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Article in *Journal of the Energy Institute* · July 2021

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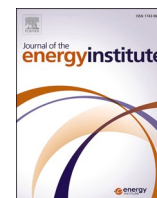
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Trends in the development and utilization of agricultural wastes as heterogeneous catalyst for biodiesel production

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ARTICLE INFO

Keywords:

Agricultural wastes
Biodiesel
Characterization
Heterogeneous catalyst
Modification
Preparation protocol
Transesterification

ABSTRACT

Biodiesel is unarguably one of the most considered substitutes for fossil-based liquid fuels. However, the high cost of biodiesel production has been a major inhibitor for its large-scale activity. Apart from the cost of feedstock, catalysts contribute to the high pump price of biodiesel. Wastes derived from agricultural sources have been seen as viable means of synthesizing cost-effective and environmentally friendly catalysts and is an appropriate disposal of wastes. In this study recent trends in converting and utilizing agricultural wastes as heterogeneous catalysts for biodiesel production were reviewed. Agricultural wastes classifications, types of catalysts for biodiesel production, and the effects of conversion and modification techniques on pore size, acidity, surface area, and other fingerprints that enhance the catalytic activity were discussed. The use of characterization methods to test the suitability of solid catalysts was analysed, and some published works on the use of some agricultural wastes-derived catalysts were scrutinized. The paper concludes that catalysts derived from agricultural wastes offer a cheap, readily available, easy to produce, and environmentally benign replacement for the imported commercial ones. Going forward, more target investigations are needed on the suitability of some unexplored agricultural wastes to convert them to green catalysts. Researchers should explore the use of optimization models and statistical tools to determine the appropriate conditions for effective performance of biofuels.

1. Introduction

With increasing world population, urbanization, and industrialization, the energy demand will continue to rise significantly. To meet this demand, the global energy consumption from oil, coal, and renewable energy sources has continued to rise, as shown in Fig. 1. Oil, a fossil resource, is still predicted to continue to dominate the energy sector till 2050. However, renewable energy sources are projected to increase from 27 exajoules (EJ) in 2018 to 114 EJ in 2040 and further to 161 EJ in 2050 [1]. Fossil fuel reserves which are the primary source of global energy have been predicted to become exhausted by 2050 going by the current depletion rate. Despite its attendant environmental effects, most fuels currently in use are still sourced from fossil-based fuels [2]. From available records, the energy sector is one of the most significant contributors to global carbon dioxide (CO₂) emissions which is emitted from the exhaust of internal combustion engines due to the use of fossil-based fuels [3,4]. Going by the current trend, global CO₂ emissions, which

were found to be about 35.3 billion metric tons in 2018, has been predicted to rise to 43.08 billion metric tons in 2050 [5]. The combinations of CO₂, carbon monoxide, sulphur dioxide, nitrogen oxides, etc discharged from fuel combustion are the major contributors to environmental degradation and contributors of global warming [6,7]. Thus, to produce energy that meets performance and environmental specifications, the application of renewable fuels has become an inevitable choice. Renewable fuels such as biodiesel, bioethanol, biogas, etc have gained prominence as viable replacements for conventional non-renewable fuels with lots of human and financial resources committed to the exploitation, production, and utilization of these fuels over the past few decades.

Biodiesel has become one of the most used renewable fuels due to its many advantages. In order to meet the ever-increasing demand for biodiesel, there is a need to speed up the biodiesel synthesis process. Uncatalyzed production of biodiesel is characterized by more reaction time, higher cost, more energy consumption, higher temperature, and

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<https://doi.org/10.1016/j.joei.2021.06.017>

Received 8 May 2021; Received in revised form 19 June 2021; Accepted 24 June 2021

Available online 8 July 2021

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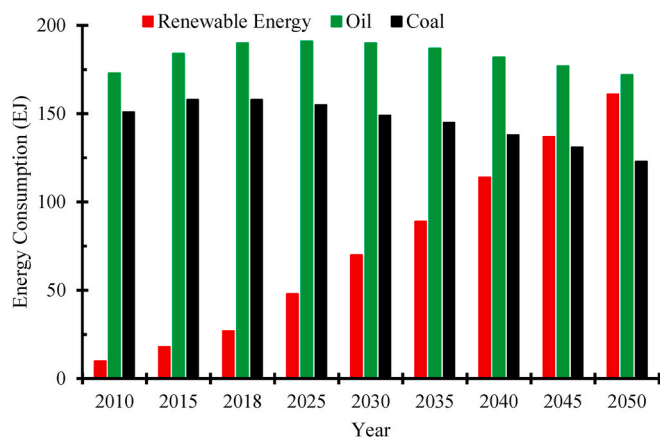


Fig. 1. Global coal, oil, and renewable energy (EJ) consumption and forecast to 2050 Adapted from [1]. Developed by the authors.

