



REVIEW ARTICLE

Renewable feedstocks and agricultural catalysts: Transforming biodiesel production

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Received: 02 January 2026; Accepted: 25 June 2026; Available online: Version 1.0: 31 July 2026

Cite this article: Aneesha S, Preeti Y, Arun KS, Yatika D, Akshita S, Khushi A, Isha C. Renewable feedstocks and agricultural catalysts: Transforming biodiesel production. Plant Science Today. 2026; 13(sp4): 1-22. <https://doi.org/10.14719/pst.13493>

Abstract

The sustainability of the energy supply has grown significantly from economic, environmental and public health standpoint. This has accelerated the search for renewable and sustainable energy alternatives. Due to challenges with feedstock availability, land use, the food vs. fuel dilemma and generation costs, biodiesel's economic and environmental sustainability is debatable. Apart from feedstock concerns, the cost of biodiesel is greatly impacted using catalysts. Recent studies have demonstrated that agricultural waste can be converted into efficient heterogeneous catalysts that are both cost-effective and environmentally sustainable. These waste-derived catalysts have achieved biodiesel yields of 85–98 % while reducing catalyst preparation costs by approximately 30–60 % compared with conventional catalysts. This review comprehensively summarises recent advances in the conversion of agricultural residues into efficient catalysts for biodiesel production. It includes important components like life cycle assessments (LCA), feedstock development, catalyst synthesis, comparative performance and economic viability. Significant developments in the catalytic use of many agricultural by-products are carefully examined.

Keywords: agricultural residues; biodiesel; biofuels; catalysts; feedstocks

Introduction

The global need for energy is escalating very fast, propelled by population growth, industrialisation and urbanisation. Electricity plays an important role in economic growth; however, petroleum-based fuels are still widely used in transportation and industrial sectors. At present, fossil fuels contribute nearly 81 % of the world's energy demand, of which about 90 % is obtained from petroleum resources (1, 2). The increasing consumption of these non-renewable fuels has created concerns related to energy availability and environmental pollution. Emission of greenhouse gases and particulate matter from fossil fuel combustion has significantly affected environmental quality and contributed to climate change. Therefore, attention has shifted toward renewable energy sources such as solar, wind, hydro, tidal, biomass and geothermal energy. Despite their advantages, these energy sources are not yet sufficient to satisfy the continuously rising global energy requirements (3). In this context, biofuels have emerged as a suitable alternative energy source. Among different biofuels, biodiesel has gained considerable importance because it is renewable, biodegradable and produces comparatively lower environmental pollution.

Biodiesel is renewable, biodegradable, nontoxic and carbon-neutral fuel created via the triglycerides transesterification from fats of animal or vegetable oils into fatty acid methyl esters (FAMEs). It is considered good compared to traditional diesel, providing comparable combustion properties along with several merits, like diminished viscosity, elevated cetane number, increased flash point

and decreased sulfur and aromatic content (4). These characteristics yield cleaner emissions and good engine performance, encompassing decreases in carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x) and particulate matter. The adaptability and ecological sustainability of biodiesel render it an excellent option for addressing energy and climate-related issues (3).

Biodiesel feedstocks are characterized into four generations. First-generation feedstocks comprise consumable oils like soybean, palm, rapeseed and sunflower. Nonetheless, these create problems to food supply, eliciting ethical and economic apprehensions (4). Second-generation feedstocks such as *Jatropha curcas* L., *Madhuca indica* J.F.Gmel. and other non-edible oils do not disrupt food production and have been more favored for biodiesel synthesis. Third-generation feedstocks such as microalgae, fats of animal and waste cooking oil provide substantial oil yields and waste valorisation. Fourth-generation biodiesel considers genetically modified organisms, such as transgenic microalgae and cyanobacteria; nonetheless, its commercial feasibility is now constrained by elevated costs and technological intricacies (2). The basic technology for biodiesel generation is transesterification, where interaction of alcohol with triglycerides in the presence of a catalyst occurs. Generally, methanol or ethanol was used as alcohol. This technique produces FAMEs and glycerol as a by-product (2). Catalyst-free procedures are inefficient because of prolonged reaction times, elevated energy demands and various operational circumstances (4).

To address these constraints, extensive studies have been conducted on homogeneous and heterogeneous acid, base and enzymatic catalysts. Although efficient, numerous catalysts are expensive and produce secondary pollutants. This has generated interest in sustainable, cost-effective alternatives, including catalysts sourced from agricultural waste, biomass and natural minerals (4).

Recent advancements have redirected attention to non-edible oils, microalgae and waste materials as feedstock for biodiesel (5). Advancements in catalyst design, especially heterogeneous systems utilising waste materials, have enhanced reaction efficiency and reusability (2). The clustered regularly interspaced short palindromic repeats (CRISPR) and other metabolic pathway modification of genetic engineering have facilitated the development of microalgae strains with increased lipid content (6). Hybrid feedstock approaches, such as combining waste cooking oils with algal oils, have shown potential in increasing yield and reducing costs (7). In recent times, the advancement of catalyst technology has involved magnetic nano catalysts, mesoporous materials and biochar supported systems that augment surface area and acidity (8–10). Computational optimisation technologies such as machine learning and response surface methodology (RSM) are used to reduce the experimental burden and optimise process variables (11). Prominent examples include ILs-OMt-0.6 mesoporous clay catalysts that produce 97.02 % yield (12) and FS-B-L-PILS magnetic nanospheres that produce 98.1 % biodiesel from high-acid *Euphorbia lathyris* L. oil and retain > 91 % efficiency after five cycles (13).

Notwithstanding considerable advancements, obstacles persist especially concerning production expenses, feedstock accessibility and industrial scalability (14). Although considerable advances have been made in the field of biodiesel research, the industrial scalability and techno-economic viability of various biodiesel generations remain a big challenge. First generation feedstocks are associated with food-for-fuel conflict and high production costs, while second and third generation feedstocks are limited by the availability of biomass, complexity of processing and commercialisation (15, 16). In this respect, heterogeneous catalysts based on agricultural wastes have gained much interest due to their low cost, reusability and the potential to reduce the biodiesel production cost while solving the waste management problem (17). Some catalysts obtained from agricultural residues showed biodiesel conversion efficiencies of 85–98 %, indicating their industrial applicability under optimised conditions (18). But catalyst stability, feedstock variability and limited pilot scale validation still hamper large scale commercialisation. However, current research aims to provide cost effective, abundant feedstocks and efficient catalytic systems as well as to conduct lifecycle and economic assessments to assess long-term feasibility (5, 19). Moreover, this review aims to critically evaluate the use of agricultural waste-derived heterogeneous catalysts for biodiesel production, with emphasis on catalyst synthesis methods, catalytic efficiency, sustainability aspects. This review seeks to summarise and assess recent advancements in biodiesel feedstock utilisation and catalytic technologies, emphasising sustainability, cost-effectiveness and industrial applicability, thus aiding the future progression of biodiesel as an excellent alternative energy source (11).

Statement of novelty

- This research primarily focuses on agriculture wastes as sustainable heterogeneous catalysts for biodiesel generation, addressing economic and environmental challenges.

- This review systematically integrates underutilised agricultural residues, sustainable catalyst preparation strategies and comparative analysis of previous studies to identify existing knowledge gaps and highlight the potential of unexplored agricultural waste-derived catalysts for efficient and sustainable biodiesel production.
- Previous reviews have mainly addressed biodiesel feedstocks or catalyst development separately, with limited focus on integrating catalyst performance, scalability, sustainability and LCA aspects. Therefore, this review provides a comprehensive framework combining agricultural waste availability, catalyst chemistry and biodiesel performance.

Biodiesel

Biodiesel is considered environmentally friendly when compared to conventional diesel that is obtained from organic oils and fats and contains oxygen. It can be generated from many plant-based oils, like soybean, rapeseed, palm, sunflower, lauric, stearic and palmitic oils, among others and is chemically characterised as a combination of fatty acid with long-chain mono alkyl esters. Glycerol and biodiesel are byproducts of a catalysed reaction between lipids (either animal or vegetable) and alcohol (20).

The cost of generation of biodiesel is higher than petroleum diesel, which is a major demerit. The current supply of animal and vegetable fats and oils can meet only about 20–30 % of the global demand for liquid fossil fuel replacement. Some other disadvantages of biodiesel include its low energy content compared to petroleum diesel, the possibility of deposit formation on tank surfaces during storage due to its degradation susceptibility and the fact that it freezes at low temperatures (19, 20).

Feedstocks for generation of biodiesel

The feedstock cost is the primary factor which impacts biodiesel generation from economic point of view (21). Previous researchers indicate that it constitutes nearly 70–75 % of the overall generation cost (22). According to earlier reports, feedstock prices are essential for the economic viability of the biodiesel business (21, 23). Enhancing production scale, reducing feedstock costs and minimising production expenses are essential for effective biodiesel synthesis. The competition for food resources renders the application of vegetable oils derived from edible plants (22).

Genetically engineered microalgae for biodiesel production:

Microalgae have long been a promising third-generation feedstocks because of their large amount of liquid content, increased growth rate and ability to thrive in wastewater and non-arable land. However, challenges like low natural lipid accumulation, elevated harvesting costs and competition with other bio-industries have limited their global application in biodiesel production. Recent improvements in genetic engineering enhance the biofuel potential of microalgae through various approaches (23, 24). One approach involves metabolic pathway engineering for higher lipid accumulation. Genetic modifications in microalgae target key metabolic pathways to increase the lipid content. For instance, overexpression of the acetyl-CoA carboxylase (*ACC*ase) gene in *Chlamydomonas reinhardtii* and *Phaeodactylum tricornutum* has been shown to enhance lipid synthesis (24). Similarly, the knockout of the phosphoenolpyruvate carboxylase (*PEPC*) gene redirects carbon flux towards lipid biosynthesis, significantly increasing triacylglycerol (TAG) accumulation (21).

Another promising strategy is CRISPR-Cas9 genome editing for enhanced biodiesel generation. Microalgal genome editing techniques, such as CRISPR-Cas9 technology, can be applied to engineer lipid biosynthesis pathways for improved lipid productivity. For example, deletion of starch synthesis genes (*sta6*) in *C. reinhardtii* resulted in a 60 % increase in lipid content with no loss in biomass productivity (25). Furthermore, regulation of the nitrogen-starvation response genes using CRISPR has been demonstrated to improve lipid accumulation without loss of growth rates, thereby increasing the efficiency of biodiesel production.

Genetically engineered strains of algae such as *Thalassiosira pseudonana* have been genetically engineered to use atmospheric CO₂ more efficiently, acting as artificial carbon sinks and reducing greenhouse gas emissions (6). The fourth generation of biofuels has a better sustainability profile with dual role of producing biodiesel and sequestering carbon. Despite these advances, genetically modified microalgae are faced with regulatory issues and environmental concerns that they may escape into natural ecosystems. But large-scale is hampered by high costs of genetic modifications and controlled cultivation. There have been several suggestions for containment strategies to reduce these risks. Traditional physical containment approaches include closed photobioreactors, sterilisation procedures, controlled fermentation systems, high-efficiency particulate air (HEPA) filtration and rigorous waste management procedures (26). More recently, intrinsic approaches to biological containment have been investigated. These include synthetic auxotrophy, engineered kill switches, toxin-antitoxin systems, CRISPR-based self-destruction mechanisms and orthogonal genetic circuits preventing survival outside of controlled industrial environments. While these approaches enhance biosafety, studies show that mutational escape, evolutionary adaptation and system instability might still undermine containment efficiency during long-term industrial operation (27). In this context, the use of multilayered containment systems combining physical and genetic safeguards is being increasingly recommended for biofuel industries

employing genetically modified (GM) strains. Therefore, future research should focus on robust risk assessment models, international regulatory coordination and the development of fail-safe biocontainment technologies to ensure sustainable and environmentally responsible biodiesel production.

Hybrid feedstocks: combining multiple generations for sustainable biodiesel production: The concept of hybrid feedstock involves blending multiple feedstocks such as first-generation vegetable oils, nonedible oils of second-generation and third-generation algal oils to optimise cost, yield and sustainability as depicted in Fig. 1. One example of this approach is the combination of waste cooking oils (WCO) with microalgal biodiesel, which can eliminate raw material costs while maintaining a good energy output. Studies have shown that a 50 : 50 blend of WCO-derived biodiesel and *Nannochloropsis* algal biodiesel results in improved oxidative stability and reduced NO₂ emissions. Another strategy is non-edible oil and algae co-processing. *Jatropha* oil, a second-generation non-edible feedstock, can be blended with algal lipids to enhance biodiesel yield and eliminate production costs (7). *Jatropha*-algal hybrid biodiesel demonstrates superior cetane number, flash point and viscosity compared to individual biodiesel types, thus making it a suitable alternative to fossil diesel.

