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Review

Plant Biomass-Derived Sulfonated Carbon Catalysts for Biodiesel Production from Waste Cooking Oil: A Systematic Review

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ABSTRACT. Growing interest in sustainable fuels has prompted research into biodiesel production from used cooking oil as a means of converting waste into a renewable energy resource. This review systematically examines plant biomass-derived sulfonated carbons as heterogeneous catalysts for this process. Fifteen selected studies were assessed in terms of biomass feedstock, catalyst preparation and characterization, reaction parameters, biodiesel quality, and catalyst reusability. Across these studies, lignocellulosic biomass emerged as the predominant precursor owing to its ability to yield carbon frameworks suitable for functionalization with catalytically active sulfonic acid groups (–SO_3H). Advances in catalyst synthesis methods show a shift from conventional two-step pyrolysis toward more energy-efficient approaches through process intensification, such as ultrasonic irradiation and microwave-assisted methods, which can significantly reduce reaction time. In general, optimal esterification conditions are achieved at 50 – 70 °C, a methanol-to-oil molar ratio of 18:1 – 22:1, and a reaction time of 1 – 4 h, resulting in biodiesel yields of 80 – 99.7%. Most biodiesel products meet the ASTM D6751 standard, although compliance with EN 14214 remains variable. Catalyst stability is generally moderate to good after several reuse cycles. Overall, this catalyst shows significant potential for industrial-scale biodiesel production, although the decline in catalytic activity due to –SO_3H group leaching and surface fouling requires further investigation.

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INTRODUCTION

National crude oil production is showing a significant downward trend, from 772 thousand barrels of oil per day (BOPD) in 2019 to only 580 thousand BOPD in 2024. This decline largely reflects diminishing production from mature oil fields, compounded by discoveries of new reserves that are insufficient to compensate for these losses (Dewan Energi Nasional, 2024). Meanwhile, growing pressure to curb CO_2 emissions has reinforced the need to diversify energy supplies and accelerate the transition toward low-carbon energy (Sethi and Dash, 2022; Rositoh *et al*., 2025). These challenges have stimulated interest in renewable fuels, including biodiesel, which is

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produced through the transesterification of triglycerides with short-chain alcohols, yielding fatty acid methyl esters when methanol is used. Biodiesel is a renewable fuel with more environmentally friendly characteristics than fossil fuels (Zahan and Kano, 2018).

Correspondingly, used cooking oil-based biodiesel is emerging as a potential alternative due to its abundant availability, relatively low cost, and contribution to waste reduction (Kolakoti *et al*., 2021). However, used cooking oil generally contains high levels of free fatty acids (FFA), water, and oxidation products, which can inhibit transesterification and degrade biodiesel quality (Cahyo *et al.*, 2024). High FFA content can trigger saponification reactions when using alkaline catalysts, leading to a decrease in yield of biodiesel and increased complexity and cost of refining processes (Gusti and Surtikanti, 2024). Therefore, the use of acid catalysts is more relevant for esterification and transesterification processes with raw materials with high FFA levels (Ramadhani *et al*., 2025). Despite their catalytic effectiveness, homogeneous catalysts present challenges in product separation and operational stability that can complicate large-scale biodiesel production (Kumar *et al*., 2020).

Heterogeneous acid catalysts offer potential advantages through easier recovery, repeated use, and comparatively high thermal stability, which may reduce downstream processing requirements (Welter *et al*., 2023). Among these materials, sulfonated carbons have attracted considerable interest for processing feedstocks with high FFA contents. Their acidic sites facilitate FFA esterification without promoting the saponification associated with alkaline catalysis, although their tolerance to water depends on catalyst properties and reaction conditions. Activity at moderate temperatures, typically 60–100 °C, may also help limit process energy requirements (Sani *et al*., 2015). The performance of sulfonated carbon catalysts depends on the properties of the carbon framework and the incorporation of sulfonic acid groups (–SO_3H). Surface area, pore architecture, and surface chemistry influence the accessibility and retention of these acid sites, thereby affecting catalytic activity and durability (Fatimah *et al*., 2023). Plant biomass residues provide promising precursors because their lignocellulosic constituents can be converted into carbon frameworks suitable for subsequent sulfonation. Their use therefore offers an opportunity to valorize biomass waste while developing catalysts for biodiesel production (Kumar *et al*., 2019; Ansari *et al*., 2025).

Nevertheless, high conversions reported under laboratory conditions do not alone establish the practical feasibility of these catalysts. Persistent challenges include the loss of activity during repeated use, leaching of sulfonic acid groups, and restricted reactant transport within inadequately developed pore networks (Naji *et al*., 2024). These limitations complicate the translation of laboratory results into reliable industrial performance. Furthermore, catalyst preparation using concentrated H_2SO_4 and the processing requirements associated with regeneration introduce additional technical, environmental, and economic considerations that require critical assessment (González *et al*., 2017; Nazir *et al*., 2021).

Although research on sulfonated carbon catalysts has expanded, substantial differences in biomass feedstocks, preparation procedures, and reaction conditions hinder meaningful comparisons across studies. A systematic synthesis is therefore needed to assess the available evidence and distinguish broadly applicable findings from results obtained under specific experimental conditions. Previous reviews have addressed related aspects of this field. Chong *et al*. (2021) examined sulfonated carbon catalysts broadly rather than focusing on used cooking oil, whereas Stepacheva *et al*. (2023) emphasized the application of carbon materials as catalyst supports. Soodesh *et al*. (2024) provided a wider assessment of carbon catalysts, with less detailed consideration of their stability and practical limitations. Together, these contributions provide a foundation for a more focused evaluation of plant biomass-derived sulfonated carbons for biodiesel production from used cooking oil.

Accordingly, this review systematically examines the relationships among biomass precursor selection, catalyst synthesis, physicochemical properties, and catalytic performance in used cooking oil conversion. Particular attention is given to reaction conditions, biodiesel quality, catalyst reusability, and stability. By integrating these aspects, the review aims to identify the principal factors governing catalyst performance, evaluate limitations in the existing evidence, and clarify the challenges that must be addressed before industrial implementation. A systematic literature review was conducted to evaluate sulfonated carbon catalysts derived from plant biomass for biodiesel production from used cooking oil. Relevant publications were retrieved from ScienceDirect and Google Scholar using the following search expression: “biodiesel” AND (“waste cooking oil” OR “waste oil”) AND (“sulfonated carbon catalyst” OR “C-SO_3H”) AND “biomass” AND “transesterification”. The search covered articles published in English or Indonesian between 2015 and 2025.

Study identification and selection were structured using the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) framework. Eligible studies investigated sulfonated carbon catalysts

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prepared from plant biomass and applied them to biodiesel production from used cooking oil. Studies were excluded if they employed non-carbon catalysts, did not involve sulfonation, or used other oil feedstocks. Review articles were also excluded from the primary evidence synthesis. The search yielded 135 records, including 88 from ScienceDirect and 47 from Google Scholar. After removing 14 duplicates and 18 review articles, 103 records remained for further screening. Assessment against the eligibility criteria resulted in the inclusion of 15 research articles for detailed analysis. Extracted data comprised biomass precursor type, catalyst preparation procedures, characterization techniques, reported optimal reaction conditions, biodiesel quality, and catalyst reusability and stability. These data were synthesized to examine recurring trends, relationships between catalyst properties and performance, and limitations relevant to practical application. Figure 1 summarizes the literature identification and selection process.

