can be presented together. The escalation from simple composition labels to process-ready validation is summarized in Figure 3.

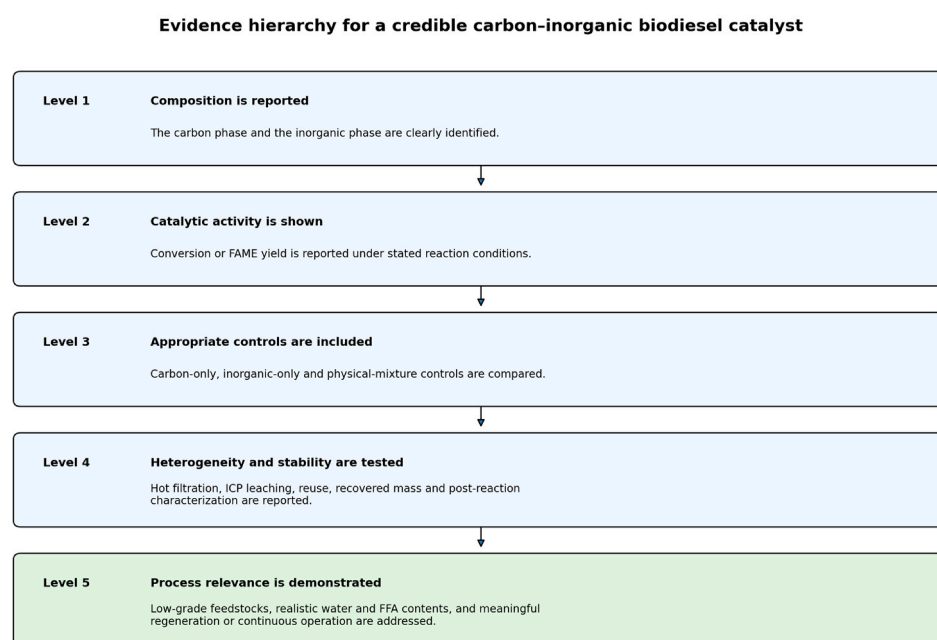


Figure 3. Evidence hierarchy for carbon–inorganic biodiesel catalysts, from a compositional label to process-ready validation. Original schematic prepared for this review.

11.2. Heterogeneity and Leaching

Hot filtration should be performed at a meaningful conversion rather than only after the reaction is complete. The solid is removed rapidly while the filtrate is returned to identical conditions; continued conversion indicates soluble or colloidal active species. ICP-OES or ICP-MS should quantify Ca, Mg, K, Na, Fe, Co, Zn, Cu, S and P as appropriate. Filtrate pH or conductivity is useful supporting information but does not replace elemental analysis.

Recovered-catalyst mass must be included because constant yield can coexist with progressive material loss if catalyst loading is initially large. Conversely, declining yield

may reflect incomplete recovery rather than intrinsic deactivation. A complete mass balance separates leaching, attrition, sampling loss and chemical transformation.

11.3. Deactivation Mechanisms and Regeneration

Figure 4 summarizes family-specific deactivation. Basic oxides lose activity through hydration, carbonation, glycerol adsorption and leaching. LDH-derived mixed oxides can reconstruct in water-containing media. Sulfonated carbons lose acid groups or become pore-blocked. Magnetic ferrites can oxidize, aggregate or dissolve. Graphenic supports can restack or lose oxygen functionality. A generic statement that the catalyst was reused five times does not identify which mechanism is operating.

Deactivation, diagnosis and regeneration in biodiesel catalysts			
Catalyst family	Typical deactivation pathway	Key diagnostic test	Representative response
CaO / basic oxides	Hydration, carbonation, glycerol adsorption, and Ca leaching	XRD, ICP, CO ₂ -TPD	Dry handling, hydrophobic support, and careful regeneration.
LDH-derived mixed oxides	Reconstruction in water-containing media and loss of basic sites	XRD before/after use; CO ₂ -TPD	Control calcination history and water exposure.
Sulfonated carbons	Loss of -SO ₃ H groups, pore blocking, and sulfur leaching	S analysis, NH ₃ -TPD, filtrate activity	Re-sulfonate only if the carbon framework remains intact.
Magnetic hybrids	Ferrite oxidation or aggregation, lower magnetization, and metal leaching	VSM, ICP, recovered mass	Use gentle washing and monitor magnetization after cycles.

Regeneration is meaningful only when activity, selectivity, material recovery, and phase integrity are all preserved.

Figure 4. Deactivation, diagnosis and regeneration pathways for the principal catalyst families discussed in this review. Original schematic prepared for this review.

Regeneration must be treated as a new synthesis step. Oxidative calcination may remove organics but burn carbon or sinter CaO. Acid washing may clean pores but dissolve ferrites or remove alkaline ash. Re-sulfonation can restore nominal sulfur while changing porosity and accessibility. Every regeneration protocol should therefore be followed by the same characterization used for the fresh catalyst (Table 6).

Table 6. Deactivation mechanisms, diagnostic methods and mitigation strategies.