other extreme production conditions. Conversion efficiency, reaction speed, and product yield are low with uncatalyzed biodiesel generation process [8,9]. The application of an appropriate catalyst can improve the solubility of alcohol which can improve the reaction rates and result into better biodiesel synthesis processes [10]. Though the addition of catalysts can escalate the production expenditure, the benefits derivable in catalytic biodiesel production far outweighs the drawbacks. In order to overcome the high cost of commercial catalysts, researchers have devised sustainable approaches to development of environmentally benign and cost-effective catalysts from a wide range of waste materials. Expensive and highly precious oxides of potassium, magnesium, calcium, zirconium, nickel, silicon, titanium, vanadium, zinc, cobalt, chromium, strontium, etc have been extracted from biological, agricultural, household, and industrial wastes with impressive techno-economic advantages [11–13]. These waste-derived metallic oxides are highly active, can perform at low temperature and under atmospheric pressure conditions.

This paper reviews recent trends in the development, conversion, and utilization of agricultural wastes as heterogeneous catalysts for biodiesel production from the available literature. This work will also develop a framework for the classification of agricultural wastes for catalytic applications. The motivation for this research is to examine the environmental, operational, and economic benefits of agricultural solid wastes-derived catalysts over conventional commercial heterogeneous catalysts. The current efforts will be limited to the review of development and utilization of heterogeneous catalysts derived from various agricultural wastes for biodiesel production using information mined from published literature. The outcomes of this investigation will provide reliable and up-to-date information on the conversion, development, utilization, and performance of various agricultural wastes into heterogeneous catalysts for the transesterification process for researchers and biodiesel refiners.

1.1. Biodiesel production techniques

The acute environmental impacts of the use of fossil-based liquid fuels and the unsatisfactory performance of vegetable oils and its blends as fuels for compression ignition (CI) engine has made the search for cost-effective, environmentally friendly and sustainable alternative fuel inevitable. Fossil-based fuels have been found to have ineffective engine performance and incomplete combustion resulting in the emission of carbon monoxide, nitrous oxide, unburnt hydrocarbon, methane, and other greenhouse gases when used for CI engines [14,15]. The high viscosity, poor volatility, high carbon residue resulting in carbon deposit in engine parts, unreliable flashpoint, unpredictable performance under cold weather, and deterioration during storage have made the

application of vegetable oil and its blend impracticable. The high price of vegetable oil, the non-consistent, non-reliable, and non-homogeneous supply chain, and the unwillingness of some engine manufacturers to accept it as fuel are also part of the more obvious problems [16,17]. As a result of these challenges, efforts are being intensified towards converting cheaper and inedible feedstocks, including waste vegetable oil, into more suitable and sustainable biodiesel. Table 1 shows some of the advantages and disadvantages of biodiesel as a CI engine fuel. Among other techniques of biodiesel synthesis, microemulsion, blending/dilution, pyrolysis/thermal cracking, superfluid/supercritical, and transesterification methods have become well-established [18,19].

Though expensive and requires additional infrastructure for distillation, pyrolysis has also been used for biodiesel production by subjecting the feedstock to thermal degradation and removal of oxygen. When vegetable oils are pyrolyzed, products such as alkanes, alkenes, aromatics, and various forms of carboxylic acids are generated. During the micro-emulsification process, alcohol is added to vegetable oil to minimize its kinematic viscosity and ease the conversion to biodiesel. Table 2 shows the advantages and disadvantages of major biodiesel production techniques. Biodiesel is produced to meet and tested according to ASTM D6751 or EN 14214 standards. Since the focus for this review is the development of an agricultural-based catalyst for biodiesel production by transesterification, more attention shall be focused on the transesterification method.

1.2. Agricultural wastes

Wastes are substances that are generated with no intention for further use and therefore has been discarded, rejected, disposed of, or abandoned [37]. Agricultural wastes are remnants or non-useful products arising from agricultural activities or processes. They can also be the residues or leftovers from domestic consumption of agricultural products or the remainders of the industrial processing of agricultural products. If the cost of collection, transportation, and processing of the material is more than its economic values, such a material can be termed a waste [38,39]. Wastes are generated during various agricultural operations and at every stage of the activities in the agricultural value chain beginning from land preparation, weeding, harvesting, to consumption or utilization of agricultural products at domestic and industrial levels. The wastes can be in a solid or liquid state, and can be generated from crops, food, fruits, woods, vegetables, meat, poultry or

Table 1
Advantages and disadvantages of biodiesel [20–24].