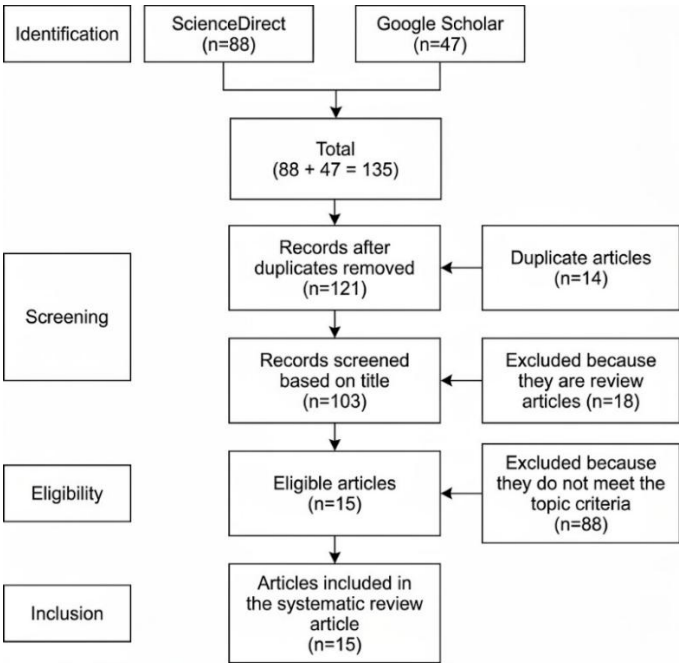


Figure 1. Literature search and study selection workflow for the systematic review.

TYPES OF BIOMASS AS PRECURSORS FOR SULFONATED CARBON CATALYSTS

Across the 15 studies reviewed, lignocellulosic biomass was the most frequently used precursor for sulfonated carbon catalysts. Its prevalence is consistent with the ability of cellulose, hemicellulose, and lignin to form carbonaceous frameworks during carbonization. The resulting framework provides a platform for sulfonic acid functionalization, while its structural characteristics influence catalyst stability and the accessibility of acid sites.

Lignin-rich precursors, including cork and bagasse-derived lignin, tend to yield carbon materials with a greater degree of aromaticity, which may enhance structural stability. Sulfonation can introduce –SO_3H groups onto these aromatic domains through electrophilic substitution, although the extent of functionalization and the retention of acid sites also depend on carbonization and sulfonation conditions (Bhatia *et al*., 2020; Nazir *et al*., 2021). Corn cobs, which contain a different distribution of lignocellulosic components, have been reported to produce relatively open, porous frameworks that can facilitate reactant access to catalytic sites (Mardina *et al*., 2024). These findings suggest that precursor composition influences both the carbon framework and its suitability for subsequent functionalization.

Other investigated feedstocks include agroindustrial residues such as red fruit (*Pandanus conoideus*) pulp and spent black tea. Their conversion into functionalized carbon demonstrates the potential of locally available waste materials as catalyst precursors (Rahmah *et al*., 2023; Jumah *et al*., 2025). High acid-site densities reported for some tea-waste-derived catalysts further suggest that precursor chemistry, together with processing conditions, affects the development of surface acidity. However, claims of lower energy requirements require comparative processing data, because susceptibility to thermal decomposition alone does not establish the energy efficiency of catalyst preparation.

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The reviewed literature also includes chemically defined organic precursors, such as glucose, xylose, glycerol, and cyclodextrins. Unlike untreated lignocellulosic residues, these compounds offer more uniform starting compositions and have been converted into carbonaceous materials through hydrothermal carbonization, often in a single carbonization step. This distinction concerns preparation of the carbon framework and does not necessarily imply that carbonization and sulfonation occur simultaneously. Glucose and xylose, as monosaccharides, are easily dehydrated and polymerize to form relatively homogeneous amorphous carbon, resulting in a more uniform distribution of acid sites (Nata and Putra, 2017; Tran *et al*., 2016). Glycerol, a by-product of biodiesel production, is interesting because the use of waste-derived precursors also offers opportunities to incorporate circular economy principles into catalyst preparation (Kumar *et al*., 2020). Cyclodextrin provides another route to carbon synthesis, as its cyclic molecular architecture may influence pore development during carbonization. The range of precursors investigated suggests considerable flexibility in carbon source selection, allowing locally available materials to be considered. However, comparable catalytic performance cannot be assumed, because precursor chemistry and processing conditions jointly determine the properties of the resulting catalyst. Effective design therefore requires synthesis strategies tailored to each feedstock to achieve suitable pore structures and accessible, well-distributed acid sites (Maneechakr *et al*., 2015).

CATALYST SYNTHESIS METHOD

Carbonization Based on Conventional Pyrolysis

In the conventional two-step synthesis, biomass is first carbonized by pyrolysis at 400 – 800 °C, after which the resulting carbon is treated with a strong sulfonating acid to introduce –SO_3H groups. This approach yields a carbon structure with a high degree of aromatization, thereby providing good thermal and mechanical stability. This is reflected in various biochar-based systems that exhibit resistance to extreme reaction conditions and relatively good reusability. However, quantitatively, these methods have limitations in the functionalization stage. For example, xylose-based catalysts are reported to have an initial surface area of 86.3 m^2/g and an acidity of 1.38 mmol/g, but experience a significant decrease after reuse, with the surface area decreasing to 10.4 m^2/g and acidity to 0.59 mmol/g, which is followed by a decrease in biodiesel yield of about 21% after three cycles (Tran *et al*., 2016). In general, the decrease in catalyst activity after 3 – 6 cycles of use ranges from 10 – 30%, depending on the synthesis method and the strength of the interaction between the –SO_3H group and the carbon matrix. This phenomenon indicates that an excessively high aromatization rate can limit the effective interaction between the –SO_3H group and the carbon matrix, thereby increasing susceptibility to leaching and catalyst deactivation. Mechanistically, high-temperature carbonization conditions lead to the loss of polar groups such as –OH and –COOH through dehydration and deoxygenation. As a result, the next sulfonation stage proceeds via electrophilic substitution of the relatively inert aromatic domain, thereby requiring harsher sulfonation conditions (such as concentrated H_2SO_4 at ≥120 °C for more than 10 hours). In addition, the high energy requirements of the carbonization stage make this method less efficient in terms of energy and process sustainability (Kang *et al*., 2025).

Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is emerging as a more energy-efficient alternative for synthesis, with a relatively low operating temperature of 180 – 200 °C. This approach yields amorphous carbon enriched in oxygen-containing functional groups, including –OH and –COOH, which influence surface chemistry and may facilitate subsequent sulfonation. The reported quantitative results also indicate competitive catalytic performance. For example, a biochar-based catalyst of red fruit pulp synthesized through the HTC and sulfonation pathway exhibits optimum reaction conditions at 60 °C for 2 hours, while corn cob-based systems require sulfonation conditions at 150 °C for 6 – 10 hours. In other systems, hydrothermal carbon catalysts have been reported to reduce FFA by up to 93.4% at 60 °C for 3 hours (Mardina *et al*., 2024; Rahmah *et al*., 2023). Mechanistically, the high oxygen group content in HTC-derived materials increases their affinity for sulfonizing agents, thereby leading to higher acid site densities without requiring extreme reaction conditions. However, the lower aromatization rate of HTC than in the pyrolysis method limits thermal stability, especially under long-term reaction conditions or at high temperatures. Comparatively, pyrolysis methods generally produce materials with surface area in the range of 5 – 180 m^2/g and acid density of 1 – 5 mmol/g, while hydrothermal methods and single-stage approaches tend to produce higher acid site densities that can even exceed 10 mmol/g, with more moderate synthesis conditions (Mardina *et al*.,

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2024). Figure 2 illustrates the preparation of biomass-derived sulfonated carbon catalysts through hydrothermal carbonization (HTC) and subsequent sulfonation.