Cellulosic biomass-derived lipids are also being explored for generations of hybrid feedstocks. Residues of agriculture like rice straw, corn stover and bagasse of sugarcane have been investigated for extraction of lipid via microbial fermentation (2). Oleaginous yeast such as *Yarrowia lipolytica* can convert lignocellulosic sugars into lipids, which are then blended with conventional biodiesel feedstocks to improve sustainability and reduce land-use conflicts (28). By integrating multiple sources, hybrid feedstock mitigates feedstock price volatility and ensures a steady supply for biodiesel generation. Lifecycle assessments indicate that hybrid biodiesel has a lower carbon footprint compared to single-source biodiesel, making it a preferred choice for sustainable energy policies.

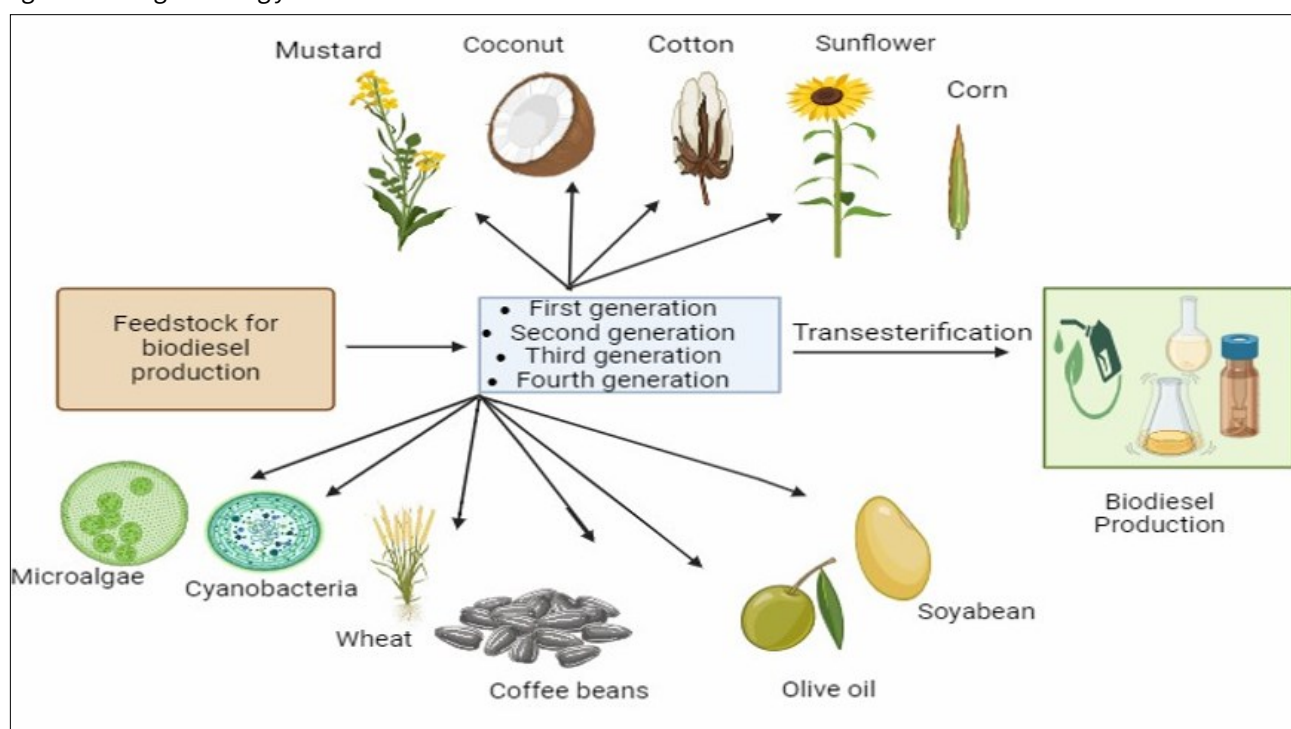


Fig. 1. Schematic representation of key steps in biodiesel production, including feedstock selection of first, second, third and fourth generation, transesterification with alcohol and biological catalyst, that leads to production of biodiesel. By-products such as glycerol are separated during the process to ensure the production of high-quality biodiesel.

Types of feedstocks

First-generation feedstocks: Soybean, palm, coconut, olive, mustard and rapeseed oils are examples of first-generation feedstocks (29). Due to their availability and ease of conversion, these edible feedstocks were previously the core of biodiesel generation (5). Previous researchers claimed that most of the global biodiesel is derived from consumable vegetable oils. The primary regions for biodiesel manufacturing are Southeast Asia, Canada and Europe, where rapeseed oil is predominantly utilised over soybean oil or palm oil (30, 14).

One of the most common vegetable oils used for cooking in the US is soybean oil. Concerns about food shortages and price spikes are important for the broad use of edible feedstocks for biodiesel. The need to adapt crops to different climatic conditions, limited arable land and high production costs are further challenges. Because of these restrictions, biodiesel producers are looking for other fuel options (5). Research shows that edible oils may be effectively replaced by non-consumable vegetable oils in biodiesel production. Growing poor soil, lowering generation costs and solving the fuel-versus-food problem are just a few of the many merits of using non-edible oil feedstocks. Earlier researchers noted that there has been extensive study on generating biodiesel from various non-edible sources of oils in recent years (21).

Second-generation feedstocks: Second-generation feedstocks include *M. indica*, *Jatropha*, rubber seed, Nagchampa and *Calophyllum inophyllum* L. The non-edible sources that are composed of second-generation fuels, such as Karanja oil, Jojoba oil and *Jatropha* oil, demonstrate reduced yields, posing a challenge for these fuels (5). Non-edible oil is a favoured option; however, its use as a biodiesel feedstock is constrained by extended cultivation periods, variability in lipid quality among different plant species, climatic conditions, geographical factors, seasonal variations and the significant land area necessary for sufficient production. Moreover, it alleviates food disparity and lessens the requirement for agricultural land (31).

Third-generation feedstocks: Biodiesel generated from used cooking oils and microalgae is classified as "third-generation biodiesel" (5). Microalgae are microorganisms that can be prokaryotic or eukaryotic, unicellular or multicellular, photosynthetic and are recognised for their fast development and adaptation to harsh environmental circumstances. Examples of eukaryotic microalgae encompass green algae, namely *Chlorophyta*, cyanobacteria, namely *Cyanophyceae* and diatoms, represented by *Bacillariophyta*, which are classified under the prokaryotic domain (32). Microalgae are easy to grow, require less labor, may employ non-potable water and effectively assimilate existing nutrients. Numerous microalgae species exhibit adaptability to diverse climatic circumstances, providing considerable benefits over alternative feedstocks of biodiesel like soybean, rapeseed, sunflower and palm oil, which frequently demonstrate suboptimal adaptation to local conditions. Microalgae have markedly superior growth rates and efficiency relative to traditional crops and other aquatic plants. For example, generating a 30 % (w/w) oil yield from rapeseed or soybean necessitates 49 to 132 times more area than microalgae.

Third-generation biodiesel, mainly microalgae-derived biofuels, encounters demerits including the requirement for constant sunlight, intricate oil extraction processes, scaling

limitations in manufacturing, elevated costs, contamination and stability concerns (5). Expanding commercial use might be arduous. It overcomes issues related to earlier biodiesel generations, like food security, environmental impact, carbon neutrality and economic viability and may be modified to meet unique needs. Alternative third-generation feedstocks, like engineered microorganisms or unconventional sources, may not encounter these specific limitations (33).

The generation of biodiesel from spent cooking oil provides a cost-effective alternative, eliminating raw material costs to around 50 % of those associated with virgin oil (19). Employing waste oils not only decreases manufacturing expenses but also addresses environmental issues by diminishing municipal trash, simplifying governmental waste collection and lessening wastewater treatment requirements. A little fraction of leftover cooking oils is utilised in soap manufacturing, whereas the bulk is underutilised (34). Frying oils provide distinct problems due to their higher free fatty acid (FFA) concentration relative to untreated oils, resulting in diminished yields and heightened catalyst usage.

Elevated cooking temperatures accelerate degradation of triglycerides, whereas food moisture also increases free fatty acid levels, resulting in stability concerns and elevated peroxide values (35). Improving the ethanolsis or methanolsis of frying oil to mitigate these challenges and to enhance biodiesel production is important. The use of waste cooking oil, particularly waste palm oil, as a feedstock significantly decreases production costs, accounting for around 70–95 % of total expenses (20). Therefore, prioritising non-edible oils and waste cooking oils above edible oils is crucial for the sustainable production of biodiesel (19).

Fourth-generation feedstocks: The fourth-generation feedstocks involve genetically engineered microalgae that improve CO absorption during photosynthesis, establishing a manmade carbon sink and increasing biofuel output. Genetically modified algal strains such as *P. tricornutum*, *C. reinhardtii* and *T. pseudonana* have been created to exhibit rapid growth and resilience under nutrient-deficient conditions. Genetically engineered microalgae offer environmental benefits, like diminished greenhouse gas emissions, carbon dioxide sequestration and prospective applications as substrates for biological wastewater treatment. Notwithstanding these benefits, the advancement of fourth-generation biofuels is still in early stage of development, concentrating on mitigating environmental effects relative to preceding generations (36).

However, challenges associated with fourth-generation biodiesel feedstocks, such as possible environmental risks, can be alleviated by more research and advancements in genetically modified microalgae and cost-effective harvesting methods. Currently, Second-generation biodiesel feedstocks provide a feasible and cost-effective alternative for biodiesel production, while investigations continue to improve the potential of fourth-generation biofuels (2).

Comparative analysis of feed stocks: A comparative assessment of biodiesel feedstocks is essential to determine their economic viability, conversion efficiency and environmental impact (37). Table 1 summarises key characteristics such as lipid content, yield, land requirement and cost efficiency of different feedstocks used in biodiesel production.

Table 1. The table below summarises key characteristics such as lipid content, yield, land requirement and cost efficiency of different feedstocks used in biodiesel production

Feedstock type	Lipid content (%)	Yield (L ha ⁻¹ year ⁻¹)	Land requirement	Cost efficiency	Reference
Soybean oil	14–21 %	450–600	High	Moderate	(38)
Palm oil	36–40 %	4000–5000	Very high	High	(39)
<i>Jatropha</i>	30–35 %	1900–2200	Moderate	Moderate	(40,41)
Microalgae	35 – 60 %	50000–100000	Low	High	(42, 43)
Waste cooking oil	5–16 %	Vary accordingly	None	Very High	(44)

Furthermore, compliance with international fuel standards such as ASTM D6751, EN 14214 and IS 15607 is essential to ensure fuel quality, safety and engine durability. Parameters including acid value, viscosity, flash point, sulfur content and oxidation stability must be carefully monitored (45). Therefore, future biodiesel research should integrate purification technologies, glycerol valorisation, storage stability enhancement and fuel standard compliance to improve industrial feasibility and commercialisation.

Classification of agricultural residues: Global agricultural waste accumulation exceeds 2 billion tonnes (46). If the substantial waste produced annually is diminished or repurposed, it will significantly contribute to alleviating food scarcity among the population (47). Annually, India generates a substantial amount of solid waste, with agricultural waste comprising around 350–990 million tonnes per year (48). Besides China, India ranks among top second producer of agricultural waste globally, generating about 130 million tonnes of paddy straw, of which half is utilised as feed and the remainder is dumped.

Furthermore, burning rice residue (parali) in the north-western region generates significant air pollution and heightens public health issues. Inadequate disposal of agricultural leftovers results in the evolution of greenhouse gases (GHGs) like carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) endangering both human and ecological systems (47). The agricultural wastes (AWs) which hindered the sustainability of agricultural systems and affect public concern encompass crop residues (leaf litter, seed pods, stalks, stems, straws, husks, weeds), poultry byproducts (spilled feed, feathers, droppings, bedding material), livestock excreta (urine, dung, wash water, residual milk, waste feed),

slaughterhouse byproducts (blood, hair, hides, flesh, bones), agro-industrial byproducts (bagasse, molasses, peels from various fruits and vegetables, pulps from multiple fruit varieties, oil-seed cakes) and aquaculture byproducts (uneaten feed, faecal matter) (48).

Agriculture is a major biological sector that generates substantial biomass, serving as a crucial input for the bioeconomy. Bioeconomic solutions based on agricultural waste management can mitigate the under utilisation of animal faeces and the indiscriminate burning of agricultural residues, thereby ensuring food and health security, valorising waste to produce value-added goods and enhancing farmers' livelihoods (47,48). Agricultural waste can act as a catalyst for biodiesel generation, contributing significantly to the circular bioeconomy (49).