Advantages	Disadvantages
Highly renewable, oxygenated, biodegradable, and non-toxic	High viscosity and pour point
Produced from renewable resources	Can deteriorate during storage
High transmissibility and miscibility	Unsuitable for cold temperature region
High energy content	High NOx emission
High cetane number	Can cause clogging in engines, fuel lines, and hoses
High flash point	Triggers food vs fuel debates
Simple production process	Some of the feedstocks can conflict with food security
Low sulphur content	Unpredictable fuel quality
Emission of less carbon and other greenhouse gases	Water shortage
Engenders high combustion efficiency	
Easily adaptable to diesel engine	
Easy to transport and store	
Feedstocks can be sourced locally	
Reduce oil importation and saves foreign exchange	
Engenders positive economic impact	
Improves air quality and health	
Less engine wear	
Helps to stabilize fossil-based fuels market	

Table 2
Advantages and disadvantages of biodiesel production methods.

Production methods	Advantages	Disadvantages	Ref
Pyrolysis/cracking	• Easy process • Free from Pollution • Formation of side products • High product yield • Uses similar infrastructure as fossil fuel refinery	• Involves elevated temperature • Costly apparatus required • Impure product • Product contains Sulphur • No environmental advantages	[25–27]
Micro-emulsification	• Uncomplicated process • Improved cetane number • Improved spray behaviors • Product causes injector sticking • Reduced emission of NOx, CO, etc.	• Reduced volatility and stability • Carbon deposit • Incomplete combustion	[25,28,29]
Dilution/blending	• Easy process	• Higher emission of smoke and CO • Inchoate combustion • Carbon deposition in engines • Gum formation	[26,30]
Transesterification	• Simple process • Industrial-scale production • Properties of biodiesel produced comparable to PBD fuel	• Multiple separation processes • High moisture and impurity levels • Costly catalysts • Generation of wastewater	[31–33]
Superfluid/Supercritical	• Short reaction time • No need for a catalyst • High conversion rate • Production efficiency	• High energy consumption • The high cost of apparatus • Varieties of feedstock can be used • Degraded products generated • High reaction temperature and pressure • High quantity of methanol required	[34–36]

dairy products [40].

Wastes from the agricultural industry constitute a substantial portion of global wastes and it is becoming a menace not only to environmentalists, town planners, but have also negatively impacted sanitation and air quality, caused environmental pollution thereby constituting health hazards to humans and animals alike. Inappropriate disposal and management of untreated agricultural waste exacerbate climate change by escalating the emission of greenhouse gases, releasing unpleasant odors, disrupting scenic landscapes [41]. Global generation of agricultural wastes is almost five times of municipal solid waste and second only to industrial waste, particularly in countries with large farming and agricultural activities [39,42]. In order to effectively manage wastes, systems of waste reduction, reusability, and recycling are being encouraged.

1.3. Classification of agricultural wastes

Agricultural wastes can be biodegradable, non-biodegradable, hazardous, or non-hazardous. Not many researchers have attempted to

classify agricultural wastes. Obi et al. [38] classified agricultural wastes based on the agricultural activities that generated the waste namely waste from cultivation activities (unused pesticides, herbicides, and fertilizers and their containers), livestock production (wastewaters, animal wastes, non-reusable animal food ruminants), and aquaculture (wastes from fish feeds and other water animals). Lakshmi et al. [39] also categorized agricultural wastes into animal waste, food processing waste, crop waste, and hazardous agricultural waste. Examples of animal waste include manure, animal carcasses, while corn stalks, sugarcane bagasse, fruits, vegetables are crop waste. However, these efforts at classifying agricultural wastes appear inadequate as they do not seem to cover all known examples of agricultural wastes. Any framework for agricultural wastes classification must be comprehensive, all-encompassing, and across-the-board. Building on the agricultural wastes classification by European Waste Catalogue [43], a more comprehensive framework for agricultural wastes classification are as follows:

1.3.1. Woody and crop residue

These are wastes generated from bush clearing, tree felling, and during post-harvesting of crops or after the crop have been processed. They are the materials left on the farm after timber or crop has been harvested [44,45]. They are mostly biodegradable and non-hazardous. Notable examples include leaves, sawdust, wood pellets, corn cob, corn husk, wheat bran, soybean hulls, molasses, rice husks, seed pods, roots citrus residues, sugarcane bagasse, palm leaves, banana trunks, etc.

1.3.2. Food and fruit residues

Food and fruit residues are the uneaten or discarded food and fruits. Examples are food wastes, eggshells, banana peels, orange peels, orange seeds, lemon peels, plantain peels, cassava peels, yam peels, groundnut shells, coconut shells, etc. This category of agricultural wastes is biodegradable and non-toxic.

1.3.3. Animal and wastewater wastes

Wastes are generated from animal husbandry, poultry, slaughterhouses, piggery, wastes from cattle, goats, cows, etc. They are generated in solid, semisolid manure or liquid (slurry) form. They usually have unpleasant odors, and are socio-culturally offensive. They include waste feed, cow blood waste, cow dung, pig manure, animal fats, residual milk, chicken fats, feathers, animal bones, chicken bones, poultry droppings, chicken feeds, bedding material, dairy wastewater, wastewater from cleaning of animal houses, etc [46,47]. Some of this category of agricultural wastes are nonbiodegradable and pose a serious threat to humans and the environment.