Figure 2. Biomass-based sulfonated carbon catalyst synthesis pathway by the HTC method. Illustrated from Mardina *et al*. (2024), with copyright 2024 Universitas Pendidikan Indonesia.

Simultaneous Carbonization and Sulfonation

Combining hydrothermal carbonization and sulfonation in a single step simplifies catalyst preparation by allowing carbon framework formation and –SO_3H incorporation to proceed concurrently at approximately 180 °C. Catalysts prepared through this route have demonstrated promising performance. For example, a cyclodextrin-derived catalyst achieved a biodiesel yield of 90.8% at 117 °C within a reaction time of 8.8 minutes. Glucose-derived catalysts prepared using comparable procedures also retained much of their initial activity over repeated reaction cycles. Incorporating sulfonic acid groups during carbon framework development may promote a more uniform distribution of acid sites and contribute to their retention. However, these performance results alone do not establish stronger covalent bonding or greater resistance to leaching than catalysts produced through two-step synthesis; such interpretations require supporting structural characterization and comparative leaching measurements. Nevertheless, the claim that this method can save energy by up to 70% should be interpreted with caution. Although some studies report reductions in process time and operating temperature, not all provide a comprehensive energy analysis. Therefore, a more precise statement is that the single-stage method has the potential to lower energy consumption through process-stage reduction, but quantitative validation at an industrial scale still requires Techno-Economic and Life Cycle Assessments (Maneechakr *et al*., 2015; Nata and Putra, 2017).

Direct Sulfonation Without Carbonization

The no-carbonization approach also shows significant potential, particularly for biomass with relatively reactive polymer structures. For example, a black tea waste-based catalyst is reported to have a very high acid site density of 34.6 mmol/g with a surface area of 58.3 m^2/g, and is capable of producing a biodiesel conversion of up to 97.3% at 50 °C within 70 minutes. However, the catalyst stability of this approach is generally lower than that of other methods, with activity decreasing by about 10 – 15% after several cycles of use. This decrease is associated with surface fouling and possible degradation of the –SO_3H group during the reaction (Jumah *et al*., 2025).

The reviewed findings suggest that two-step pyrolysis-based synthesis can produce structurally stable catalysts, although its high carbonization temperatures may increase energy requirements. Hydrothermal routes, including those integrating carbonization and sulfonation in a single step, have achieved biodiesel yields above 90% at reaction temperatures of 50 – 120 °C, with reaction times ranging from minutes to hours. These results highlight the importance of jointly optimizing acid-site density, pore accessibility, catalyst durability, and energy consumption rather than selecting a synthesis route solely on the basis of initial activity. Single-step hydrothermal synthesis therefore warrants further investigation for industrial application, particularly through extended reuse experiments, measurements of sulfonic acid group leaching, and comprehensive techno-economic assessment. Table 1 summarizes the principal advantages and limitations of the synthesis routes.

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Table 1. Comparison of catalyst synthesis methods.

Precursors	Carbonization			Sulfonation			References
	Method	Temperature (°C)	Time (hours)	Agents	Temperature (°C)	Time (hours)	
Cyclodextrin	One-step hydrothermal carbonization	180	4	$C_2H_6O_4S$ + $C_6H_8O_7$	180	4	(Maneechakr *et al.*, 2015)
Xylose	Hydrothermal carbonization	190	24	H_2SO_4 98%	150	15	(Tran *et al.*, 2016)
Oat husk	Slow pyrolysis	600	3	H_2SO_4 98%	140	0.5	(González *et al.*, 2017)
Glucose	Simultaneous Carbonization and Sulfonation	180	4	$C_2H_6O_4S$	180	4	(Nata and Putra, 2017)
Coconut coir	Pyrolysis	600	3	H_2SO_4 98%	100	24	(Sontakke and Jha, 2018)
Coconut pulp residue	Simultaneous Carbonization and Sulfonation	–	–	H_2SO_4 98%	100	1	(Thushari and Babel, 2017)
Rice husk	Fast pyrolysis	480 – 510	0.0027	H_2SO_4 98%	150	15	(Mohamed *et al.*, 2020)
Cork biochar	Pyrolysis	600	2	H_2SO_4 98%	100	12	(Bhatia *et al.*, 2020)
Glycerol	Simultaneous Carbonization and Sulfonation	180	0.5	H_2SO_4 98%	180	10	(Kumar *et al.*, 2020)
Lignin sugarcane residue	Pyrolysis	400	1	H_2SO_4 98%	180	2	(Nazir *et al.*, 2021)
Microalgae biomass	Pyrolysis	600	4	H_2SO_4 98%	110	6	(Roy and Mohanty, 2021)
Corn cobs	Hydrothermal carbonization	200	10	H_2SO_4 98%	150	10	(Mardina *et al.*, 2024)
Red fruit residue	Pyrolysis	500	1	5 M H_2SO_4	150	2	(Rahmah *et al.*, 2023)
Spent black tea	Direct Sulfonation Without Carbonization	–	–	H_2SO_4 95%	100	3	(Jumah *et al.*, 2025)
Seed shell *V. montana*	Pyrolysis	450	3.5	H_2SO_4 98%	120	16	(Kang *et al.*, 2025)

CATALYST CHARACTERIZATION

Characterization of sulfonated carbon catalysts focuses on textural properties, surface acidity, functional group chemistry, and carbon structure. Relevant measurements include specific surface area, pore size distribution, total acid-site density, the incorporation and retention of sulfonic acid groups (–SO_3H), and morphological features and structural ordering. Together, these properties influence reactant access, catalytic activity, selectivity, and durability during esterification and transesterification. The reviewed studies reported substantial differences in specific surface area, ranging from 1.33 m^2/g for coconut-pulp-derived carbon to 179.66 m^2/g for glycerol-derived carbon (Thushari and Babel, 2017; Bhatia *et al.*, 2020). Although a larger surface area can provide more opportunities for acid-site exposure, the number of catalytically accessible sites also depends on the extent of functionalization and the accessibility of the pore network. However, empirical data show that the relationship

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between surface area and catalytic performance is not linear. For example, glycerol-based catalysts with a very high surface area (179.66 m^2/g) do not always exhibit the best catalytic performance. In contrast, catalysts with relatively lower surface areas, such as black tea waste-based catalysts (58.3 m^2/g), can achieve biodiesel conversions of up to 97.3%. This phenomenon indicates that surface area is not the dominant parameter in determining catalytic activity. The sulfonation effect is known to cause pore clogging by the $–SO_3H$ group as well as the restructuring of the carbon skeleton, so that although the surface area decreases, the density of the acid site increases. Therefore, catalytic activity is determined more by the number and accessibility of the $–SO_3H$ group than by the value of the total surface area. Thus, the interpretation of BET data should be conducted critically, taking into account changes in surface chemistry rather than relying solely on absolute surface area values (Naji *et al*., 2024).

The pore size distribution in sulfonated carbon catalysts shows a wide range, ranging from about 1.03 nm in wheat husk-based catalysts to 31 nm in cork-based catalysts. Differences in pore architecture influence reactant transport, particularly during transesterification involving bulky triglyceride molecules. Microporous catalysts (<2 nm), exemplified by wheat-husk-derived carbon with a reported pore size of 1.03 nm, may restrict access to internal acid sites and limit their contribution to the reaction. By comparison, the larger pores reported for cork-derived carbon (31 nm) and bagasse-lignin-derived carbon (~9.44 nm) can facilitate molecular transport and improve site accessibility. The higher biodiesel yields and faster reactions associated with mesoporous catalysts are consistent with reduced diffusion resistance, although comparisons across studies cannot isolate pore size from other catalyst properties and operating conditions. Pore-size distribution therefore helps explain the relationship between measured acidity and catalytic performance, where the activity depends on the availability of acid sites to reactants, rather than total acid-site density alone (Tamborini *et al*., 2016).