Failure Mode	Most Affected Systems	Cause	Diagnosis	Mitigation
Hydration/carbonation	CaO and Ca-rich hybrids	H ₂ O/CO ₂ exposure; storage; esterification water	XRD, TGA, CO ₂ -TPD	Dry storage; controlled recalcination; hydrophobic microenvironment
Leaching	K/Ca/Na-loaded biochar; sulfonated carbon; ferrites	Methanol, water, acids, weak anchoring	Hot filtration, ICP, filtrate activity	Stronger anchoring; lower soluble loading; spatial separation
Pore fouling	All porous carbons and oxides	Glycerol, soaps, polymers, feed solids	BET, TGA, Raman, microscopy	Solvent cleaning; feed pretreatment; hierarchical porosity

Table 6. Cont.

Failure Mode	Most Affected Systems	Cause	Diagnosis	Mitigation
LDH reconstruction	Calcined LDH/MMO	Water/carbonate contact	XRD, TPD, cation analysis	Control water; choose stable composition; re-calcine with caution
Magnetic decay	Fe ₃ O ₄ /ferrite hybrids	Oxidation, dissolution, aggregation	VSM, XRD, ICP	Protective shell; milder acid exposure; reduce attrition
Support degradation	GO/rGO or biochar under harsh regeneration	Oxidation, high-temperature burn-off	Raman, XPS, TGA	Low-temperature regeneration; non-oxidative cleaning

12. Process Translation: Continuous Operation, Shaping and Sustainability

The strongest laboratory catalyst may not be the most useful process catalyst. Fine powders can float, agglomerate, form stable emulsions or create difficult filtration. Pressing a powder into pellets can block pores and reduce exposed basicity. Carbon–inorganic hybrids should therefore be evaluated as process materials: pellets, coated monoliths, packed beds, magnetically recoverable particles or structured porous bodies.

Continuous biodiesel production requires stable activity over time rather than high conversion in a single batch. Fixed-bed operation is particularly demanding because water, glycerol, soaps and feed impurities can accumulate. Time-on-stream, pressure drop, product composition and regeneration frequency are more informative than cycle number. Carbon can aid shaping and pore hierarchy, but binder choice and mechanical strength must be reported.

A realistic benchmark should test the same catalyst against three feeds: a dry refined oil, a waste cooking oil with measured acid value and water content, and a deliberately high-FFA feed. This sequence distinguishes a clean-oil base catalyst from a water/FFA-tolerant hybrid and from a genuinely bifunctional system. The catalyst should then be operated in a continuous or semi-continuous configuration long enough to reveal leaching and fouling.

Techno-economic analysis (TEA) and life-cycle assessment (LCA) must include catalyst preparation, not only the origin of the carbon. A material derived from waste may still require high-temperature pyrolysis, KOH activation, concentrated H₂SO₄, multiple washing steps, and short catalyst lifetimes. These burdens can outweigh the benefit of waste feedstock. Conversely, a slightly less active catalyst may be preferable if it uses mild preparation, low metal loading, simple recovery, and a long lifetime [25].

Machine-learning-ready datasets could assist catalyst selection, but only after reporting becomes consistent. Useful inputs include carbon source, pyrolysis and calcination conditions, ash composition, surface area, pore distribution, acid/base-site density, inorganic phase, particle size, contact angle, feed acid value, water content, alcohol ratio, and mixing. Outputs should include FAME yield, normalized rate, leaching, recovered mass, and deactivation rate. A dataset containing only maximum yield will reproduce the current bias toward severe conditions and incomplete stability evidence.

13. Conclusions and Design Rules

Refocusing the carbon–inorganic catalyst literature on a single reaction scenario reveals a clearer set of design rules. Biodiesel production from low-grade lipid feedstocks is governed by acid/base chemistry, oil–alcohol–solid transport, water and FFA tolerance, heterogeneity, and separation. Carbon can be valuable, but only when it changes one of those constraints in a measurable way.

CaO/biochar and related basic hybrids can deliver high FAME yields, yet hydration, carbonation and leaching remain central. LDH-derived mixed oxides offer better compositional control, but direct evidence for carbon–LDH synergy is still limited. Sulfonated carbons address high-FFA feeds, provided that acid groups remain attached under methanol/water exposure. Magnetic hybrids can simplify recovery, but magnetization does not compensate for loss of Ca, K, S or Fe. Graphenic supports should be justified against less expensive carbon supports because conductivity is rarely the controlling variable in conventional transesterification.

The strongest evidence chain is straightforward: define the carbon and inorganic phases; compare inorganic-only, carbon-only and physical-mixture controls; report feed-stock acid value and water; measure acid/base sites; test hot filtration; quantify leaching and recovered mass; and characterize the catalyst after use. Only then can improved yield or durability be assigned to the interface.

Future progress should prioritize simpler architectures, realistic low-grade feeds, structured catalysts, continuous operation, and transparent TEA/LCA. The field does not need a larger catalogue of multifunctional powders. It needs catalysts whose interfacial function survives the chemical and engineering conditions of biodiesel production.

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