1.3.4. Fishing and aquaculture wastes

These are wastes generated from agricultural activities at the aquatic habitat mainly from feed, chemicals, and pathogens. They can be in solid state wastes which originates from the uneaten feed and fecal droppings or dissolved wastes derived from food metabolism or decayed, discarded feed [48,49]. They include dead fishes, fish fins, uneaten feed, fecal droppings of fish, exoskeleton of shrimp, etc. Though some of this category of agricultural wastes is biodegradable, they, however, generate offensive odors, socially unpleasant, litter the environment, and pollute terrestrial and aquatic habitats if not appropriately disposed of.

1.3.5. Wastes from agricultural activities

These are the categories of wastes generated from agricultural activities like farming, horticulture, hunting, etc. Notable examples include used wooden pallets and crates, foils, plant trimming, shrubs, grasses, animal skin, tree trunks and branches, wastewater, discarded guns, unsold flowers, dead animals, recovered decayed animal, cans, trays, etc [50,51]. Some of them are biodegradable and produce nasty

odors and an environmental nuisance when decaying. Those that are non-biodegradable are discarded indiscriminately and increase farm wastes.

1.3.6. Food preparation and processing wastes

These include waste foods, wastewater, eggshells, rice husks, wheat powder, coffee husks, waste barley, brewery wastewater, sugar refinery wastewater, banana peels, oil palm empty fruit bunch, olive mill wastewater, sugarcane bagasse, dairy wastewater, and other wastes generated at every stage of food preparation and processing, etc [52,53]. Some of these wastes are biodegradable though with social, environmental, and health consequences, if not well handled. For example, wastes from the kitchen, such as food leftovers, wastewater, etc attract rodents, flies, mosquitoes, cockroaches, and other pests which are carriers of disease-causing agents.

1.4. Development of agricultural wastes into heterogeneous catalysts

Over the past few decades, commercial heterogeneous catalysts have been severally used and reported in the literature for the conversion of various feedstocks into biodiesel. Some of the metal oxides and mixed metal oxides obtained from commercial sources include calcium oxide (CaO) [54], calcium methoxide [55], calcium diglyceroxide [56], magnesium oxide [57], magnesium zirconate ($\text{Mg}_2\text{Zr}_5\text{O}_{12}$) [58], aluminium oxide supported molybdenum oxide [59], aluminium oxide supported calcium oxide [60], magnesium pyrophosphate [61], sulphated zirconia [62], sodium molybdate [63], etc. Though some of these catalysts are reported to have high conversion efficiency, they are unsustainable as catalysts for biodiesel production owing to their complex and labour-intensive methods of preparation. Since they are commercial catalysts and produced from non-renewable sources, their application poses disposal problems and raises environmental concerns [64,65].

Catalysts derived from agricultural wastes are low-cost, non-toxic, non-corrosive, generates no wastewater, and are readily available. They have a high conversion rate, biodegradable, and a viable means of disposing of agricultural wastes by biodiesel producers [66–68]. In recent years, various agricultural wastes have been developed, converted, and utilized as low-cost and eco-friendly catalysts for the synthesis of biodiesel, using various low-grade feedstocks. Some of the agricultural wastes derived heterogeneous catalyst with high catalytic activities include eggshells [69], shrimp shell [70], animal bones [71], oyster shell [72], chicken bones [73], coal fly ash [74], banana peel [75], banana trunk ash [76], *musa balbisiana* peel ash [77], cocoa pod husk ash [78], coconut husk ash [79], pineapple (*Ananas comosus*) leaves ash [80], waste fish (*Labeo rohita*) scale [81], waste fish bone [82], etc. Table 3 shows the sources of agricultural wastes that have been used as green solid catalysts, their availability, and other potential uses.

1.5. Preparation methods for catalysts derived from agricultural wastes

Over the years, various techniques have been used by various researchers to convert agricultural wastes to catalysts. These procedures are carefully selected to enhance their catalytic potentials. Awogbemi et al. [109] employed washing, drying, grinding, sieving, and calcination to convert waste chicken eggshells into catalysts as depicted by the flowchart in Fig. 2. Farooq et al. [73] converted chicken bones into the catalyst by first washing the bones in hot water, drying them in the sun, drying them in the oven maintained at 110 °C for 6 h before pulverizing. The resulting powder was subjected to calcination at different temperatures for 4 h. Basumatary et al. [65] adopted two routes in converting agricultural wastes to a heterogeneous catalyst, as shown by the flowchart in Fig. 3. Similar procedures were followed by other authors for wastes from chicken eggshells and coconut wastes as shown Fig.