Reported total acid-site densities varied considerably, from approximately 1.38 mmol/g for xylose-derived catalysts to 34.6 mmol/g for catalysts prepared from black tea waste. Higher acidity was generally associated with greater biodiesel conversion, although this trend was not consistent across all systems. A high concentration of acid sites offers limited benefit when reactants cannot readily access them or when these sites are lost or deactivated during operation. Declining activity over successive reaction cycles has been attributed to sulfonic acid group leaching and surface fouling. These observations indicate that catalytic performance depends on the accessibility, spatial distribution, and chemical stability of acid sites, alongside their abundance. Accordingly, surface acidity and pore architecture should be optimized together to support sustained catalytic activity (Yadav *et al*., 2023).

Fourier transform infrared spectroscopy (FTIR) provides qualitative evidence of sulfonation through absorption bands assigned to the stretching vibrations of S–O bonds in sulfonic acid groups. However, overlapping signals in the 1020 – 1190 cm^{-1} wavenumber region can complicate band assignments and limit the distinction between sulfur-containing functionalities. FTIR findings therefore require complementary analyses to establish the chemical identity and bonding environment of the incorporated sulfur species more confidently (Lim *et al*., 2020).

X-ray photoelectron spectroscopy (XPS) offers additional insight into surface sulfur chemistry. In the studies employing this technique, sulfur signals were assigned predominantly to highly oxidized species consistent with sulfonic acid or sulfonate functionalities associated with the carbon framework. Such assignments support the interpretation of successful surface functionalization but do not, by themselves, establish resistance to leaching. Although stable attachment of $–SO_3H$ groups may contribute to catalyst durability, this relationship is best evaluated by combining XPS characterization with sulfur-leaching measurements and activity retention over repeated reaction cycles (Kumar *et al*., 2020).

Scanning electron microscopy (SEM) observations suggest that sulfonation generally increases surface roughness and morphological irregularity. Descriptively, these changes reflect the formation of heterogeneous structures with an increase in the area of contact between the catalyst and the reactant (Jumah *et al*., 2025). Especially, increased surface roughness can enhance legality and improve liquid–solid phase contact, thereby improving the efficiency of external mass transfer and the opportunity for interaction between the reactant and the active site. However, not all morphological changes are beneficial. In some cases, particle agglomeration or pore-structure collapse actually inhibits diffusion and reduces the accessibility of the active site. Therefore, the interpretation of SEM results needs to be linked to the extrasurface data (BET) and pore size distribution to produce a more comprehensive understanding of catalytic performance (Nazir *et al*., 2021). The results of the SEM morphological analysis of the sulfonic carbon catalyst based on used black tea are shown in Figure 3.

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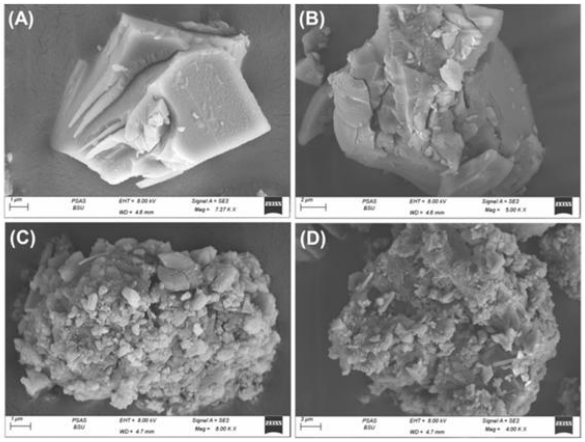


Figure 3. SEM image of raw black tea powder and sulfonated black tea catalyst: (a) raw black tea powder, (b) raw black tea after sulfonation, (c) sulfonated black tea powder, and (d) sulfonated black tea catalyst after sulfonation. Adapted from Jumah *et al.* (2025) by license *Creative Commons Attribution 4.0 International* (CC-BY 4.0).

The results of X-ray diffraction (XRD) analysis indicate that most sulfonated carbon catalysts are amorphous, with no sharp crystalline peaks. This characteristic indicates a high degree of structural irregularity. Particularly, amorphous structures have a greater density of defects, which serve as sites for anchoring the –SO_3H group, thereby increasing the density of acid sites and their more even distribution on the catalyst surface. Nevertheless, there are trade-offs between reactivity and stability. Highly disordered carbon frameworks may exhibit limited thermal stability, whereas extensive crystalline ordering can hinder surface functionalization. An appropriate degree of structural disorder is therefore important for facilitating sulfonation while maintaining catalyst stability under reaction conditions (Kumar *et al.*, 2020).

Taken together, the characterization findings indicate that sulfonated carbon catalyst performance cannot be attributed to a single physicochemical property. Rather, catalytic activity reflects the combined influence of acid-site density, pore-size distribution, accessible surface area, structural stability, and morphology. Catalysts with medium or even low surface area may exhibit high activity if they have a homogeneous distribution of –SO_3H groups and are located in an easily accessible pore structure. In contrast, catalysts with high surface area but suboptimal pore distribution or low stability tend to exhibit inadequate performance. A comprehensive summary of the physicochemical characteristics of sulfonated carbon catalysts is presented in Table 2.

Table 2. Characteristics of sulfonic carbon catalysts.

Precursors	Morphology			Structure			References
	BET		SEM/TEM	NH_3-TPD/Titration	FTIR, XPS	XRD	
	Surface Area (m^2/g)	Pore Size (nm)		Acid Density (mmol/g)			
Cyclodextrin	8.2	22.1	Irregular surface	1.87	SO_3H, S 2p (168 eV)	amorphous	(Maneechakr *et al.*, 2015)
Xylose	86.3	6.6	Pore structure develops and is distributed	1.38	SO_3H, S 2p (169 eV)	–	(Tran *et al.*, 2016)
Oat husk	5.43	1.03	Solid structure, dominant micropores	7.0	SO_3H, S 2p 3.2 wt% (168 eV),	–	(González *et al.*, 2017)
Glucose	25.72	–	Homogeneous morphology	1.99	SO_3H, S 2p 3.79 wt%	amorphous	(Nata and Putra, 2017)
Coconut coir	–	–	Rough surface, irregular structure	3.2	SO_3H	–	(Sontakke and Jha, 2018)
Coconut pulp residue	1.33	13.2	Solid surface, there is a sulfur distribution	3.8	SO_3H, S 2p (168 eV)	–	(Thushari and Babel, 2017)

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Precursors	Morphology			Structure			References
	BET		SEM/TEM	NH_3-TPD/Titration	FTIR, XPS	XRD	
	Surface Area (m^2/g)	Pore Size (nm)		Acid Density (mmol/g)			
Rice husk	39.11	9.19	Porous and open structure	10.0	SO_3H	amorphous	(Mohamed *et al.*, 2020)
Cork biochar	179.66	2.1	Highly porous structure	–	SO_3H, S 2p 1.05 wt%	amorphous	(Bhatia *et al.*, 2020)
Glycerol	6.53	31	Large pore structure	0.035	SO_3H, S 2p (168 eV)	amorphous	(Kumar *et al.*, 2020)
Lignin sugarcane residue	30.31	9.44	Open and distributed pore structure	4.74	SO_3H	amorphous	(Nazir *et al.*, 2021)
Microalgae biomass	68.13	2.63	Delicate structure, relatively small pores	3.249	SO_3H, S 2p (169 eV)	amorphous	(Roy and Mohanty, 2021)
Corn cobs	–	–	The porous structure is not homogeneous	1.47	SO_3H	amorphous	(Mardina *et al.*, 2024)
Red fruit residue	7.51	2.08	Small pore structure	–	SO_3H	amorphous	(Rahmah *et al.*, 2023)
Spent black tea	58.3	–	Expanded pore structure	34.6	SO_3H	amorphous	(Jumah *et al.*, 2025)
Seed shell *V. montana*	20.0	8.3	Porous and relatively stable surface	3.65	SO_3H, S 2p 3.14 wt%	amorphous	(Kang *et al.*, 2025)