Crops, fruit, vegetables, meat and dairy product remnants are all examples of agricultural waste that develop because of the production and processing of agricultural commodities. The classification of agricultural waste into crop residues, animal residues, industrial wastes and fruit and vegetable wastes (FWs) is illustrated in Fig. 2 (50). An effective feedstock for biodiesel production is residual oils, agro-industrial byproducts and processed agricultural wastes like de-oiled rice bran, de-oiled cakes from oil seeds, coffee grounds and discarded vegetable oil from food manufacturing, households and restaurants. In addition, biodiesel synthesis makes use of a wide variety of feedstocks sourced from various inedible agricultural seeds ensure that you choose the best and most often used inedible oils, Table 2 provides a detailed list of oil-rich plants along with their oil concentrations (%) reported in different plant parts, highlighting their potential as feedstocks for biodiesel production.

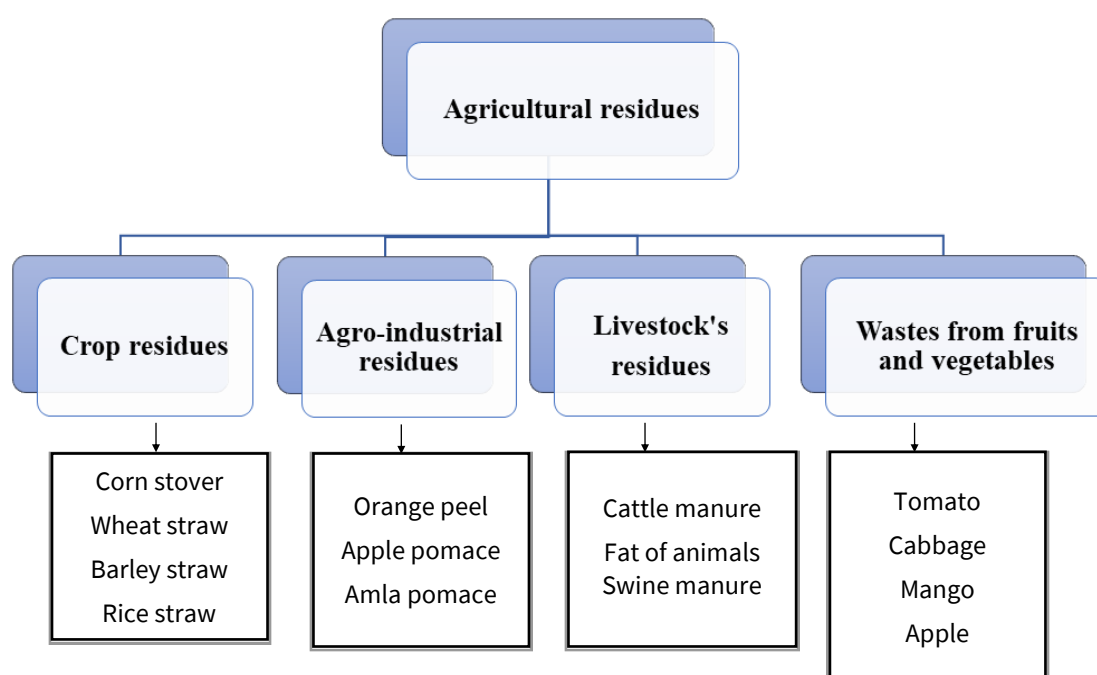


Fig. 2. Classification of agricultural residues into various categories: Crop residues, livestock's residues, agro-industrial residues, fruit waste and vegetable waste.

Table 2. Oil-enriched plant species and their corresponding oil concentration (%) reported in different plant parts, highlighting their potential as feedstocks for biodiesel production

Botanical name	Local name	Oil concentration (%)	References
<i>Datura stramonium</i> L.	-	10.3 – 23.2	(51)
<i>Pistacia chinensis</i> L.	-	30	(52)
<i>Euphorbia lathyris</i> L.	-	48	(53)
<i>Nicotiana tabacum</i> L.	Tobacco	36 – 41	(51)
<i>Ricinus communis</i> L.	Castor	45 – 50	(54)
<i>Schleichera trijuga</i> Wild.	Kusum	10 – 65	(55)
<i>Madhuca indica</i> J.F.Gmel.	Mahua	35 – 50	(56)
<i>Azadirachta indica</i> A.Juss.	Neem	20 – 30	(57)
<i>Pongamia pinnata</i> (L.) Pierre	Karanja, Pungam	25 – 50	(58)
<i>Jatropha curcas</i> L.	<i>Jatropha</i> , Ratanjyot	20 – 60	(55)

Catalysts obtained from agricultural waste have emerged as a sustainable and economical solution for biodiesel synthesis, providing great catalytic efficiency and environmental advantages (59). Diverse plant residues, such as banana peels, cocoa pod husks, orange peels, walnut shells and sugarcane bagasse, were investigated for their role as heterogeneous catalysts in transesterification reactions. The generation procedure often involves drying, burning and calcination at temperatures from 500 °C to 900 °C, which considerably influences their chemical composition, surface area and catalytic activity. Research shows that *Musa balbisiana* Colla peel, cocoa pod husk, walnut shell, tamarind fruit shell and *Tectona grandis* L.f. leaf catalysts can produce biodiesel yields greater than 90 %. Catalysts prepared from *M. balbisiana* peel showed very high efficiency with a 99.3 % yield of biodiesel in only 2 min under microwave irradiation. On the other hand, orange peel ash, rich in potassium with a mesoporous structure, reached 98 % conversion with good reusability up to five cycles (2). These catalysts showed good reusability and catalytic activity for several cycles and recalcination was helpful to recover their catalytic efficiency. Agricultural waste catalysts offer a feasible alternative for large-scale biodiesel production, merging economic feasibility with environmental sustainability. Subsequent investigations ought to concentrate on improving catalyst stability, reusability and industrial scalability (59). Physicochemical properties of heterogeneous catalysts are important to determine the efficiency of conversion to biodiesel, reaction kinetics and stability of catalyst. The surface area is one of the most important properties in the catalytic performance, since the higher the surface area, the more active sites are available for triglyceride-methanol interactions, which increases the efficiency of transesterification (60). The porous structure and proper pore size distribution of catalysts promote the mass transfer of bulky triglyceride molecules to the internal active sites, alleviating the mass transfer limitation and improving the biodiesel yield (61). Thus, optimization of catalyst surface area, pore structure, crystallinity and acid-base properties are necessary for high biodiesel yield, improved catalyst reusability and stable industrial scale biodiesel production.

Although there is increasing interest in the use of heterogeneous catalysts derived from agricultural waste for biodiesel production, several concerns related to catalyst stability, metal leaching and fuel contamination are still poorly addressed. One of the major limitations affecting the industrial applicability is catalyst leaching, where active metal species such as Calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na) may leach into the reaction medium during transesterification, especially in the presence of moisture and free fatty acids (3). Ash-derived catalysts and calcium oxide (CaO)-based biowaste catalysts, such as eggshell and plant ash catalysts, are particularly susceptible to leaching, which causes soap

formation, catalyst deactivation and reduced biodiesel purity (62). Residual metals and ash particles may also contaminate biodiesel products, negatively affect engine components, fuel injectors and combustion efficiency while increase sediment and ash content (63). Consequently, future research should focus on developing highly stable, low-leaching and regenerable catalysts with improved structural durability and minimal contamination risks to ensure sustainable industrial biodiesel production.

Crop residues: The predominant form of agricultural waste comprises straws, stovers, leaves and seed pods, produced during the agricultural phase. Previous researchers reported that global agricultural waste generation is around 2802 million tonnes annually. Biofuels are predominantly derived from agricultural leftovers, like rice straw, wheat straw, maize stover and wheat straw which are accessible throughout the year (64). Nonetheless, a minor fraction is utilised for biofuel or animal feed, whilst the predominant amount is incinerated, causing ecological damage. Rice straw, a prevalent and rich biomass resource, is mostly generated in Asia, yielding an annual production of 731 million tonnes (50).

By 2030, waste like rice straw in India is anticipated to total 221.8 million tons annually (65). Wilmar's research demonstrates that 482 million metric tonnes of rice produce approximately 38.5 million metric tonnes of rice bran. Crude rice bran oil, including roughly 17.5 % oil and 8 % FFA, possesses significant promise as a biodiesel feedstock. Rice bran oil necessitates a two-step pretreatment method for biodiesel synthesis because of its elevated free fatty acid concentration (50, 59).

Agro-industrial residues: Agricultural processing waste is a category of secondary agricultural waste, consisting of byproducts produced by the food industry. This encompasses vegetable and fruit peels, starch byproducts from starch production, molasses from sugar processing, fruit pulp, sugarcane bagasse, chicken skin, eggs, animal fat and meat from the meat business, along with defatted seeds from the edible oil sector (50).

Sugarcane bagasse, a residue of sugarcane processing post-juice extraction, as a notable agro- industrial waste. Palm oil is the most extensively produced edible oil worldwide. The processing of fresh palm fruit produces nearly 35.19 million tonnes of waste from an overall total of 85.84 million tonnes. Supplementary agro-industrial waste includes orange peels, apple pomace and assorted fruit by-products from sectors including cider production, fruit juice manufacture and food processing businesses (59, 64).

Livestock's residues: In numerous rural homes, the breeding of livestock and crop cultivation serve as the foundation of sustenance. Livestock manure is extensively utilised as an energy source in certain areas, especially for biogas generation or the manufacture of compost briquettes for combustion (50). This procedure

encompasses the digestion of animal slurry, the cremation of poultry litter and the utilisation of straw as fuel in combined heat and power facilities. These projects attain economic viability when markets are available for the produced heat (e.g., industrial applications) and by-products like fertilisers for agricultural purposes.

Waste heat can be harnessed on agricultural sites or transmitted to adjacent towns (66). The primary categories of animal waste include solid manure (farmyard manure), liquid manure (urinary excrement) and wastewater. Unregulated manure can considerably exacerbate water and air pollution. Liquid manure can pollute surface water by pathogen infiltration, wastewater release, nutrient leaching (mostly nitrogen and phosphorus) and various other contaminants. Conversely, solid manure can intensify air pollution, emitting up to 18% of CO₂ and 37% of CH₄ as greenhouse gases (50).

Wastes from fruits and vegetables: Raw fruits and vegetables, including citrus fruits, pineapples, mangoes, oranges, jackfruits, tomatoes and bananas, are categorised as fruit and vegetable wastes (FWWs). A substantial amount of these fruits and vegetables is produced by processing facilities and health-oriented markets (66). The very perishable nature of these organic wastes complicates landfill disposal and increases the danger of contamination. The substantial quantity of FWWs generated contributes to the operational expenses of markets (50). In earlier reports, the generation, packaging, utilisation and packaging of fruits and vegetables generate 15 million tonnes of trash in the United States, 6.5 million tons in the Philippines, 32 million tonnes in China and 1.8 million tonnes in India. In India, food waste totals approximately 5.6 million tonnes per year, frequently discarded in areas outside metropolitan centers (66).

Methods for production of biodiesel

Vegetable oils can be transformed into diesel-like fuels via several techniques, including transesterification, pyrolysis, dilution and micro emulsification. Transesterification is the predominant and favored method for biodiesel generation. This approach provides numerous benefits, including the generation of high-quality biodiesel with substantial output under regular conditions for operation (5).

Transesterification: Transesterification is the most widely used method for biodiesel production which involves mixing triglycerides in oils and fats with alcohol, commonly methanol, producing fatty acid mono alkyl esters (biodiesel) and glycerol as byproducts, using suitable catalyst as illustrated in Fig. 3 (67). The primary catalysts utilised in this approach are enzymatic, acidic and alkaline types, which significantly enhance the reaction rate and yield. Catalyst selection depends on conversion efficiency, corrosion susceptibility and the ease of separating the final products.

Transesterification can occur without catalysts; nevertheless,

it necessitates high temperatures, increased pressures, prolonged reaction durations and supplementary pre- and post-treatment processes (50). Its simplicity and efficiency make transesterification the preferred biodiesel production method. The conventional transesterification process involves extensive pretreatment and posttreatment operations (66). If the feedstock contains more than 2.5 wt. % FFA, the pretreatment procedure is esterification with acid catalyst (H₂SO₄). Post-treatment consists of purification and quality control of crude biodiesel. Recent research has been directed toward novel approaches such as the use of ionic liquids and supercritical technology for catalyst-free transesterification, aiming to improve efficiency and sustainability. These methodologies lower energy consumption, increase reaction rates and ease biodiesel purification. Enzymatic processes are moving forward as immobilised lipases improve reusability and cost-efficiency (68). Biodiesel production could be revolutionised by improvements in these areas.