The preparation approaches for the conversion and development of agricultural wastes to solid catalysts involve the collection of the various

Table 3

Description, availability, and applications of some notable agricultural wastes.

Agricultural waste	Description	Availability	Other applications	Ref.
Plantain peels	Plantain peels are obtained from ripe or unripe plantain fruits.	Cameroon, Ghana, Uganda, Colombia, and Nigeria are the leading plantain producers with 4.3, 4, 3.7, 3.5, and 3.5 million metric tons (MT) annually.	- Plantain peels are for skincare products. - Rubbing plantain peels can help to treat skin disorders and defects. - It helps wound healing. - It speeds up cell regeneration.	[83]
Groundnut shells	Groundnut shells are the external cover or peels of groundnut seed	China, India, Nigeria, the USA, and Myanmar are the leading groundnut producers globally, with China producing 17.52 MT in 2019.	- Useful in animal feed, fertilizer, and pulp and paper industries - Used for enzyme, hydrogen, and bioenergy production - Used in dye and heavy metal degradation. - Used for plastic, wardrobes, metal casting, insulation board, and pesticides production	[84–87]
Banana peels	Banana peels are removed from the banana fruit before eating the banana fruit.	About 63.14 million MT, 21.48 million MT, 17.59 million MT, and 10.14 million MT of bananas are produced in Asia, Africa, South America, and Central America respectively in 2019.	- Used for skincare, pharmaceutical, beauty care, hair product, and food industries. - Used for teeth whitening, first aid, household cleaning products, and wastewater treatment.	[88,89]
Orange peels	Orange peel is the skin of orange fruit.	About 46.06 million MT of orange were produced globally in 2019/2020 with Argentina, South Africa, Brazil, and Australia as leading producers.	- Orange peel helps combat inflammation, makes skin glow, enhances food digestion, improves lung and heart health. - Tea, candies, air fresheners, and wooden polish can be made from orange peels.	[90]
Chicken eggshells	Chicken eggshells are gotten when chicken eggs are broken.	Global chicken egg production was above 82.17 million MT in 2019	- For water treatment and removal of copper (II) from water. - As calcium supplement in human foods.	[91,92]

(continued on next page)

Table 3 (continued)

Agricultural waste	Description	Availability	Other applications	Ref.
Cocoa pod	Cocoa pods are gotten when cocoa is harvested	Over 4.85 Million Tonnes of cocoa was produced in 2019. Ivory Coast, Ghana, Nigeria, and Cameroon are the four largest producers of cocoa	- Used as a pest repellent in gardens - Used as a natural bandage - Used for compost or natural manure for farms - Used as feed for livestock	[93]
Cocoa pod husk	Cocoa pod husk is obtained after removing cocoa beans from the fruit.		- Used in animal feed production - Used in the food processing industry - Used in the production of soap	[94,95]
Rice husks	Rice husks are the hard-protecting coverings for rice grains	About 700 million tons of rice are produced globally, every year.	- Used for compost or fertilizer - Used as a building material - Used in pet's food formulation - Used in the construction industry, as fillers and insulation materials.	[96,97]
Oil palm trunk	Oil palm trunk is a by-product of the felling of a palm tree.	The oil palm tree grows mainly in Asia, Africa, and Latin America. In 2020, about 75.45 million MT of palm oil were produced with Indonesia, Malaysia, Thailand, Colombia, and Nigeria as the major producers.	- Used as raw material in pulp and paper industry - Production of particleboards and bio-composites - construction of walls and flooring	[98–100]
Coconut husk	Coconut husk is obtained from the outer covering of coconut.	About 62.46 million MT of coconut are produced annually with Indonesia as the leading producer with 17.13 million MT of coconuts produced in 2019.	- As a source of charcoal and fuel - Used in the production of carpets, ropes, floor mats, brushes, mattresses, and other household products. - Used as mosquito repellent	[101,102]
Kola nut pod	Kola nut pod is the	A total of 306.420		[103–105]

Table 3 (continued)

Agricultural waste	Description	Availability	Other applications	Ref.
	covering of the kola nut that must be broken during harvesting to access the kola nut seed	metric tons of kola nut was produced globally in 2019. Nigeria, Ivory Coast, and Cameroon produced about 52.6%, 19.6%, and 16.5% of global kola nut, respectively.	- Used as bio-sorbents and detoxifier - Used in poultry and snail feed formulation - Used for liquid detergent - Used as organic fertilizer - Used as a paint additive	
Palm kernel shell	Palm kernel is the leftover from the palm kernel mill	8.77 million MT of palm kernel oil are produced in 2020 globally.	- Used as adsorbent for contaminated water treatment - Used for cooking - Used as reinforcement for Portland cement	[106–108]

waste materials from the farms, markets, factories, sorting of the wastes, and their transportation to the laboratories for further processing. The waste material is then subjected to cleaning to remove any unwanted object that has adhered to its body and drying, either in the sun or in an oven. Oven drying is faster and the drying rate can be controlled, but the cost of energy for drying is high. Sun-drying is cheaper but time-consuming and the waste material is susceptible to contamination. After drying, the waste materials are ground using mortar and pestle. Further grinding into smaller particle sizes is done by an electrically powered grinder. The particle sizes are confirmed using a suitable sieve of appropriate meshes. The waste material, now in powdered form, is subjected to high-temperature calcination over some time. The calcination temperature and time of calcination affect the performance of the catalyst and are carefully selected [110]. Apart from calcination, there are other modification processes to enhance the performance and catalytic properties of the materials.