OPTIMAL CONDITIONS OF TRANSESTERIFICATION REACTIONS

Biodiesel can be produced through triglyceride transesterification or FFA esterification with methanol. In used cooking oil-based systems, Sulfonic carbon catalysts play an important role as solid acid catalysts that effectively facilitate both reaction pathways**.** The production stage begins with the conversion of biomass precursors through thermal treatment to produce carbon material with an aromatic framework containing surface functional groups such as carboxyl (–COOH) and hydroxyl (–OH). This material is then sulfonated, typically with sulfuric acid (H_2SO_4), to introduce a sulfonate group (–SO_3H) that serves as an active site. In particular, the –SO_3H group will act as a proton (H^+) donor that activates the carbonyl group in fatty acids or triglycerides, thereby increasing the electrophilicity of the carbon atom. Methanol subsequently attacks the activated carbonyl carbon, forming a tetrahedral intermediate that undergoes proton transfer and elimination to yield a fatty acid methyl ester. Esterification releases water, whereas triglyceride transesterification proceeds through successive di- and monoglyceride intermediates, ultimately producing glycerol. Regeneration of the catalyst's acidic sites completes the catalytic cycle. In water-containing feedstocks, partial triglyceride hydrolysis may generate additional free fatty acids that subsequently undergo esterification, alongside direct transesterification. The relative contributions of these pathways depend on feedstock composition and reaction conditions, with glycerol formed through the conversion of glycerides rather than FFA esterification (Kang *et al.*, 2025; Yadav *et al.*, 2023). The reaction mechanism for the synthesis of biodiesel using sulfonated carbon catalysts is illustrated in Figure 4.

Optimization of reaction conditions in biodiesel production is generally evaluated using a number of interrelated operational parameters, including the methanol-to-oil molar ratio, reaction temperature, reaction time, and catalyst concentration. Collectively, these parameters control reaction kinetics, mass transfer phenomena, and thermodynamic equilibrium, thus exerting a significant influence on the conversion and yield of biodiesel. Based on a literature analysis, the molar ratio of methanol to oil shows a fairly wide range, from 10:1 to 30:1, with a non-random distribution. Ratios in the range of 18:1 – 22:1 are the most dominant conditions, followed by lower ratios (10:1 – 15:1) and higher ratios (≥25:1). Quantitatively, low ratios such as 10:1 have been able to produce high conversions, for example, by 97.3% in black tea waste catalysts, which have a very high acid site density. In contrast, in other systems, higher methanol ratios such as 25:1 and 30:1 are required to achieve maximum yields

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of 98.58% and 99.7%, respectively, as reported for cork- and shell-based catalysts of *V. montana*. These findings suggest that the use of high methanol ratios does not necessarily reflect the catalyst's intrinsic efficiency, but is often employed as a strategy to overcome kinetic limitations and mass-transfer barriers. Excess methanol favors methyl ester formation by shifting the reaction equilibrium toward the products and may influence phase behavior and reactant contact. However, increasing the methanol-to-oil ratio also raises downstream recovery requirements and associated energy consumption. Therefore, methanol ratios in the moderate range are more relevant for industrial-scale applications, as they strike a balance between reaction performance and process efficiency (Nazir *et al*., 2021; Bhatia *et al*., 2020).

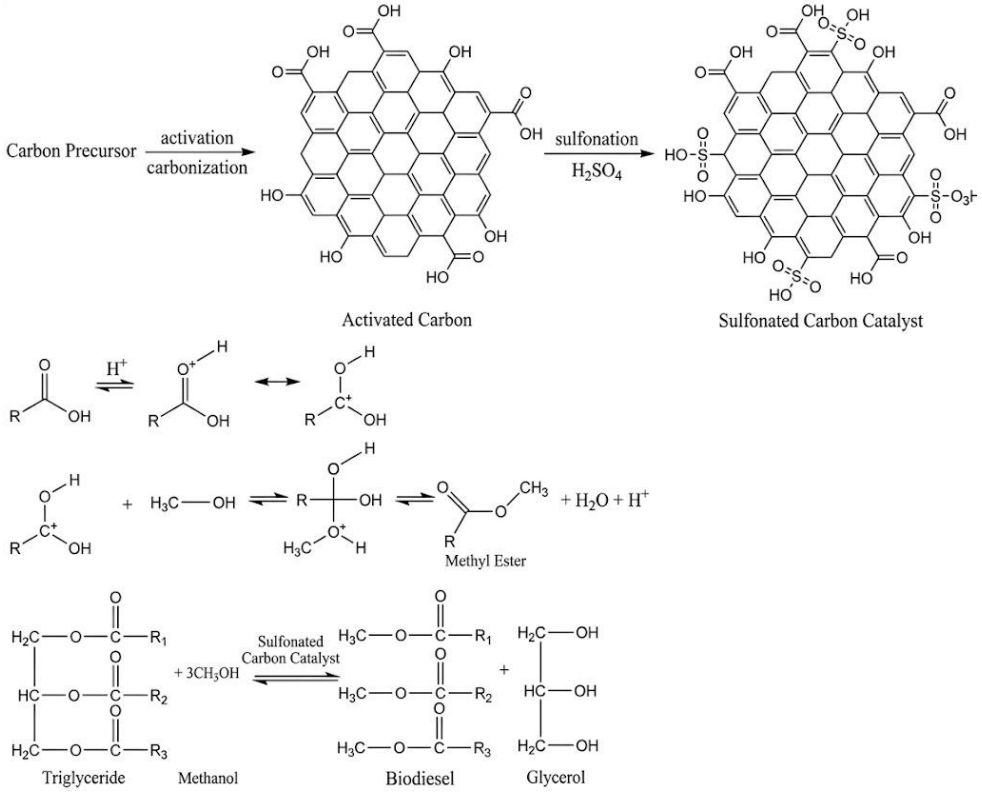


Figure 4. The reaction mechanism in biodiesel synthesis uses sulfonated carbon catalysts. The reaction mechanism was created by the author based on the concept of –SO_3H-based heterogeneous acid catalysis for biodiesel synthesis.

The temperature distribution of the reaction showed a consistent pattern, with most studies operating in the range of 50 – 70 °C, close to the boiling point of methanol. At this range, the increase in reaction kinetics took place optimally without causing significant methanol loss. Nevertheless, some studies have reported the use of high temperatures (≥117 °C), particularly in systems employing process intensification, such as ultrasonic and microwave processing. For example, a biodiesel yield of 90.8% can be achieved at 117 °C in 8.8 minutes, and about 90% at 140 °C in 15 minutes. Although this increase in temperature significantly accelerates the reaction kinetics, this approach has important technical implications. Operation at temperatures above the methanol boiling point requires the use of a closed reactor system with an autogenic pressure of ±2.3 bar (autogenous pressure), which increases the design complexity of safety risks and operational costs. Therefore, although high-temperature systems demonstrate superior kinetic efficiency, moderate-temperature conditions (50 – 70 °C) remain a more realistic option for industrial-scale applications, as they do not impose additional stress and offer better operational stability (Sontakke and Jha, 2018; Jumah *et al*., 2025). Quantitatively, systems with moderate methanol molar ratios (18:1 – 22:1) at temperatures of 50 – 70 °C consistently produce biodiesel yields exceeding than 85%. On the other hand, increasing the methanol molar ratio to ≥25:1 yields only a relatively small increase (~2 – 5%) and is followed by increased separation load and process energy consumption (Bhatia *et al*., 2020; Kang *et al*., 2025).