Various forms of transesterification methods are available:

Base-catalysed transesterification: This technique, employing catalysts such as NaOH and KOH, is prevalent. Base catalytic transesterification is not a superior alternative when utilising feedstock oil with elevated free fatty acid concentration (66). Furthermore, water utilised for purification may lead to increased soap formation following the decomposition of triglycerides into free fatty acids and diglycerides or glycerides. Pretreatment with acid catalysts (H₂SO₄) is necessary for oils with free fatty acid content over 1.0 wt % (69).

Acid-catalyzed transesterification: Strong acids such as HCl and H₂SO₄ can process high-FFA feedstocks; however, they entail slow reaction rates and necessitate neutralisation steps. This method of transesterification is not widely utilised in industrial applications due to its propensity to corrode metallic vessel surfaces, its relatively slow kinetics and its facilitation of metal oxide production. The yield of biodiesel may diminish due to the alkali base catalyst; therefore, acid pretreatment is conducted prior to the reaction with the base catalyst (67, 68).

Heterogeneous catalysis: During this process, a chemical reaction occurs between the feedstock oil and an alcohol, which results in the generation of glycerol and biodiesel in the presence of a heterogeneous catalyst. Inorganic catalysts like CaO, TiO₂ and MgO facilitate simpler separation, prevent soap production and enable catalytic reusability. Co-solvents are necessary to enhance mass transfer (69).

Supercritical methanol transesterification: In this transesterification process, no catalyst is employed; biodiesel is generated through the reaction between feedstock oil (triglyceride) and alcohol under supercritical conditions, characterised by elevated pressure and temperature. This process functions at elevated temperature and

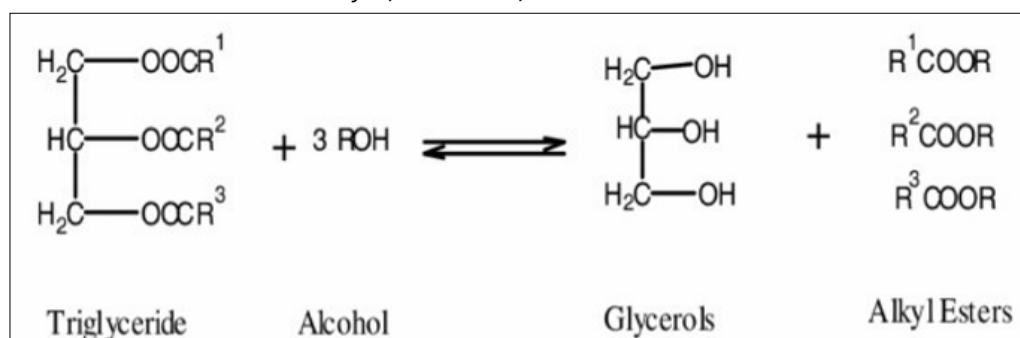


Fig. 3. Transesterification reaction; a chemical reaction wherein triglycerides (fats or oils) interact with an alcohol (usually methanol or ethanol) in the presence of a catalyst, yielding biodiesel (methyl or ethyl esters) and glycerol as a by-product.

pressure, negating the necessity for catalysts and rendering it unaffected by free fatty acids and water. Despite providing high yields and preventing soap production, its economic viability continues to pose a difficulty (59, 64).

Enzymatic transesterification: Lipase enzymes facilitate an eco-friendly method that achieves high biodiesel output, operates at low temperatures (~40 °C) and produces no glycerol byproduct. Lipase may catalyse a diverse array of substrates, having free fatty acids. Other primary inputs for biodiesel synthesis include acyl and oil and acyl, like alcohol. The enzymatic reaction is superior due to its moderate reaction conditions, facile product recovery, absence of wastewater formation, lack of saponification and enhanced product quality (67). The elevated expense of the enzyme renders it somewhat expensive. However, this limitation can be mitigated by the repeated utilisation of the enzyme, leading to the application of immobilised lipase. An effective approach is to develop a novel strain of lipase or recombinant lipase that exhibits high tolerance to methanol, elevated catalytic efficiency, robust resilience to severe conditions and sustained efficacy after several applications. Consequently, the genetic engineering of lipase and its expression is a domain requiring additional advancement (68).

Industrial suitability of transesterification: Base-catalysed transesterification is widely applied in the industry due to its simplicity and fast reaction rate, but it is restricted especially for the feedstocks with high content of FFA. In such cases, additional pretreatment operations (acid esterification) are required, thus increasing complexity and costs. Other approaches, such as supercritical methanol, heterogeneous catalysis and enzymatic transesterification, have advantages, but face some obstacles. Thus, transesterification is the dominant technology, but its practical application is dependent on feedstock characteristics and on process optimisation (59, 66). Table 3 compares the major transesterification methods used for biodiesel production based on their advantages, limitations and industrial suitability.

Downstream processing and commercial applicability of biodiesel

Significant progress has been made in renewable feedstocks and catalysts from agricultural waste for biodiesel production, but comparatively little attention has been paid to downstream processing, fuel quality and commercial applicability. The purification of downstream biodiesel is an important step as crude

biodiesel contains impurities such as residual methanol, glycerol, catalyst residues, soaps and unreacted triglycerides which have adverse effects on the engine performance and fuel stability (70). The most widely used method is conventional water washing, but membrane separation, dry washing and adsorption-based purification methods are increasingly preferred due to their lower water consumption and environmental impact (71).

Glycerol valorisation is also crucial for the economic sustainability of biodiesel industries. The crude glycerol produced during transesterification can be converted into valuable products such as hydrogen, biogas, propylene glycol and glycerol carbonate, thus supporting circular bioeconomy approaches (72). Furthermore, engine compatibility and storage stability are still major issues for large-scale biodiesel utilisation. In general, biodiesel improves lubricity as well as reduces CO and particulate emissions, but high biodiesel blends can lead to increased NO₂ emissions and affect cold-flow properties and oxidative stability (73). Oxidation, moisture absorption, microbial contamination and polymer formation may also occur during long term storage, particularly in biodiesel derived from highly unsaturated feedstocks (74).

Pyrolysis and catalytic cracking: Pyrolysis is a process that transforms one substance into another through the utilisation of heat, with or without a catalyst. This method involves heating materials in an oxygen-free environment, breaking chemical bonds to produce smaller molecules. Common feedstocks for pyrolysis include oils of vegetable, fats of animals, natural fatty acids and fatty acid methyl esters. Soybean oil has experienced thermal deterioration and distillation using a standard, American Society for Testing and Materials distillation apparatus in both air and nitrogen atmospheres (19).

Research has also explored the catalytic cracking of vegetable oils for biofuel production. A study showed that copra and palm oil was subjected to cracking at 723 K with a standard SiO₂/Al₂O₃ petroleum catalyst. The concentrated organic phase was isolated to produce biodiesel and gasoline, with the chemical composition of the resulting liquid fuel closely resembling that of conventional petroleum diesel. In comparison to alternative cracking techniques, pyrolysis is more rapid, cleaner and efficient. Nonetheless, its utilisation has diminished as contemporary methods for biodiesel manufacturing have gained prominence (19).

Table 3. Comparative analysis of different biodiesel transesterification methods, including their advantages, limitations, conversion efficiency and Industrial suitability for biodiesel production

Transesterification method	Advantages	Limitations	Industrial suitability	References
Base-catalysed transesterification	High reaction rate and widely used for biodiesel production	Not suitable for feedstocks with high free fatty acid content; soap formation may occur	Commercially established for low-FFA feedstocks	(66, 69)
Acid-catalyzed transesterification	Suitable for high-FFA feedstocks	Slow reaction rate, corrosive nature and additional neutralization steps required	Mainly used for pretreatment processes	(67, 68)
Heterogeneous catalysis	Easy catalyst separation, catalyst reusability and reduced soap formation	Requires co-solvents to improve mass transfer	Promising for sustainable large-scale production	(69)
Supercritical methanol transesterification	Catalyst-free process and unaffected by free fatty acids and water	Requires high temperature and pressure; high operational cost	Limited industrial application due to economic constraints	(59, 64)
Enzymatic transesterification	Eco-friendly process, mild reaction conditions and improved product	High enzyme cost and lower operational stability	Potential for future industrial applications	(67, 68)

Dilution: Vegetable oil has been used with diesel to decrease its viscosity for engine application. In 1980, Caterpillar Brazil integrated 10 % vegetable oil into pre-combustion chamber engines, sustaining consistent power output without modifications to the engine. During that period, vegetable oil did not entirely supplant diesel; but rather it included 20 % vegetable oil and 80 % diesel demonstrated efficacy. Short-term trials evaluated a 50/50 mixture, while a combination of 75 % diesel and 25 % sunflower oil demonstrated encouraging outcomes (19, 37). Although dilution is primarily considered a fuel modification approach, it is important because diluted biodiesel systems can influence catalyst efficiency, fuel viscosity, combustion behavior and overall energy demand. Understanding these interactions is important for evaluating the practical applicability of agricultural waste-derived catalysts in biodiesel production and downstream fuel utilisation (15).

Microemulsification: The high viscosity of vegetable oils can be diminished by employing microemulsions with solvents like ethanol, 1-butanol and methanol. A microemulsion is a stable colloidal mixture characterised by the dispersion of optically isotropic fluid structure, formed from two typically immiscible liquids and a variety of ionic or non-ionic surfactants, with diameters of particles ranging from 1 to 150 nm. These mixtures improve spray properties by rapidly vaporizing all low-boiling-point components within micelles. Engines have exhibited comparable performance utilising microemulsions of 25 % and 53 % sunflower oil by weight mixed with diesel (19). Microemulsification has been briefly due to its role in improving fuel properties and combustion efficiency of biodiesel produced using agricultural waste-derived catalysts. The technique supports better fuel atomisation and reduced viscosity, thereby complementing catalyst-assisted biodiesel production and enhancing the practical feasibility of renewable fuel applications (75).

Catalysts for biodiesel synthesis

Multiple endeavours have been made to synthesise biodiesel from numerous feedstocks; Studies to generate biodiesel from diverse feedstocks have concentrated on creating effective catalysts to enhance production scalability (38). Primary catalyst types for biodiesel production encompass enzymes, acids and bases.

Catalysts are essential in the transesterification process. At present, various catalysts are under examination, each possessing distinct advantages and disadvantages. In extensive applications, these catalysts are anticipated to be economically viable and ecologically sustainable. Catalysts employed in transesterification can be categorised according to their composition and reactivity (76).

Homogeneous catalysts: The selection of catalysts is a crucial factor in biodiesel synthesis to lower synthesis costs. The catalyst selection is contingent upon the FFA level in the feedstock oils. Homogeneous catalysts like reactants reside in the same phase. H_2SO_4 , HCl , H_3PO_4 , sulfonic acid, KOH and NaOH are some commonly used homogenous catalysts.

Homogenous acid catalyst: Acid catalysts, including H_2SO_4 , HCl and sulfonic acid, are utilised in the manufacture of biodiesel. The procedure is dissolving the catalyst in methanol and incorporating the mixture into oil with vigorous agitation. Bronsted acids, such as sulfonic and sulfuric acids, effectively accelerate transesterification, yielding significant amounts of alkyl esters, though the process proceeds at a reduced rate. Homogeneous acid catalysts, although efficient, are problematic due to their corrosive properties, necessity for high pressure and temperature and extended reaction times,

making them commercially unviable (2).

Homogenous base catalysts: Alkali catalysts, including KOH and NaOH , are solubilised in methanol and combined with oil during the transesterification process catalysed by alkali. This procedure, conducted at 340 K under atmospheric pressure, produces ester and crude glycerol phases. Vegetable oils transesterify more rapidly with base catalysts than with acid catalysis. Although homogeneous base catalysts attain elevated conversion rates and reduced manufacturing durations. They encounter obstacles such as soap generation and issues in catalyst separation, which impede their cost-efficiency (2, 3, 24).

Heterogenous catalysts: Heterogeneous catalysis is considered good compared to homogeneous catalysis for the generation of economical biodiesel fuel. Recent years have witnessed significant advancements in the generation of excellent and economically viable heterogeneous catalysts for the transesterification of triglyceride (oils or fats) into biodiesel. The transesterification reaction with heterogenous catalyst is regarded as the most viable approach for biodiesel synthesis because it is cost effective (69, 77).

Heterogeneous base catalysts are increasingly recognised for their benefits, such as functioning in gentler circumstances, recyclability and facilitating a soap-free reaction, hence enhancing environmental sustainability. Metal oxides and mixed metal oxides have enhanced catalytic activity and are under investigation for increased efficiency. Nonetheless, these catalysts are expensive owing to intricate preparation methods, including calcination and raise sustainability issues due to their dependence on non-renewable minerals.