Generally, agricultural wastes can be converted to solid catalysts by adopting the preparation methods as shown in Fig. 7. The catalysts can be used after grinding and sieving without any form of modification. The various modification processes are to improve the performance of the catalyst and allow further reusability. Major modification techniques include physical mixing, calcination, carbonization, wet impregnation, hydration, co-precipitation, calcination-hydration, etc.

1.6. Modification techniques for agricultural wastes derived catalysts

Modification of agricultural wastes-derived catalysts is the various preparation methods and additional actions employed in the conversion process to enhance the performance of the catalysts. The modification techniques are introduced to improve the physicochemical properties, morphological features, selectivity, catalytic activity, simplicity, safety, economy, performance, and effectiveness of the catalysts for biodiesel production [114,115]. A good heterogeneous catalyst is expected to have a large pore size, large surface area, strong basic site, and less leaching for better catalytic performance and effectiveness. From the economic and safe handling points of view, a suitable solid catalyst is expected to be non-toxic, less corrosive, safe to handle, easy to separate, readily available, highly reusable, and cost-effective [116,117]. Various modifications have been applied to achieve these properties and boost

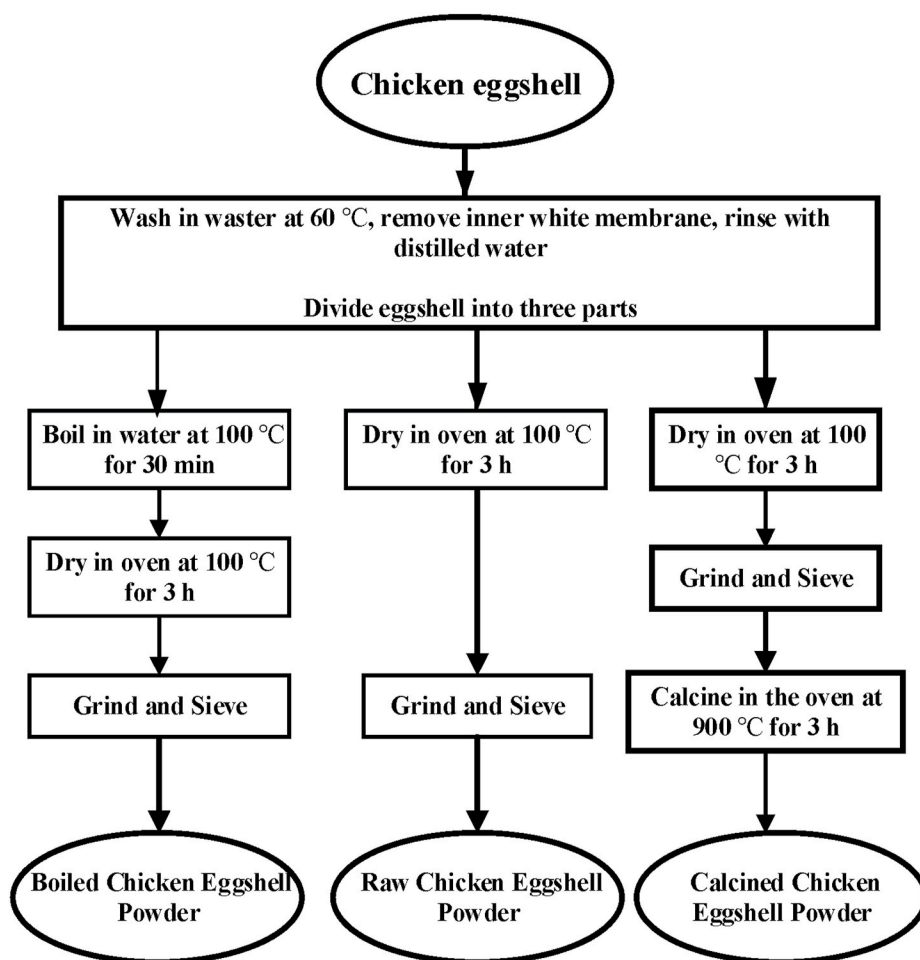


Fig. 2. Flowchart for modification of waste chicken eggshells into catalyst [109].