The reaction times in the analyzed studies showed a wide range, from minutes to several hours, with the main distribution in the 1 – 4 hours range, followed by fast (<1 hour) and conventional (>6 hours) systems. Conventional systems generally take longer, i.e., about 6 – 8 hours, to achieve high conversion, which indicates limitations in

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the internal diffusion and kinetics aspects of the reaction. In contrast, process intensification methods, such as ultrasonic and microwave processing, can significantly reduce reaction times to the minute scale. Nevertheless, reaction times cannot be evaluated in isolation. The decrease in time in intensification systems is due not only to an increase in temperature but also to improved mass transfer efficiency, a more homogeneous energy distribution, and intensified interactions between reactants and catalysts. The longer reaction times reported for conventional systems may partly reflect mass-transfer constraints associated with heterogeneous catalysis (Nazir *et al*., 2021).

Catalyst loadings across the reviewed studies ranged from 1 to 15 wt%, with most falling between 3 and 10 wt%. Increasing the loading generally provides additional active sites and can accelerate conversion, although the benefit diminishes when reactant transport becomes limiting. In some systems, loadings of ≥10 wt% provided little improvement in yield and could impair mixing by increasing slurry viscosity and diffusion resistance. Catalysts with high acid-site densities achieved optimal yields at approximately 3 wt%, whereas systems with less accessible sites required loadings of 10 – 15 wt% to attain comparable conversion. These comparisons suggest that catalyst dosage should balance accessible acidity against the transport constraints introduced by higher solids concentrations (Jumah *et al*., 2025).

Collectively, these findings indicate that suitable reaction conditions depend on catalyst properties and the interaction between reaction kinetics and mass transfer. High methanol-to-oil ratios and elevated temperatures may compensate for limitations in a particular system and should therefore not be interpreted as evidence of superior intrinsic catalytic activity. Process optimization should assess biodiesel yield alongside energy demand, separation requirements, operational complexity, and scalability. Such an assessment is necessary to determine whether laboratory performance can be sustained under industrially relevant conditions. Table 3 summarizes the reported optimal transesterification conditions for biodiesel production from used cooking oil using sulfonated carbon catalysts.

Table 3. Optimal conditions of transesterification reactions for biodiesel production using sulfonated carbon catalysts.

Precursors	Molar Ratio Methanol : Oil	Reaction Temperature (°C)	Reaction Time (hours)	Catalyst Content (wt%)	Yield (%)	References
Cyclodextrin	20:1	117	0.15 (Ultrasonic)	11.5	90.8	(Maneechakr *et al*., 2015)
Xylose	9.35:1	110	4	10	89.6	(Tran *et al*., 2016)
Oat husk	10:1	140	0.5 (microwave)	10	~90.0	(González *et al*., 2017)
Glucose	20:1	60	3	10	93.4	(Nata and Putra, 2017)
Coconut coir	18:1	65	7	5	84.92	(Sontakke and Jha, 2018)
Coconut pulp residue	12:1	65	12	5	92.7	(Thushari and Babel, 2017)
Rice husk	20:1	70	6	10	90.37	(Mohamed *et al*., 2020)
Cork biochar	25:1	65	6	1,5	98.58	(Bhatia *et al*., 2020)
Glycerol	22:1	100	3	5	92.3	(Kumar *et al*., 2020)
Lignin sugarcane residue	18:1	60	0.25 (microwave)	15	89.19	(Nazir *et al*., 2021)
Microalgae biomass	11:1	60	6	3	96.25	(Roy and Mohanty, 2021)
Corn cobs	15:1	60	3	3	80.4	(Mardina *et al*., 2024)
Red fruit residue	12:1	60	1	1	64.77	(Rahmah *et al*., 2023)
Spent black tea	10:1	50	1.17	3	97.3	(Jumah *et al*., 2025)
Seed shell *V. montana*	30:1	120	8	9.6	99.7	(Kang *et al*., 2025)

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QUALITY OF BIODIESEL PRODUCED

Biodiesel quality provides an integrated measure of reaction performance, purification effectiveness, and the properties of the final product. Commonly assessed fuel characteristics include kinematic viscosity, density, cetane number, flash point, and acid value. Comparison with the corresponding requirements of ASTM D6751 and EN 14214 helps determine whether the biodiesel satisfies relevant fuel specifications.

Most reported kinematic viscosities fell between 3.62 and 5.74 mm^2/s, within the stated ASTM D6751 limits of 1.9 – 6.0 mm^2/s, although values above 5.0 mm^2/s exceeded the narrower EN 14214 range of 3.5 – 5.0 mm^2/s. Higher values reported for biodiesel produced using xylose-derived catalysts (6.40 mm^2/s) and *V. montana* shell-derived catalysts (10.76 mm^2/s) may indicate residual triglycerides or partial glycerides associated with incomplete conversion or insufficient purification. Conversely, the lower viscosity obtained with black-tea-waste-derived catalysts (3.62 mm^2/s) is consistent with effective conversion to fatty acid methyl esters (FAME). Nevertheless, viscosity alone cannot establish conversion or ester purity, because feedstock composition and measurement temperature also influence this property.These findings suggest that viscosity is a sensitive parameter for product quality, as it reflects the interaction between reaction efficiency and purification effectiveness. Therefore, viscosity is not necessarily directly correlated with biodiesel yield, but must be interpreted in conjunction with other quality parameters (Tran *et al*., 2016).

The reported density values of biodiesel ranged from 0.83 to 0.93 g/cm^3, with most studies reporting 0.87 – 0.89 g/cm^3, which is consistent with the EN 14214 standard (0.860 – 0.900 g/cm^3). By comparison, the density parameters showed the highest level of conformity among the quality parameters. The stability of this density value indicates that most biodiesel products are dominated by the FAME fraction. However, lower values such as 0.83 g/cm^3 in bagasse-based lignin-based systems indicate variations in fatty acid composition or differences in measurement methods. Density, therefore, reflects more of product composition than catalyst effectiveness, hence, the variation is smaller than that of other quality parameters (Nazir *et al*., 2021).

The reported biodiesel cetane values ranged from 49.34 to 65.3, where all data met the ASTM D6751 standard (≥45). However, only about half fit the EN 14214 standard (≥51). The highest value, 65.3 (in black tea waste-based systems), indicated excellent combustion quality, while the lower values, around 49 – 50 (in cyclodextrin- and lignin-based systems), only met ASTM standards. This suggests that the cetane number is determined more by the fatty acid composition of the feedstock, specifically its saturation level and carbon chain length, than by the type of catalyst used. Catalysts play a role in increasing reaction conversion, but do not directly affect the distribution of FAME composition. Therefore, the variation in cetane values between studies reflects differences in feedstock characteristics rather than in catalytic methods (Maneechakr *et al*., 2015).

The reported biodiesel flash point is in the range of 100 – 194 °C, with most studies meeting ASTM standards (≥93 °C) and some meeting EN standards (≥120 °C). High flash point values, such as 194 °C in cyclodextrin-based systems and 167 °C in xylose-based systems, indicate a good purification rate with a low residual methanol content. In contrast, lower values, around 100 °C in glucose-based systems, indicate the possibility of residual methanol in the product. Thus, the flash point reflects the effectiveness of the post-reaction purification process more than the catalyst activity (Nata and Putra, 2017).