Categories of heterogeneous catalysts encompass heteropoly acid, carbon, zeolite, hydrotalcite and waste materials, metal oxides, enzymes and ion exchange resins.

Base catalysts include CaO and titanium dioxide (TiO_2), magnesium oxide (MgO), having good reusability and minimal soap production; however, they necessitate co-solvents for optimal reaction efficiency. Acid catalysts include sulfated zirconia and tungstated zirconia, which are appropriate for high free fatty acid oils; nevertheless, their reaction rates are inferior to those of base catalysts.

Montmorillonite has attracted significant attention as an efficient heterogeneous catalyst for biofuel synthesis, principally due to its cost-effectiveness, availability, stability and superior plasticity (69,78). Chitosan-derived sulfonated solid acid catalysts are a category of heterogeneous catalysts. Chitosan-derived sulfonated catalysts, being solid acids, are classified as heterogeneous catalysts. Chitosan-derived sulfonated solid acid catalysts have demonstrated high efficacy in biodiesel generation. A previous report explained that the biodiesel output from these catalysts may get up to 98.6 % under optimised conditions (79).

Enzymes (Biocatalysts): Enzymes are utilised in biodiesel production. Enzymes, especially lipases derived from diverse microorganisms, are extensively utilised in biodiesel production owing to their capacity to catalyze reactions at moderate temperature, pressure and pH conditions. These biocatalysts enhance biodiesel yields, reduce soap production and streamline purification operations (19).

Research has investigated the ability of lipases derived from *Chromobacterium viscosum*, *Candida rugosa* and pig pancreas to transesterify oils including *Jatropha*, soybean, sunflower and used cooking oil. *C. viscosum* lipase exhibited the most favorable

outcomes for a solvent-free transesterification reaction utilising *Jatropha* oil. The immobilisation of *C. viscosum* lipase on Celite-545 that reported to enhance biodiesel yield to 71 % during an 8hr reaction at 113 K. Nonetheless, enzyme-mediated transesterification is infrequent owing to its sluggish reaction rate, enzyme inhibition and elevated costs (35, 47).

Lipase enzymes facilitate an eco-friendly method characterised by high biodiesel yield, low temperature operation (about 40 °C) and the absence of glycerol byproduct. Lipase may catalyse a diverse array of substrates with free fatty acids. Two other primary input materials for biodiesel synthesis are oil and acyl acceptors, such as alcohol. The enzymatic reaction is preferable due to its mild reaction conditions, facile product recovery, absence of wastewater formation, lack of saponification and superior product quality. The elevated expense of the enzyme renders it somewhat expensive. However, this limitation can be mitigated by the repeated utilisation of the enzyme, leading to the application of immobilised lipase (64, 79). An effective approach is to develop a novel strain of lipase or recombinant lipase that exhibits high tolerance to methanol, enhanced catalytic efficiency, robust resistance to extreme conditions and sustained efficacy after several applications. Consequently, the genetic engineering of lipase and its expression represents a domain requiring future advancement.

Calcium oxide-based catalysts: The synthesis of catalysts from waste products, including CaO derived from biomass, is a cost-efficient and environmentally sustainable alternative. Biomass substrates employed for the synthesis of CaO catalysts comprise shells from mussels, shrimp, clams, crabs and eggs, in addition to animal bones and scales (37). The CaO-derived catalysts obtained from eggshells and mollusk shells exhibit strong basicity, excellent catalytic activity and improved reusability over multiple cycles, resulting in biodiesel yields above 95 % with relatively low energy consumption (80). Despite their elevated reactivity, CaO catalysts encounter problems including active site pollution and storage difficulties. To improve their stability, CaO catalysts undergo modifications such as wet impregnation and recalcination; nonetheless, these techniques elevate production costs and diminish scalability (2, 25).

Green catalysts: Catalysts produced from plant ash have emerged to be good sustainable and economical approach for biodiesel generation. Ash-based catalysts such as banana peel ash and coconut husk ash have demonstrated high biodiesel yields (90–98 %) due to the presence of alkali metals like potassium, which enhance transesterification efficiency under shorter reaction times (18). But, these green catalysts, derived from agricultural and botanical byproducts, mitigate numerous issues related to other catalyst types (37, 46). Heterogeneous catalysts derived from waste biomass, especially those comprising metal oxides and carbonates, exhibit remarkable catalytic efficiency and recyclability. These characteristics render them appropriate for extensive biodiesel production while reducing environmental impact in comparison to homogeneous catalysts (2).

Montmorillonite as green catalyst:

Montmorillonite has attracted significant attention as an effective heterogeneous catalyst for biofuel generation, principally due to its cost-effectiveness, availability, stability and superior plasticity. Too far, it has only garnered little attention and interest in the manufacturing of various biofuels utilising montmorillonite-based catalysts (78).

Montmorillonite has been utilised as a catalyst in various applications, particularly in biodiesel synthesis and organic reactions, providing several advantages. The reactions facilitated by montmorillonite are often conducted at mild conditions, yielding good selectivity and efficiency, with a straightforward workup including simply catalyst filtering and solvent evaporation. Montmorillonite catalysts can be readily recovered and reutilised. non-hazardous, reusable, cost-effective, capable of waste reduction and conducive to atom economy (81). It may reduce the energy of activation by stabilising the transition state. Ecologically benign and the utilisation of clays as catalysts facilitates their recycling, hence enhancing their economic efficiency (78).

Some other catalysts are:

Heteropoly acid-based catalysts: Heteropoly acid (HPA) comprise of acidic hydrogen-oxygen-addenda atoms (V, Mo, W) and heteroatoms (Si, As, P). They are multi-functional green catalysts with good oxidation, acidity and thermal stability. The HPAs are classified into Keggin-type and Wells-Dawson-type and Keggin-type HPAs can be further improved (82).

Catalysts based on zeolite: Zeolites are aluminosilicate microporous materials with tunable catalytic properties, well-defined active sites and shape selectivity. Their porous structures act as nanoscale reactors, facilitating chemical reactions (83).

Catalysts based on hydrotalcite: Hydrotalcite (HT) are eco-friendly heterogeneous catalysts with a layered hydroxide structure. They have gained significant interest in catalyst development (84).

Catalysts based on carbon: Carbon-based materials are promising, cost effective and efficient heterogeneous catalysts for biodiesel generation. They offer chemical inertness, thermal stability, structural diversity and high acid density, making them suitable for acid-catalysed reactions (77).

Waste-based catalysts: The growing waste generation due to urbanisation necessitates sustainable utilisation. Waste materials, including biomass-based sources, clay and mineral derived catalysts, plant and animal shell derived catalysts, sea based derived catalysts have been explored as potential catalysts for biodiesel generation, contributing to environmental sustainability (85).

Ion exchange resin-based catalysts: Ion exchange resins (IERs) are generated with divinylbenzene and styrene copolymers with quaternary ammonium or sulfonic acid functional groups on their backbones. The IERs can be categorised as heterogeneous catalysts that are easily obtained. However, its manufacturing is not feasible due to the high-cost relative to new ones (77).

Preparation of agricultural wastes catalyst for biodiesel generation

Plant waste has been effectively used to produce catalysts for diverse uses, functioning as active precursors and components (58). Plant waste is significantly utilised in the development of solid base catalysts (2). Agricultural residues mostly consist of organic components abundant in C, O, K, Na, Ca, Mg and trace elements. The incineration of plant materials yields ashes predominantly composed of alkali metal oxides and carbonates, due to the significant reduction of carbon and oxygen during burning (67). Researchers have employed diverse approaches to transform agricultural waste into catalysts, meticulously choosing methods to optimise their catalytic efficacy. Table 4 summarises preparation conditions, advantages and performance of different biodiesel catalyst preparation methods

Table 4. Summary table of preparation conditions, advantages and performance of different biodiesel catalyst preparation methods

Method	Preparation conditions	Advantages	Performance Metrics	References
Calcination	Heating at 300–1200 °C for 2–4 hr	Increase surface area, removes impurities, improves catalyst stability	Biodiesel yield: 90–98 % (dependent on temperature & feedstock)	(2, 67)
Physical Mixing	Simple mixing of materials, sometimes followed by calcination at 900 °C	Low-cost, high scalability, environmentally friendly	Requires additional processing for optimal catalytic performance	(86, 56)
Calcination, hydration and dehydration	Rehydration at 60–80 °C for 4–6 hr, calcinations at 500–650 °C	Improves surface area and catalytic active sites	Biodiesel yield: 85–95 % (depends on hydration conditions)	(86, 94)
Co-precipitation	Mixing catalyst precursors with a basic solution (NaOH, KOH) at high speeds, dehydration at 100–120 °C, calcination	Precise control over catalyst composition, homogeneous material production	High biodiesel yield (~ 92 %) but requires additional processing	(15, 80)
Wet impregnation	Mixing catalyst with support material, drying and calcinations at 250–600 °C	Enhances surface area and catalyst stability	Biodiesel yield: 90–98 % depending on support material	(71, 38)
Bifunctional modification	Combining acidic and basic sites for simultaneous esterification and transesterification	Ideal for high-free fatty acid (FFA) feedstocks, eliminates need for two-step reactions	Biodiesel yield: 95 %+, reduces soap formation	(56, 87)
Machine learning and RSM Optimisation	Uses statistical models and AI to optimise reaction parameters	Reduces experimental costs, predicts optimal conditions	Yield improvements of 90 % + with optimised conditions	(11, 53)

Calcination: Calcination is a heat treatment at high temperatures to remove volatile chemicals, decompose carbonates and enhance properties of material. The efficiency of this protocol is dependent on several optimisation parameters such as temperature control, residency time, heating rate and ambient atmosphere (86). Calcination is a widely used method for catalyst fabrication (Fig. 4). It is generally carried out at temperatures from 300 °C to 1200 °C for 2–4 hr to produce solid catalysts from plant sources (38). The calcination temperature has a significant influence on the catalyst composition, alkalinity, porosity and catalytic activity (2).

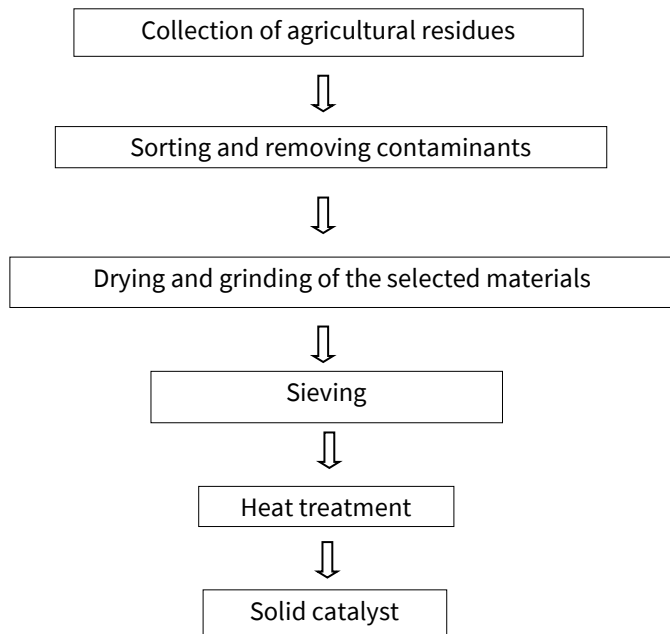
Experimental validation through pilot studies is crucial to tune these parameters and, in turn, ensure scalability and industrial

feasibility. The sugarcane bagasse ash was calcined at a temperature in the range of 600 °C to 900 °C to improve the catalytic properties by previous researchers and resulted in a biodiesel conversion efficiency of 95.5 %, where the calcination was carried out at 800 °C, increasing silica content and catalytic activity. Samples calcined at 500 °C or without calcination showed low conversion of 40.2 % and 38.7 %, respectively (87). A study on the calcinations of rice husk ash (RHA) exhibited a great enhancement in the silica purity (98 %) and surface area and it was very efficient for biodiesel synthesis (88).

The calcination at 1200 °C resulted in a decrease in catalyst efficiency, with biodiesel conversion falling to 60.5 %, potentially due to a reduced alkalinity. Table 5 presents the calcination temperatures for various feedstocks. Catalytic properties can be improved by methods besides calcination, such as wet impregnation, physical mixing, co-precipitation and hydration. One of the main advantages of calcination is that it can be easily scaled up and employed at the industrial level using relatively simple equipment. The method also provides stable catalysts with strong catalytic properties. However, calcination is an energy intensive process with high operational costs due to long heating times at high temperatures. Furthermore, the process produces emissions of CO and therefore has a moderate impact on the environment (94). Consequently, optimising process parameters and investigating sustainable adjustments are required for enhancing the efficiency and sustainability of calcination-based catalyst production.