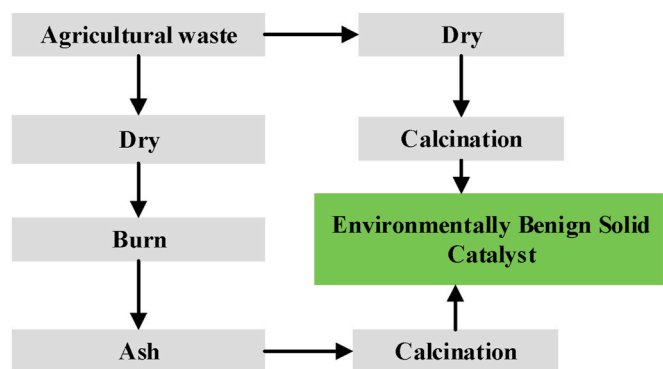


Fig. 3. Flowchart for the conversion of agricultural wastes into solid catalyst [65].

the performance of the agricultural wastes-derived solid materials for transesterification as well as purity and integrity of the products. Table 4 shows the summary of some of the processes and effects of the modification methods.

1.7. Physical mixing method

The physical mixing method involves the direct mixing or blending of two or more powdery materials. This is done before, during, or after pulverization of the materials in a mortar or grinder. By this, the output of the blended materials can benefit from the compositional, structural

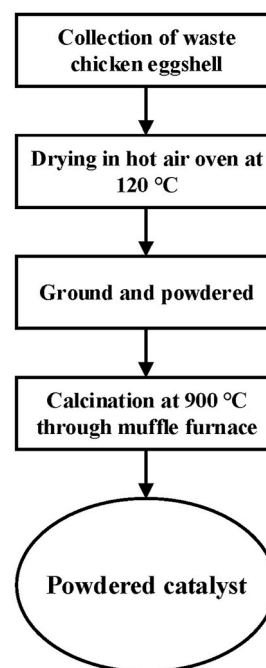


Fig. 4. Flowchart for the conversion of waste chicken eggshell into solid catalyst [111].

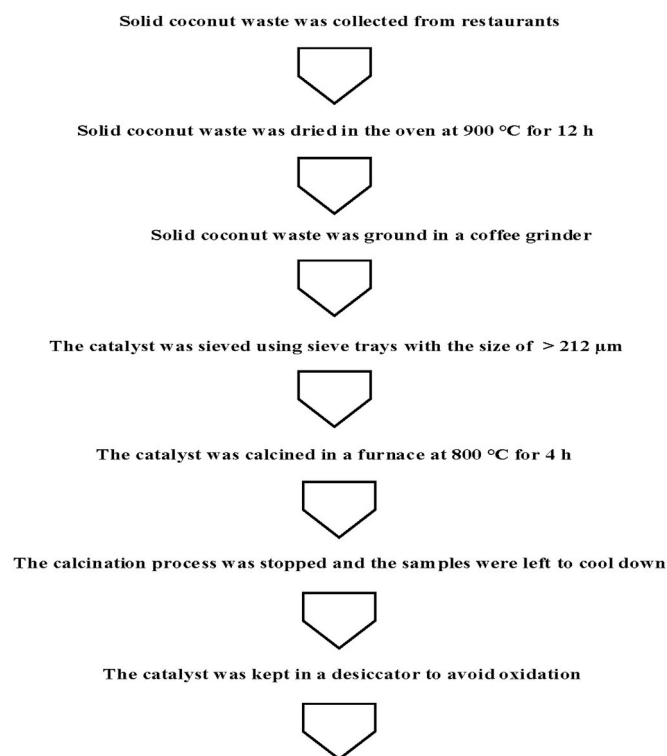


Fig. 5. Flowchart for the conversion of coconut waste into solid catalyst [112].

features, and physicochemical properties of the constituents of the mixture. In a recent research, Mansir et al. [114] mixed a metal oxide with CaO derived from waste eggshell for the conversion of WCO into biodiesel. The two metal oxides were converted into a slurry, thoroughly dispersed in a beaker, and calcined at a temperature of 900 °C in an oven. Similarly, Joshi et al. [113] mixed CaO derived from waste eggshell with Zinc oxide (ZnO) to transesterify *Jatropha* and *Karanja* oils into biodiesel.

In another research, Barium was mixed with CaO derived from waste *T striatula* shells for biodiesel production using WCO as feedstock. The resulting heterogeneous catalyst achieved better catalytic activity resulting into 98% FAME conversion rate, and high reusability [118]. Also, Ofori-Boateng and Lee [119] derived a bifunctional catalyst by physically mixing potash extracted from cocoa pod husks and MgO for the transesterification of soybean oil into biodiesel under optimum conditions. Similar results were reported by Jazie and Albaaji [120] when they used the mixture of eggshells and animal bones as a catalyst for the conversion of WCO into FAME. In all these instances, the blended catalysts performed better than the individual catalyst in converting WCO into biodiesel thereby justifying the extra efforts expended in modifying the catalysts by physical mixing.