The reported biodiesel acid values ranged from 0.17 – 0.45 mg KOH/g, which generally met the maximum limit set by international standards (≤0.5 mg KOH/g). Most studies showed compliance with these standards, although some higher values, such as 0.72 mg KOH/g (xylose-based system) and 2.47 mg KOH/g (wheat husk-based system), indicated imperfect esterification or the possibility of degradation during the process. In contrast, very low values such as 0.098 mg KOH/g (red fruit pulp-based system) indicated a high FFA conversion efficiency. These findings indicate that acid levels are strongly influenced by process control, particularly regarding water content, oxidation levels, and the effectiveness of the post-reaction purification stage (Jumah *et al*., 2025).

Critically, the influence of the catalyst precursor type on biodiesel quality is indirect. Biomass with a high lignocellulose content, such as tea waste, straw, or lignin, tends to produce catalysts with higher acid-site densities, thereby contributing to more efficient FFA conversion and a decrease in acid counts (Mohamed *et al*., 2020; Nazir *et al*., 2021; Jumah *et al*., 2025). In contrast, catalysts with lower acid density or limited pore accessibility tend to produce biodiesel with higher viscosity, owing to the presence of mono- or diglyceride residues (Tran *et al*., 2016; Kang *et al*., 2025). However, the difference in biodiesel quality between precursors is not always significant if the refining process is carried out optimally. This shows that the post-reaction stage plays an equally important role in determining the final quality of biodiesel, alongside the characteristics (Nata and Putra, 2017; Kumar *et al*., 2020).

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Based on the integration of all quality parameters from the 15 studies analyzed, sulfonated carbon catalysts are generally capable of producing biodiesel that meets ASTM standard D6751, but still require further optimization to achieve compliance with the more stringent EN standard 14214. These findings show that the quality of biodiesel is determined not only by the performance of the catalysts but also by a complex interaction among the composition of the raw material, the reaction conditions, and the effectiveness of the product refining process. Therefore, the evaluation of the quality of biodiesel cannot be done partially, but must be carried out comprehensively considering the relationship among reaction conversion, product distribution, and overall process conditions. This approach is important to ensure that the resulting quality parameters truly present the feasibility of biodiesel as a fuel. A detailed summary of biodiesel quality parameters is presented in Table 4.

Table 4. Biodiesel quality parameters.

Precursors	Kinematic Viscosity ($mm^2 s^{-1}$)	Density ($g\ cm^{-3}$)	Cetane Number (CN)	Flash Point (°C)	Acid number (mg KOH g^{-1})	References
Cyclodextrin	4.15	0.88	50.0	194	0.45	(Maneechakr *et al.*, 2015)
Xylose	6.40	–	–	167	0.72	(Tran *et al.*, 2016)
Oat husk	5.21	0.89	–	–	2.47	(González *et al.*, 2017)
Glucose	5.742	0.89	–	100	–	(Nata and Putra, 2017)
Coconut coir	–	–	–	–	–	(Sontakke and Jha, 2018)
Coconut pulp residue	–	–	–	–	–	(Thushari and Babel, 2017)
Rice husk	5.45	0.87	–	90	0.18	(Mohamed *et al.*, 2020)
Cork biochar	3.90	0.87	50.56	–	–	(Bhatia *et al.*, 2020)
Glycerol	4.35	0.87	–	–	<0.5	(Kumar *et al.*, 2020)
Lignin sugarcane residue	3.92	0.83	49.34	133	0.39	(Nazir *et al.*, 2021)
Microalgae biomass	4.23	0.93	61.53	–	–	(Roy and Mohanty, 2021)
Corn cobs	–	–	–	–	–	(Mardina *et al.*, 2024)
Red fruit residue	–	–	–	–	0.29	(Rahmah *et al.*, 2023)
Spent black tea	3.62	0.84	65.3	152	0.29	(Jumah *et al.*, 2025)
Seed shell *V. montana*	10.76	0.88	–	–	0.28	(Kang *et al.*, 2025)

REUSABILITY AND STABILITY OF THE CATALYST

Reusability is an important parameter for assessing the feasibility of sulfonated carbon catalysts for biodiesel production. Among the 15 studies, 13 studies reported catalytic reuse data, while 2 studies did not explicitly present such information. Quantitatively, about 8 studies were included in the high-stability category, 4 studies in the moderate-stability category, and 1 study in the low-stability category. This distribution indicates that most catalysts exhibit relatively good resistance to reuse, as evidenced by the number of operational cycles and the rate of performance degradation. Catalyst activity losses vary, ranging from about 2 – 9% to more than 70%, which indicates that the stability of the catalyst is strongly influenced by the strength of the $–SO_3H$ group interaction with the pore structure carbon matrix, resistance to fouling, as well as the effectiveness of regeneration methods (Kumar *et al.*, 2020; Bhatia *et al.*, 2020).

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Catalysts can be classified into three stability categories. The high-stability category includes catalysts with a loss of activity ≤15% after several cycles of use, such as rice straw-based catalysts, cyclodextrins, glucose, bagasse lignin, shells of *V. montana*, microalgae biomass, coconut dregs, and black tea waste. For example, rice straw-based RS–SO_3H catalysts showed only a decrease in conversion from 90.37% to 88.56% after eight cycles, with relatively stable FFA conversion up to seven cycles (Mohamed *et al*., 2020). Similarly, coconut pulp-based catalysts are capable of producing more than 80% FAME after four reuses, with an initial acid site density of 3.8 mmol/g (Thushari and Babel, 2017).

The moderate-stability category includes catalysts with a decrease in activity of about 15 – 35%, such as catalysts based on xylose, glycerin, corn cob, and oat husk. In this group, the deactivation process generally occurs gradually due to the combined effects of rotation of the –SO_3H group, fouling by glycerol or residual oil, and reduced pore accessibility. For the xylose-derived catalyst, total acidity declined from 1.38 to 0.59 mmol/g after three reuse cycles, accompanied by decreases in surface area from 86 to 10.4 m^2/g and pore volume from 0.09 to 0.01 cm^3/g. These concurrent changes suggest that acid-site loss and reduced pore accessibility jointly contributed to catalyst deactivation, consistent with possible leaching and pore blockage (Tran *et al*., 2016).

The low-stability category is mainly observed in cork-based catalysts, indicating a drastic decrease in biodiesel yield from 98.58% to 26.4% after five cycles of use. This significant decrease indicates serious catalytic deactivation, likely due to the loss of the active acid site, surface fouling, and changes in carbon structure. Overall, the average loss of activity across all studies reporting reusability data was 18 – 20%. Nevertheless, this value was strongly influenced by such extreme cases. When these anomalous data were released, the average decrease in activity was about 13 – 15%, indicating that most sulfonated carbon catalysts were sufficiently stable for reuse (Bhatia *et al*., 2020; Kumar *et al*., 2020; Roy and Mohanty, 2021).

The most commonly reported main deactivation mechanisms involve leaching of the –SO_3H group, which is the main Brønsted acid site in esterification and transesterification reactions. These findings are supported by post-reaction characterization results from several studies. For example, in glycerol-based catalysts, CHNS analysis showed a decrease in sulfur content from 3.50% to 1.45% after a reaction with Waste Cooking Oil (WCO). This decrease was consistent with a significant reduction in total acidity from 35,117 μmol/g to 8,895 μmol/g. This decrease in sulfur and acidity content provided strong evidence that sulfonate groups undergo leaching during the reuse cycle. In addition, the study found that the decrease in catalyst activity was the combined result of active-site blockage, a decrease in total acidity, and leaching of –SO_3H groups, as confirmed by CHNS analysis (Kumar *et al*., 2020).

Similar evidence was also reported on microalgae biomass-based catalysts. In the study, reusability was systematically evaluated, and the mechanism of activity decline was examined through various characterization techniques, including EDX, CHNS, XPS, and NH_3-TPD. Although the catalyst maintains a FAME yield of more than 90% through the fourth cycle, its activity decreases in subsequent cycles, attributed to changes in the composition of active species and a reduction in certain active components after reuse (Roy and Mohanty, 2021).