Table 5. Calcination temperature reported for preparation of catalysts derived from various feedstocks

Temperature (°C)	Feedstocks	References
	<i>Lemna perpusilla</i> Torrey ash	(89)
550	<i>Musa balb</i>	(90)
800	Ginger leaves	(91)
	<i>Carica papaya</i> peels	(92)
700	Elephant-ear tree pod husk	(93)

**Fig. 4.** Flow chart depicting the process for catalyst production from agricultural residues, highlighting key steps such as the collection and pretreatment of agricultural residues, followed by the processing of residues and conversion of these materials into active catalysts.

Physical mixing: Physical mixing entails the direct amalgamation of two or more granular substances. This transpires prior to, during, or after the comminution of substances in a mortar or grinder. The composition, structural attributes and physicochemical qualities of the mixture's constituents can be successfully included into the product resulting from the mixture (86). Previous researchers used CaO derived from waste eggshells to synthesise a mixed metal oxide catalyst for biofuel production from spent cooking oil. The metal oxides were combined into a slurry, uniformly mixed and subsequently calcined at 900 °C (56).

The primary merit of this method is its low cost and high scalability, as it does not require specialised equipment or extensive energy consumption. Additionally, it is an environmentally friendly method since it avoids hazardous chemicals. However, one limitation is that physical mixing alone may not always provide strong chemical interactions between the catalyst components, potentially leading to lower performance compared to chemically modified catalysts (44).

Calcination-hydration dehydration: This approach is a variant of the calcination process. The treated material can be dried and rehydrated to improve the catalytic surface area and essential active sites. (86). The ideal parameters for the Calcination-hydration dehydration are 200–600 rpm at 60–80 °C for 4 to 6 hr for refluxing and 500–650 °C for calcination, 105–120 °C for 24 hr for hydration (92). In an earlier report, it was observed that CaO catalysts prepared by Calcination-hydration dehydration employed oil and methanol in molar ration of 1 : 5.15 within time interval of 133.1 min at 65 °C temperature and a mixing rate of 500 rpm, showed the biodiesel efficiency of 95.8 % (40).

Biochar generated from biomass is subjected to calcination to eliminate impurities, hence augmenting its surface area and porosity for improved catalytic efficacy. The processes of hydration and dehydration introduce functional groups, such as sulfonic ($-SO_3H$) or carbonyl ($-COOH$) groups, hence augmenting acid catalysis in biodiesel synthesis.

Hydration methods are beneficial as they enhance catalyst performance without requiring additional chemicals, making them environmentally sustainable. However, the process is moderately scalable, as it requires careful control of hydration conditions. Additionally, water usage and drying steps may add to the overall cost and processing time (95).

Co-precipitation: This method for catalyst modification involves vigorously mixing catalyst precursors with distilled water at high speeds. To sustain a pH of 10, aliquots of basic precipitating agents, such as K_2CO_3 , NaOH, NH_4OH and KOH are then added to the mixture and agitated for three hours. Following the coagulation of the mixture, it undergoes dehydration for 24 hr at temperatures between 100–120 °C in a hot air oven (56). The dehydrated sample undergoes calcination at ambient temperature and the resulting powder is utilised.

A study revealed that mixed iron and tin oxide catalysts prepared by co-precipitation employed 6 g methanol within time interval of 3 hr at 200 °C temperature with the biodiesel efficiency of 90 % (40). Co precipitation is also employed for preparation of iron (III) -doped ZnO with biodiesel efficiency of 91 % within 50 min at 55 °C and HPA-ZnO coated with a biodiesel efficiency of 98 % at 55 °C within 5 hr (76, 96). Mn-doped ZnO showed efficiency of 97 % at 50 °C within 50 min (54).

Catalysts obtained from agricultural waste, synthesised through co-precipitation, can effectively catalyse the transesterification of oils and fats into biodiesel. Co-precipitated catalysts have exceptional stability, recyclability and enhanced activity, resulting in increased biodiesel output. The CaO-based catalysts derived from eggshells, co-precipitated with MgO or ZnO, exhibit improved catalytic efficacy for biodiesel production.

Co-precipitation allows precise control over catalyst composition, making it highly effective for producing homogeneous materials. However, it requires additional processing steps, controlled pH conditions and extensive washing to remove residual impurities, making it moderate in scalability and cost (97).

Wet Impregnation: The technique involves utilising a stirrer to homogenously mix the catalyst and supporting compounds, yielding a slurry that is subsequently dried to synthesis a dry cake. The desiccated cake is subsequently processed, grounded and exposed to elevated temperatures for calcination (86). Previous researchers discovered KOH, NaOH and Na_2SO_4 as auxiliary chemicals (92). The preparation process entailed stirring for 4–6 hr, hydration in a hot air oven for 12–24 hr at 100–120 °C and calcination for 2–3 hr at 250–600 °C (92). In a report by previous researchers demonstrated that CaO/KF catalysts prepared by wet impregnation methods employed oil and methanol in molar ratio of 1 : 7 within time interval of 6 hr at 75 °C temperature, 98.95 % biodiesel efficiency. While Li-CaO showed 99 % of biodiesel efficiency (41).

Catalysts obtained from agricultural waste, infused with acidic or basic active sites (such as CaO from eggshells and sulfonated biochar), promote the transesterification of triglycerides for biodiesel generation (86). The regulated distribution of active species through wet impregnation proves the rate of reaction, yield and reusability of the catalyst.

The wet impregnation technique, when utilised with support obtained from agricultural waste, can facilitate the creation of economical, sustainable solid catalysts for biodiesel synthesis. This method not only fosters waste valorisation but also improves catalyst efficacy in green energy applications (98). The wet impregnation method enhances catalyst stability, surface area and dispersion, making it highly effective for biodiesel production. It is scalable and customisable but requires expensive precursor materials and precise process control, leading to higher costs and potential environmental concerns due to hazardous waste.

Bifunctional modification method: This method yields amphoteric catalysts that possess both basic and acidic characteristics. The augmentation of acidic and basic sites results in improved performance. This method can reduce costs, tackle issues related to the high FFA feedstocks for transesterification, decrease the moisture content of inferior feedstocks and improve product yield by incorporating the physical-chemical qualities that each catalyst lacks (40, 96).

For feedstocks having high FFA concentrations, a catalyst will be made bifunctional, facilitating both the esterification and transesterification in a one reaction under favourable conditions, thus eliminating the need for a two-step conversion process. The CaO was combined with tungsten-zirconia ($WO_3-Zr_2O_3$) for simultaneous esterification and transesterification of high FFA palm oil in a one-stage process (56).

The bifunctional modification method allows for simultaneous esterification and transesterification, making it ideal for high-FFA feedstocks while reducing processing time and soap formation. However, it involves complex synthesis, expensive raw materials and scalability challenges, requiring further optimisation for industrial applications (99).

Optimisation trends: Machine learning and response surface methodology in catalyst development: The biodiesel production process is gradually developing and the researchers are more and more integrating machine learning (ML) algorithms and optimising statistical tools such as RSM to improve catalyst performance and efficiency. Traditional catalyst optimisation is based on trial-and-error experiments, which can be time-consuming, costly and resource-intensive. The ML and RSM integration enable the prediction of the optimal parameters for synthesis, improvement of reaction efficiency and minimisation of the waste generated in the development of biodiesel catalysts.

Machine learning and response surface methodology in catalyst optimisation for biodiesel production: The ML, especially using learning algorithms such as artificial neural networks (ANNs), support vector machines (SVMs) and random forests, has revolutionised catalyst design by predicting optimal reaction conditions and synthesis parameters. The ML models are trained on the experimental data to correlate the preparation variables (like calcination temperature, precursor ratios, reaction time, etc.) with the biodiesel yield, thereby limiting the extensive physical experiments. Previous researchers used ML to optimise CaO-based catalysts, enhancing biodiesel yields by 95 %. Decision tree models further help rank influential factors, making catalyst design more efficient and sustainable. However, ML's effectiveness relies on high-quality data and rigorous validation (11).

The RSM is approach that optimises catalyst performance through experimental design and quadratic regression models. It efficiently fine-tunes key reaction parameters like methanol-to-oil ratio, catalyst loading and temperature. Earlier studies optimised CaO-based catalysts using RSM, achieving a 90 % biodiesel yield with minimal experimental runs. While RSM reduces workload and predicts performance, its effectiveness depends on the smoothness of the response surface in complex catalytic systems (53). A previous study investigated biodiesel production from used cooking oil using acid-catalysed transesterification in a microwave reactor. The authors combined Box-Behnken Design (BBD)-based RSM with ANN modeling to optimise biodiesel yield. The study reported that ANN models exhibited higher predictive capability compared to conventional RSM models, demonstrating the effectiveness of ML-assisted optimisation in biodiesel process intensification (100).

Innovative techniques for catalyst modification: Novel modification strategies to increase durability, reusability and efficiency have been offered by recent developments for the formation of biodiesel catalysts. By employing cutting-edge materials and processing methods, these technologies aim to increase catalytic activity, decrease leaching and improve sustainability (67).

Nano-structured catalysts: The emergence of nanotechnology has transformed catalyst design by enabling the synthesis of nano-sized catalysts with high surface area and enhanced reactivity. Use of nano-structured catalysts such as CaO nanoparticles, ZnO nanocomposites and mesoporous silica-based catalysts has been reported to improve the biodiesel conversion due to increased mass transfer. For example, nano-CaO catalysts prepared by the sol-gel

method exhibited better dispersion, higher surface basicity and greater resistance to deactivation than conventional bulk CaO (8). These catalysts improve the reaction kinetics, reduce the catalyst consumption and increase the reusability for multiple reaction cycles. However, the production of nano catalysts at a large scale is still difficult due to high costs of synthesis and the requirement of precise control of particle size (37).

Magnetic catalysts for easy separation and reusability: Magnetic catalysts, usually iron oxide (FeO) based composites, have attracted attention because of their simple separation and reusability. Traditional catalysts usually need filtration or centrifugation for recovery, which increases the cost of operation. On the contrary, magnetic catalysts can be easily separated from the reaction mixture by an external magnetic field, leading to a decrease in processing time and catalyst loss. The FeO-CaO catalysts exhibited excellent stability and reusability over several reaction cycles without significant loss of catalytic activity (10). These catalysts also avoid contamination of the biodiesel product thereby improving overall cost-effectiveness. However, the magnetic particles still have challenges of stabilisation under high-temperature conditions and further modifications are required to prevent oxidation and aggregation (36).

Biochar-supported catalysts for sustainability: Biochar obtained from agricultural and forestry waste is emerging as an excellent catalyst support material due to its high porosity, thermal stability and eco-friendliness. Biochar-supported catalysts stabilise the catalysts, reduce leaching and provide a sustainable alternative to synthetic supports. Recent studies have shown that biochar-supported KOH catalysts improve biodiesel yield and reduce catalyst deactivation, making them an economical and environmentally friendly alternative. However, further research is needed to enhance their catalytic efficiency and mechanical strength through the surface functionalisation of biochar (9).

Ionic liquid-modified catalysts: Ionic liquids (ILs) are thermally stable, nonvolatile solvents that have been studied for the modification of heterogeneous catalysts to improve the performance of the reaction. The ILs modified catalysts improve mass transfer, reduce the leaching and allow better interaction between catalysts and reactants. The KOH-impregnated IL-modified catalysts and obtained biodiesel yields of more than 98 % at lower reaction temperatures. The non-volatility of ILs makes them environmentally friendly and reduces harmful emissions. However, the high cost of synthesis of these composites and their limited commercial availability are still the major challenges (101).

Potential of agricultural wastes as catalysts

Agricultural waste-derived catalysts have gained significant attention for their sustainability and effectiveness in biodiesel synthesis. Various studies have demonstrated the catalytic potential of different agricultural residues. High biodiesel yields using a heterogeneous solid acid catalyst obtained from corncob for the transesterification of algal oil. Similarly, abandoned cotton stalks have been identified as excellent catalysts for transesterification and other chemical processes (2, 102). Sugarcane bagasse, a common product of the sugar industry, has been extensively studied for its role as a precursor for heterogeneous catalysts, demonstrating considerable catalytic activity in biodiesel production (67, 103). Additionally, another researchers highlighted the effective use of jute sticks, obtained post fibre extraction, in the generation of activated carbon for catalytic applications (104).

Another promising agricultural residue is tea waste, which has been utilised to develop heterogeneous catalysts for the transesterification of free fatty acids into biodiesel (105). Sugarcane bagasse, with an annual global availability of 180.73 million tonnes, is one of the most abundant agricultural residues suitable for catalyst development. Coconut coir has also been investigated as a precursor for heterogeneous catalysts in biodiesel generation (2, 106, 107). Furthermore, discarded coffee grounds have shown significant potential as catalysts for esterification and glucose isomerisation. Chitosan-derived sulfonated catalysts are solid acids, classified as heterogeneous catalysts. Sulfonated chitosan is generated from crustacean shells, bacterial cellulose, or algae-based carbon. Table 6 provides further details on various agricultural waste-derived catalysts for biodiesel production from different oil feedstocks, including reaction conditions, biodiesel yield and catalytic efficiency.

Chemical mechanisms enhancing biodiesel synthesis: Agricultural waste-derived catalysts facilitate biodiesel synthesis due to their alkaline and acidic oxide content. Alkaline oxides like CaO, K₂O and MgO, found in sugarcane bagasse ash, banana peels and eggshell catalysts, serve as strong basic sites for transesterification. CaO generates methoxide ions (CH₃O) in methanol, which react with triglycerides to form biodiesel and glycerol, while K₂O enhances catalytic activity. Acidic oxides such as SiO₂, Al₂O₃ and Fe₂O₃, present in tea residue and jute stick-derived catalysts, aid esterification by donating protons to FFA (105). Carbon-based catalysts from jute sticks and coffee grounds further improve efficiency through surface-mediated reactions, enhancing fatty acid conversion.

Preparation methods for maximizing catalytic efficiency: The efficiency of agricultural waste-derived catalysts depends on preparation techniques. Calcination (600–900 °C) removes impurities, increases surface area and enhances catalytic activity, as seen in CaO catalysts from eggshells and banana peels. Impregnation introduces alkali metal salts (KOH, NaOH) onto biochar or silica-rich residues, improving basicity and performance. Hydrothermal carbonisation modifies biomass (e.g., coconut coir, jute sticks) into high-surface-area carbon catalysts (104). Acid/alkali treatments using H₂SO₄ or NaOH create active sites, further enhancing catalytic efficiency.

Comparison with conventional catalysts: Agricultural waste-derived catalysts are cost-effective, renewable and environmentally sustainable, reducing production costs and minimising wastewater treatment compared to conventional NaOH and KOH catalysts. These catalysts, such as CaO from banana peels and activated carbon from jute sticks, achieve biodiesel yields over 90 % with high reusability (37, 103). Their scalability makes them viable for global biodiesel generation (2). Performance is comparable to commercial heterogeneous catalysts, with corn-cob-derived catalysts yielding 92 % biodiesel in 4 hr and cotton stalk-derived catalysts exceeding 95 % yield in three hours with reusability up to five cycles. Their efficiency stems from alkaline metal oxides (CaO, MgO and K₂O) enhancing transesterification, while silica-alumina catalysts from tea residues aid esterification. Carbon-based catalysts improve stability by preventing active site leaching.

Challenges include CaO leaching, mitigated by carbon coatings or biochar immobilisation and surface deactivation, addressed through mild calcination (500 °C) or methanol-acetone washing. High-temperature calcination (700–900 °C) enhances stability, with sugarcane bagasse-CaO catalysts retaining 90 % activity for six cycles. Future research should explore transition of metal doping and protective coatings to improve long-term stability and commercialisation (103).

Composition of catalysts derived from agricultural residues

Ash from burning plant materials is primarily made up of inorganic substances, including metal carbonates and oxides (such as CaO, SiO₂, K₂CO₃, MgO, Fe₂O₃, K₂O and P₂O₅) (38). Although the components differ depending on the source, they all contribute to the high alkalinity and efficiency of the catalysts, especially because of the high quantities of carbonate and potassium oxide (2). Previous researchers reported that ash derived from *M. balbisiana* contained alkali and alkaline earth metal carbonates and oxides and that its high potassium oxide content enhanced catalytic efficiency for biodiesel production (90). Similarly, the addition of MgO and calcium oxide increased the catalytic potential of *Mangifera indica* L. peel ash, which is high in K₂O.

Table 6. Performance evaluation of plant-based catalysts derived from agricultural residues for biodiesel production from different oil feedstocks, including reaction conditions, biodiesel yield and catalytic efficiency

Oil used	Agricultural residues as catalysts	Parameters			Biodiesel yield (%)	References
		Catalyst load (%)	Temp. (°C)	Time (min)		
Soybean oil	Banana peels (<i>Musa acuminata</i>)	0.7	25	240	98.95	(52)
Waste cooking oil	<i>Musa balbisiana</i> peels	2	60	180	100	(108)
<i>Azadirachta indica</i> oil	Cocoa pod husk	5	65	180	98	(87)
Waste cooking oil	Waste rice-straw	3.5	65	150	93.7	(109)
Honne seed oil	Cocoa pod husk-plantain peel blend	4.5	65	150	98.98	(110)
Palm kernel oil	Cocoa pod husk	4	65	65	100	(111)
Sunflower oil	Walnut shell	5	60	10	98	(108)
<i>Jatropha curcas</i> oil	Calcined <i>Jatropha</i> cake	1	60	60	94	(112)
Soybean oil	Waste peanut husk	5	65	240	98.4	(113)
<i>Jatropha</i> oil	<i>Musa paradisiaca</i> peels	5	65	12	97.56	(67)
Sunflower oil	Walnut shell ash	5	60	10	98	(114)
Sunflower oil	Ginger leaves	1.6	60	90	90.13	(89)
Sunfloweroil	Wheat straw	11.6	60.3	124	98.6	(37)
Palm oil	Pomelo peels	6	65	150	>98	(114)
Waste cooking oil	<i>Tectona grandis</i> leaves	2.5	25	180	100	(113)
Corn acid oil	Waste orange peel	5	65	274	91.68	(113)
<i>Jatropha</i> oil	Sugarcane bagasse	10	65	285	92.84	(37)

Potassium and calcium are typically found in various agricultural waste ashes, such as those from banana, orange and tucuma peels, which increase catalytic activity during transesterification. In these procedures, mixed metal oxides perform better than pure metal oxides (38). Plant species, age, growing conditions, climate, soil type and processing parameters like burning and calcination all have an impact on the highly diverse chemical composition of plant-derived ash. Even among the same plant species, variations in maturity, harvesting conditions and pollution exposure may impact the mineral content (2). This variation makes it difficult to draw broad conclusions about ash content and its catalytic effectiveness, which could have an impact on the results of biodiesel generation. Nonetheless, agricultural waste ashes, typically associated with environmental concerns, can be converted into valuable catalysts for renewable energy production. These ashes have potential applications beyond biodiesel, such as in chemical transformations and wastewater treatment (38).

Agricultural residues, including rice husk ash, corn stover, sugarcane bagasse and wheat straw are abundant in silica (SiO_2), carbon and other minerals, rendering them appropriate for biochar-based catalysts or as substrates for metal oxides in biodiesel generation (48). Moreover, the amalgamation of various agricultural waste sources can improve catalytic efficiency, stability and reusability. Animal-derived agricultural waste, including eggshells, seashells and bones, is abundant in CaCO_3 , which further be calcined to produce CaO , an efficient base catalyst for biodiesel transesterification. Moreover, bone-derived hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})_2$) functions as a promising solid acid/base catalyst, whilst fish scales and shellfish debris can be carbonized and modified for catalytic purposes (37, 46, 49).

Microbial and biopolymer-based catalysts, such sulfonated chitosan generated from crustacean shells and bacterial cellulose or carbon sourced from algae, have exceptional catalytic efficacy for biodiesel generation. Industrial byproducts, such fly ash, red mud and wasted catalysts from refineries, are frequently disposed of yet include important metal oxides such as Al_2O_3 , Fe_2O_3 and TiO_2 , which can be extracted and altered to function as heterogeneous catalysts. Furthermore, wastes from fruit and vegetable wastes, such as banana peels, orange peels, shells of coconut and potato peels, are abundant in cellulose, lignin and pectin, which can be transformed into biochar-based acid catalysts following sulfonation (81). Hybrid catalysts, such biochar or rice husk ash combined with CaO derived from eggshells, demonstrate enhanced performance, while co-doping techniques utilising metal oxides (ZnO and MgO) on biochar or CaO -based supports can further refine catalytic characteristics (69). The amalgamation of several waste sources in catalyst synthesis improves catalytic efficiency, stability and sustainability.

Comparative metrics of catalytic efficiency: Several reports have demonstrated that waste-derived catalysts can have high biodiesel yields with comparable reaction rate constants to commercial catalysts. However, differences in their surface morphology and active site availability impact overall performance. For example, *M. balbisiana* peel ash has been shown to exhibit a yield of 100 % at optimal conditions, having reaction rate constant of 0.032 min^{-1} (108). In contrast, commercial CaO catalysts have a slightly higher reaction rate constant of 0.040 min^{-1} , yielding 98.5 % biodiesel (2). Additionally, waste-derived catalysts such as waste rice straw and sugarcane bagasse ash provide yields of 93.7 % and 92.84 %, respectively (37, 109). These results highlight the cost-effectiveness of agricultural residues as viable alternatives to already available catalysts.

Commercial CaO catalysts typically maintain activity for six to seven cycles, whereas biomass-derived catalysts such as sugarcane bagasse and banana peel ash can be reused for 4 to 5 cycles before significant deactivation occurs (37, 52). The high catalytic efficiency and renewability of agricultural residues make them promising candidates for large-scale biodiesel production.

Mechanistic insights into catalytic activity: The surface chemistry and porosity of materials obtained from agricultural waste have a major impact on their catalytic performance. Strong basic sites are provided by its metal oxides (CaO , K_2O , MgO and Fe_2O_3) and carbonates (K_2CO_3 and Na_2CO_3), which are essential for promoting transesterification reactions. Because of its strong alkalinity and large surface area, CaO , which is frequently extracted from eggshells, mollusk shells and plant-based ash, functions as a very active catalyst. Similarly, by stabilising intermediate products and enhancing mass transfer, potassium carbonate (K_2CO_3), which is frequently present in rice husk ash and banana peel, increases reaction rates (87).

The surface area and porosity of catalysts significantly affect their catalytic performance. Studies have shown that catalysts with an elevated surface area provide good active sites, increasing biodiesel yield. For instance, sugarcane bagasse ash calcined at 800°C exhibited a surface area of $132.6 \text{ m}^2\text{g}^{-1}$, leading to a biodiesel yield of 92.84 % (37). Conversely, uncalcined catalysts or those with lower surface areas tend to exhibit reduced catalytic activity, with yields dropping below 50 % due to poor active site availability.

Reusability and stability of agricultural waste catalysts: The long-term stability and reusability of catalysts produced from agricultural waste provide a significant issue. Heterogeneous catalysts made from biomass sources can be recovered and used repeatedly, in contrast to homogeneous catalysts like KOH and NaOH , which dissolve in the reaction solution. However, because of CO poisoning, moisture absorption and active component leaching, their activity tends to decrease. For example, when exposed to ambient moisture, CaO -based catalysts undergo hydration and carbonation to create $\text{Ca}(\text{OH})_2$ and CaCO_3 , which decrease catalytic efficiency over several reaction cycles (37, 67). Researchers have investigated several modification strategies to increase catalyst stability and reusability. Catalytic activity can be restored by recalcination at $700\text{--}800^\circ\text{C}$, which can help regenerate active sites and remove adsorbed CO and moisture (2). Moreover, doping with Zn , Fe , or Al transition metals enhances catalyst durability and prevents leaching. Encapsulation within porous silica or alumina frameworks further improves structural stability by reducing active site degradation.

Studies indicate that certain agricultural waste-based catalysts show over 85 % of their catalytic performance after five cycles. For example, banana peel ash catalysts retained 91 % efficiency even after four cycles, making them viable alternatives to conventional catalysts (52). Similarly, waste sugarcane bagasse-derived life cycle assessment (LCA) catalysts showed stable performance over six reaction cycles, making them suitable for continuous industrial applications (37).

Environmental and economic impacts of agricultural waste-derived catalysts

The sustainability of biodiesel generation is greatly enhanced by the utilisation of agricultural waste as catalysts, offering both environmental and economic benefits (115). This section expands on the life cycle analysis (LCA), economic feasibility and broader policy implications of adopting these sustainable catalysts in large-scale biodiesel production.