In addition to leaching, fouling and pore blockage are important factors contributing to catalyst deactivation. In xylose-based catalysts, a decrease in surface area and pore volume after reuse indicates a reduction in internal surface area and pore closure by the reaction product. Decreased acidity is also associated with the leaching of the sulfonic acid group and the closure of the active site by the reaction-resulting compound, as confirmed by a decrease in the peak intensity of NH_3 desorption at about 250 °C. Meanwhile, in glycerol-based catalysts, a decrease in total pore volume and average pore size after reusability tests was attributed to FAME or glycerol deposition within the pores, resulting in pore blockage (Tran *et al*., 2016).

The qualitative characterization also indicates the presence of changes in the active site after reuse. In coconut dreg-based catalysts, a decrease in the intensity of characteristic bands in FTIR and XPS after reuse indicates a possible loss or weakening of the active group, contributing to a decrease in catalytic activity. Thus, a decrease in biodiesel yield is not only interpreted as a decrease in reaction performance but also as the result of complex interactions among acid-site leaching, pore blockage, and chemical changes on the catalyst surface (Thushari and Babel, 2017).

To maintain the sustainability of catalyst use, cleaning and regeneration methods play a very important role. The use of organic solvents such as n-hexane, acetone, or methanol has been shown to effectively dissolve clogged-pore oil and glycerol residues, thereby restoring access to the active site and extending the catalyst's lifetime. In addition, chemical regeneration techniques via resulfonation (re-sulfonation) using concentrated H_2SO_4 have been

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reported to restore catalytic activity to near-initial conditions (up to 98 – 99%), especially in catalysts that have experienced significant sulfur leaching (Kumar *et al*., 2020).

Critically, reusability evaluations indicate that most sulfonated carbon catalysts are highly reusable, but comprehensive mechanistic evidence remains limited to a few studies. Studies reporting changes in sulfur content and post-reaction acid site density provide a stronger basis for confirming the mechanism of leaching –SO_3H group. Preferably, studies that rely solely on yield are insufficient to identify specific deactivation mechanisms. Therefore, future studies need to systematically report post-action characterization parameters, such as sulfur content (CHNS/EDX), total acid site density, NH_3-TPD profile, XPS/FTIR analysis, surface area (BET), and pore size distribution. This approach is important for clearly distinguishing the relative contributions of leaching, fouling, and changes in carbon structure to the decreased catalyst performance. A summary of data on the reusability of sulfonated carbon catalysts in biodiesel production is presented in Table 5.

Table 5. Data on the reuse of sulfonated carbon catalysts in biodiesel production.

Precursors	Number of Reuse Cycles	Initial yield (%)	Final yield (%)	Performance Loss (%)	References
Cyclodextrin	4	90.00	82.00	~8.00	(Maneechakr *et al*., 2015)
Xylose	3	89.60	70.20	~19.40	(Tran *et al*., 2016)
Oat husk	3	90.00	60.00	~30.00	(González *et al*., 2017)
Glucose	5	95.00	93.00	~2.00	(Nata and Putra, 2017)
Coconut coir	–	–	–	–	(Sontakke and Jha, 2018)
Coconut pulp residue	4	92.70	80.00	~12.70	(Thushari and Babel, 2017)
Rice husk	8	97.71	88.56	~9.15	(Mohamed *et al*., 2020)
Cork biochar	5	98.58	26.40	~72.18	(Bhatia *et al*., 2020)
Glycerol	5	92.30	65.40	~26.90	(Kumar *et al*., 2020)
Lignin sugarcane residue	6	87.52	79.37	~8.15	(Nazir *et al*., 2021)
Microalgae biomass	5	96.25	82.10	~14.15	(Roy and Mohanty, 2021)
Corn cobs	5	80.40	62.70	~17.70	(Mardina *et al*., 2024)
Red fruit residue	–	–	–	–	(Rahmah *et al*., 2023)
Spent black tea	5	97.30	85.20	~12.10	(Jumah *et al*., 2025)
Seed shell *V. montana*	5	99.84	90.94	~8.90	(Kang *et al*., 2025)

Across the reviewed studies, no sulfonated carbon catalyst consistently outperformed the others in activity, reusability, and biodiesel quality. Instead, performance depended on the balance among acid-site density, pore accessibility, sulfonic acid group retention, and operating conditions. Catalysts derived from lignocellulosic wastes with abundant oxygen-containing functionalities appeared to offer a favorable combination of properties, particularly their suitability for sulfonation and the development of acidic surfaces.

Several studies combined these materials with microwave or ultrasound-assisted processing, shortening reaction times from hours to minutes while maintaining moderate operating temperatures. For example, a black-tea-waste-derived catalyst exhibited a reported acid-site density of 34.6 mmol g^{-1} and achieved high biodiesel conversion at 50 – 60 °C using relatively low methanol-to-oil ratios and short reaction times. However, these results reflect the combined effects of catalyst properties and processing conditions. Enhanced mass transfer or energy delivery may contribute substantially to the observed performance, limiting direct attribution to the catalyst's intrinsic activity. Practical implementation remains constrained by uncertainties regarding long-term durability, sulfonic acid group leaching, and the equipment requirements of elevated-temperature operation in closed reactors. Integrating waste-derived precursors, tailored pore structures, and intensified processing therefore

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represents a promising development strategy, but its industrial feasibility requires extended stability testing and comprehensive techno-economic assessment.

CONCLUSION

This systematic review identifies plant biomass-derived sulfonated carbons as promising heterogeneous catalysts for converting used cooking oil into biodiesel. Lignocellulosic residues were the predominant precursors, providing carbon frameworks suitable for sulfonic acid functionalization, while non-lignocellulosic materials expanded the available synthesis options. Catalytic performance reflected the combined influence of surface chemistry and pore architecture. Specific surface area alone was insufficient to explain activity; acid-site density, accessibility, and retention were more informative when considered alongside pore-size distribution. Commonly reported operating conditions included methanol-to-oil molar ratios of 18:1 – 22:1, temperatures of 50 – 70 °C, reaction times of 1 – 4 hours, and catalyst loadings of 3 – 10 wt%. Process intensification shortened reaction times but introduced additional operational complexity. Reported fuel properties generally fell within the corresponding ASTM D6751 limits, whereas conformity with EN 14214 was less consistent. These outcomes emphasize that biodiesel quality depends on feedstock composition and purification effectiveness as well as catalytic conversion. Repeated-use experiments commonly showed activity losses of approximately 13 – 20%, although differences in testing protocols limit direct comparisons of catalyst durability. Deactivation was principally associated with sulfonic acid group leaching, by-product deposition, and changes in pore structure. No catalyst consistently combined superior activity, durability, and fuel quality. Future development should therefore prioritize stable acid-site incorporation, accessible pore networks, and standardized reuse assessments, supported by techno-economic and environmental evaluations to establish the feasibility of larger-scale application.

CONFLICT OF INTEREST

There are no conflicts of interest in this article.

AUTHOR CONTRIBUTION

RHH: Conceptualization, Methodology, Software, Data Analysis, Manuscript Draft Writing; FK: Study Design, Manuscript Draft Writing, Manuscript Review and Editing, Supervision; AK: Study Design, Manuscript Review and Editing, Supervision.

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DECLARATION OF GENERATIVE AI

During the drafting of this manuscript, the author used ChatGPT to refine and simplify the text in terms of language and content, as well as to generate ideas for developing graphical abstracts. After using this tool, the author critically reviews and edits the manuscript as needed and takes full responsibility for the content and integrity of the published article.

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