Life cycle analysis of agricultural waste-derived catalysts

The LCA acts as a comprehensive tool for evaluating the atmospheric impacts along with the generation, utilisation and disposal of catalysts. Conventional catalysts, including homogeneous acids (e.g., H_2SO_4 , HCl) and alkali catalysts (e.g., NaOH and KOH), contribute significantly to environmental burdens due to their energy-intensive manufacturing processes, hazardous waste generation and non-recyclability. In contrast, heterogeneous catalysts derived from agricultural waste exhibit a lower environmental footprint due to their renewable nature, reduced energy requirements and minimal waste byproducts. Recent LCA studies comparing conventional catalysts with bio-based catalysts indicate that waste-derived catalysts effectively reduce greenhouse gas (GHG) emissions, energy requirement and chemical waste. Another study revealed that CaO catalysts synthesised from eggshell waste achieved a 40 % reduction in CO emissions compared to commercial CaO catalysts (86). Earlier studies used LCA to evaluate the environmental performance of the CaO catalyst from eggshells and compared it with the conventional homogeneous catalysts such as NaOH and KOH . The study showed that the application of waste-based CaO catalysts substantially reduced environmental loads by utilising biowaste materials, reducing landfill disposal and limiting chemical consumption in the preparation of the catalysts (116).

Similarly, catalysts derived from sugarcane bagasse and banana peels exhibited superior sustainability profiles, with a 50–60 % reduction in cumulative energy demand (CED) due to their low-temperature processing and avoidance of harmful chemical treatments (37). Moreover, agricultural waste-derived catalysts enhance circular economy practices by converting waste into useful materials, thereby reducing landfill burdens and environmental pollution. The implementation of such catalysts aligns with the green chemistry principles, promoting a sustainable approach to biodiesel production while mitigating the environmental risks posed by conventional catalysts. The LCA results of the agricultural waste-derived catalysts are highly case-dependent and depend on the biomass source, catalyst synthesis route, calcination temperature, transportation distance, energy consumption and system boundary assumptions. Studies reporting lower environmental burdens and lower production costs compared with conventional catalyst systems generally use locally available agricultural residues and low-energy catalyst preparation methods (117). However, not all these benefits are universally applicable, as energy-intensive calcination, feedstock transportation and catalyst regeneration may significantly alter the overall sustainability performance (118). Thus, while existing studies suggest a general trend towards better waste valorisation and lower environmental burden, LCA findings should be interpreted within the specific methodological and operational context of each study and not generalised to all biodiesel production systems.

Economic feasibility and cost reduction in biodiesel generation

The cost of producing biodiesel is still a major obstacle, with catalysts accounting for a large portion of total costs. Despite their effectiveness, basic homogeneous catalysts frequently result in higher purifying costs because of soap production and challenges with catalyst recovery. The technique is less economically feasible on a wide scale when leftover catalysts are removed from biodiesel because this raises production costs. By permitting catalyst recyclability, limiting chemical usage and lowering waste disposal costs, heterogeneous catalysts made from agricultural residues, on

the other hand, provide a more affordable option (67). From an economic perspective, these benefits make bio-based catalysts a viable way to increase the production of biodiesel. A comparative cost analysis was conducted earlier which demonstrated that biodiesel production using conventional catalysts costs approximately $\$0.80$ – $\$1.20 \text{ L}^{-1}$, whereas agricultural waste-derived catalysts lower this to $\$0.50$ – $\$0.80 \text{ L}^{-1}$ (102).

This cost reduction is the result of several reasons. First, because waste materials like rice husk, eggshells and fruit peels are either readily available or significantly less expensive than synthetic catalysts, raw material costs are much lower. Second, compared to the high-temperature production procedures needed for commercial catalysts, bio-based catalysts require less energy-intensive processing, especially in low-temperature calcination (600 – 800°C). During production, this leads to significant energy savings (52). The increased reusability of catalysts derived from agricultural waste is another significant economic benefit. These catalysts are cost-effective since they can be used for up to 5 or 10 reaction cycles, which reduces the need for frequent catalyst replacement. Heterogeneous catalysts also minimise the need for lengthy post-reaction washing and neutralisation by preventing the development of soap.

This leads to a 15–20 % reduction in downstream processing costs, further improving overall economic efficiency. Beyond direct cost savings, agricultural waste valorisation also presents economic benefits for the agricultural sector. Farmers and agro-industrial producers can generate additional revenue by selling agricultural residues for catalyst production. This practice not only eliminates waste disposal costs but also fosters sustainable rural economies by generating new income streams for small-scale agricultural businesses (2). The integration of agricultural waste-derived catalysts into biodiesel generation represents a win-win scenario, promoting cost reductions in biofuel synthesis while supporting environmental sustainability and economic growth.

Policy and industry adoption for sustainable catalysis

Global implementation of agricultural waste-obtained catalysts in biodiesel production requires supportive policies and industrial commitment. Governments worldwide are recognising the need to transition towards sustainable biofuel production and agricultural waste-derived catalysts can play a critical role in reducing reliance on fossil-based chemicals. To accelerate their adoption, targeted policies and industrial collaborations must be developed.

Providing tax breaks and subsidies to biodiesel manufacturers that use catalysts produced from agricultural waste is an effective policy approach to encourage the adoption of waste-based catalysts (119). Bio-based catalysts are more appealing than traditional alternatives since these financial incentives might help offset initial investment expenses. To promote innovation in bio-catalysis methods, governments can also provide grants and funds for research and development (R&D). Catalyst efficiency, stability and large-scale application can progress more quickly with more financing for research institutions and partnerships with the corporate sector. Another important governmental strategy is to promote circular economic integration. Industries can align with zero-waste and sustainability goals by encouraging the use of agricultural leftovers for catalyst development, which will lower manufacturing costs and reduce overall environmental impact (52).

This initiative would also encourage industries to adopt resource-efficient and environmentally friendly manufacturing processes, making biofuels more sustainable in the long run. Furthermore, establishing standardisation and certification frameworks for bio-based catalysts can facilitate regulatory approval and commercial viability. Standardised guidelines on catalyst performance, reusability and environmental impact can provide clarity to biodiesel manufacturers and policymakers, ensuring that agricultural waste-derived catalysts meet industry standards for efficiency and safety. Finally, fostering public-private collaborations is essential for scaling up bio-based catalysts (120). Partnerships between biodiesel manufacturers, agricultural sectors and government agencies can strengthen supply chains, improve technology transfer and create opportunities for real-world testing of these catalysts in industrial biodiesel production. Collaborative efforts between academia and industry can further drive research in catalyst development, ensuring that agricultural waste-derived catalysts become a commercially viable alternative to traditional catalysts in the biodiesel sector (2).

Challenges in industrial translation and future prospects

Biodiesel is eco-friendly and renewable, thus making it more effective than petroleum diesel, primarily produced through the transesterification of triglycerides. Heterogeneous catalysts generated from agricultural waste offer a sustainable and cost-effective solution, reducing dependence on conventional catalysts while utilising biomass residues. Catalysts derived from agricultural wastes are promising in terms of catalytic efficiency, but some limitations are still existing in their large-scale industrial application. The catalyst deactivation during repeated reaction cycles, such as the active site poisoning, leaching of alkaline components, pore blockage and structural degradation can decrease the long-term catalytic stability and the biodiesel yield. In addition, seasonal and geographical variation in the composition of agricultural feedstocks may affect catalyst consistency and reproducibility (117, 16). Many waste-derived catalysts also need high temperature calcination during preparation, which increases energy consumption and operation cost. And the regeneration and recovery of spent catalysts are still economically challenging for industrial scale. However, the global application of such catalysts in industrial biodiesel production is restricted due to several demerits such as research gaps, scalability and industrial feasibility (121). Therefore, it is required to establish decentralised systems for biomass collection along with the efficient storage infrastructure to ensure continuous feedstock supply for the biodiesel industries. Moreover, the expansion of the biodiesel market is greatly contingent upon policy and regulatory restrictions. Poorly harmonised fuel quality standards, inconsistent biofuel policies, inadequate financial incentives and limited subsidies restrict industrial investment especially in developing economies (122). Supportive government policies to promote renewable energy adoption, carbon reduction targets and agricultural waste utilisation are needed to accelerate commercialisation.

Another significant challenge is the underutilisation of various agricultural residues (19). While rice husk, sugarcane bagasse, banana peels and eggshells have demonstrated catalytic efficiency, many other residues, such as corn husks, peanut shells, coconut coir and Jute waste remains largely unexplored. Further research is needed to assess their catalytic activity, stability and reusability (36). Expanding the range of residues studied could lead to the discovery of new, cost-effective and highly efficient catalysts.

Another key issue is the need to characterise the catalysts for optimisation of their performance. The structural and chemical properties of the obtained catalysts from agricultural waste have an impact on their efficiency, which needs to be precisely analysed by using techniques such as X-ray photoelectron spectroscopy (XPS), synchrotron-based techniques, high-resolution transmission electron microscopy (HR-TEM) and nuclear magnetic resonance (NMR) (123). Better characterisation will enable fine-tuning of catalyst properties for improved reaction efficiency and stability. Durability of catalysts is still a challenge as many agricultural waste-based catalysts suffer from active site leaching, deactivation with multiple cycles of reaction and decrease in catalytic efficiency with time. The stability of the catalyst can be enhanced by using nano-structuring, co-precipitation and protective coatings, which may enable multiple reuse cycles, thus reducing the economic and environmental burden of frequent catalyst replacement (19).

Several emerging technologies present opportunities for improving agricultural waste-derived catalysts. One promising approach is integrating these catalysts into biorefinery models, where agricultural residues will be simultaneously used for biodiesel generation, biochar synthesis and value-added chemical extraction. Additionally, the development of multifunctional catalysts helps in catalysing both esterification and transesterification thus enhancing process efficiency and reduce production costs (86).

Another key advancement is coupling these catalysts with novel feedstock-processing techniques. Agricultural waste-derived catalysts must be optimised for compatibility with alternative biodiesel feedstocks, such as algal oils, microbial lipids and lignocellulosic biomass. Tailoring catalysts to work with low-quality, high FFA oils could eliminate the need for complex pre-treatment steps, simplifying biodiesel production and increasing yield efficiency (38).

Nanotechnology also offers potential for catalyst improvement. Nano-structured catalysts such as CaO-ZnO, MgO-TiO₂ and Fe₂O₃-supported catalysts may improve reaction kinetics, surface area and catalytic stability, which may result in improved biodiesel conversion rates (124). Hybrid catalysts with biochar-supported active sites and metal oxide promoters could be further optimised in porosity for better mass transfer and reaction efficiency. For the agricultural waste-derived catalysts to move from research stage to large scale industrial applications, it is important that there is a strong collaboration between academia and industry. Partnerships with biodiesel manufacturers can help translate real-world testing, bridging the gap between small-scale laboratory studies and commercial production. Pilot scale testing facilities will be developed to test the catalyst performance under industrial conditions (19, 37).

Government support, such as tax incentives for biodiesel manufacturers and subsidised research grants for industrial scale testing, could accelerate uptake. In addition, standardisation and certification of bio-based catalysts must be developed to ensure regulatory approval and commercial viability. Techno-economic feasibility studies, including comparative cost-benefit assessments can be used to show economic advantages and attract industry investment. The LCA and RSM modeling will be used to further optimise production parameters to ensure cost-effective biodiesel manufacturing (125). With continuous progress in nanotechnology, optimisation based on ML and collaboration with industry, catalysts derived from agricultural waste can play an excellent role in achieving economically viable and sustainable biodiesel production (2).

Conclusion

Agricultural residues as heterogeneous catalysts offer a promising alternative for the shift to sustainable biodiesel production. Through trash valorisation and circular economy techniques, this review emphasises the catalytic potential of underutilised residues and preparation strategies, highlighting their economic feasibility and environmental benefits. Industrial adoption is still hampered by issues including catalyst stability and regulatory licensing, despite significant advancements. To improve performance and scalability, future research should concentrate on underutilised residues, improved preparation techniques and sophisticated characterisation. To enable large-scale implementation and guarantee energy sustainability, strong cooperation between researchers, industry stakeholders and policymakers-backed by incentives and research and development (R&D) investment-will be crucial.

Acknowledgements

The authors express their gratitude to the Department of Biosciences and Biotechnology, Banasthali Vidyapith, Tonk 304022, Rajasthan, India, for providing the necessary research facilities and support to carry out this research.

Authors' contributions

AS¹ conceptualised, designed and planned the study and prepared the original draft of the manuscript with input from all authors. PY supervised the manuscript preparation, critically revised the manuscript, prepared and organised the figures and tables, revised the reviewer response sheet and contributed substantially to the final version of the manuscript. YD, AS², KA and IC contributed to the preparation and revision of the final manuscript. AKS supervised the entire work. All authors read and approved the final manuscript [AS¹-Aneesha Singh; AS²-Akshita Saxena].

Compliance with ethical standards

Conflict of interest: Authors do not have any conflicts of interest to declare.

Ethical issues: None

Declaration of generative AI and AI-assisted technologies in the writing process: During the preparation of this work the authors used Quillbot and Grammarly to paraphrase and make it grammatically correct. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Peer review: Publisher thanks Sectional Editor and the other anonymous reviewers for their contribution to the peer review of this work.

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