1.8. Calcination method

During calcination, the solid catalysts, usually in powdery form, are subjected to high-temperature treatment in an oven or furnace. The purpose is to enhance the physicochemical properties and catalytic activity of the materials. During calcination, the specific surface area, pore size and volume, and active site concentration are improved for better catalytic performance [121]. Calcination temperature and time have been reported as the two major factors that have a great influence on the activity of heterogeneous catalysts [122]. Farooq et al. [73] and Sirisomboonchai et al. [123] who experimented with waste chicken bones and scallop shell respectively reported that calcination of these wastes at appropriate temperature and time led to improved conversion efficiency, reusability, and active surface area during transesterification.

When calcined CaO derived from waste oyster shells was used to convert WCO to FAME, the process witnessed reduced reaction time from 3 h to 2 h, lower reaction temperature from 75 °C to 65 °C, and increased biodiesel yield from 80% to 94.5% [124].

In a similar research, a mixed catalyst consisting of MgO and CaO derived from waste chicken eggshell was subjected to calcination at 900 °C for 4 h and applied for the transesterification of WCO into biodiesel. The calcined catalyst showed better product yield, purity, and reusability when compared with an uncalcined catalyst [125]. Basri et al. [126] experimented on the effect of calcination on mussel shell, cockle shell, and scallop shell at 700–1000 °C for 4 h. Due to the effects of the calcination, CaO, which is the major mineralogical component in mussel, cockle, and scallop shell was found to be 98.367%, 99.17%, and 97.529% respectively while the surface area was 89.91 m²/g, 59.87 m²/g, and 74.96 m²/g for mussel shell, cockle shell, and scallop shell respectively. The samples demonstrated a high degree of activity, product yield, and reusability. In a study, coconut husk was converted to a heterogeneous catalyst for the transesterification of *Jatropha* oil at room temperature of 45 °C. The coconut waste was converted into powder form according to the preparation methods and modified by calcination at 350 °C and showed higher conversion efficiency of 97% after 30 min reaction time when compared with uncalcined catalyst [127]. Similar outcomes were reported in the investigation conducted by Chakraborty et al. [81], Suryaputra et al. [128], Lih Lee et al. [129], and Roschat et al. [130] who improved the activity, selectivity, surface area, pore volume, conversion efficiency, and reusability of agricultural wastes derived heterogeneous catalyst by calcination.

1.9. Calcination-hydration-dehydration method

This modification method is an extension of the calcination method. It is to enhance the basic active site and the surface area of the catalysts by subjecting the calcined powder to hydration and drying. The calcined powder or ash is dispersed in deionized or distilled water and refluxed at an appropriate speed, temperature, and time. The resulting mixture is filtered and dried in the oven at a suitable temperature and duration. The solid product gotten from the oven is subjected to further dehydration by calcination to obtain pure oxides with better catalytic properties. Etim et al. [117] reported the optimal conditions for the process to include 200–600 rpm at 60–80 °C for 4–6 h for refluxing, 105–120 °C for 24 h for hydration, and a temperature range of between 500 and 650 °C for calcination. In a research, Asikin-Mijan et al. [131] subjected the waste powder derived from waste clamshell (*Meretrix*) to calcination at 900 °C for 4 h, refluxing at 60 °C at various duration, hydration at 100 °C for 24 h, and dehydration at 600 °C for 3 h. The CaCO₃ in the waste clamshell powder was converted to calcium hydroxide (Ca(OH)₂) which influenced the formation of Brønsted basic sites for higher basicity. The sample refluxed for 12 h was found to exhibit the best surface area, pore volume, and pore size distribution of 30.30 m²/g, 3.21 cm³/g, and 3.39–80.08 nm respectively. A conversion efficiency of 98% was achieved with the use of WCO as feedstock.

Calcium oxide derived from waste eggshells was modified by calcination-hydration-dehydration and used for the transesterification of waste frying oil. The waste eggshell was subjected to calcination at 900 °C for 2.5 h, followed by hydration at 60 °C for 6 h, and lastly by dehydration by calcination at 600 °C for 3 h. The modified CaO catalyst was found to be more active with a conversion efficiency of 94.52% when compared with 79.62% achieved with waste eggshell calcined at 900 °C and 67.57% recorded with uncalcined commercial CaO. The surface area and basic strength of the commercial CaO, waste eggshell calcined at 900 °C, and waste eggshell subjected to calcination-hydration-dehydration was found to improve with modifications. The modified catalyst was reused six times as a result of improved properties and performance [132]. The impact of the calcination-hydration-dehydration waste-derived solid catalyst modification technique was also demonstrated by Roschat et al. [133] when

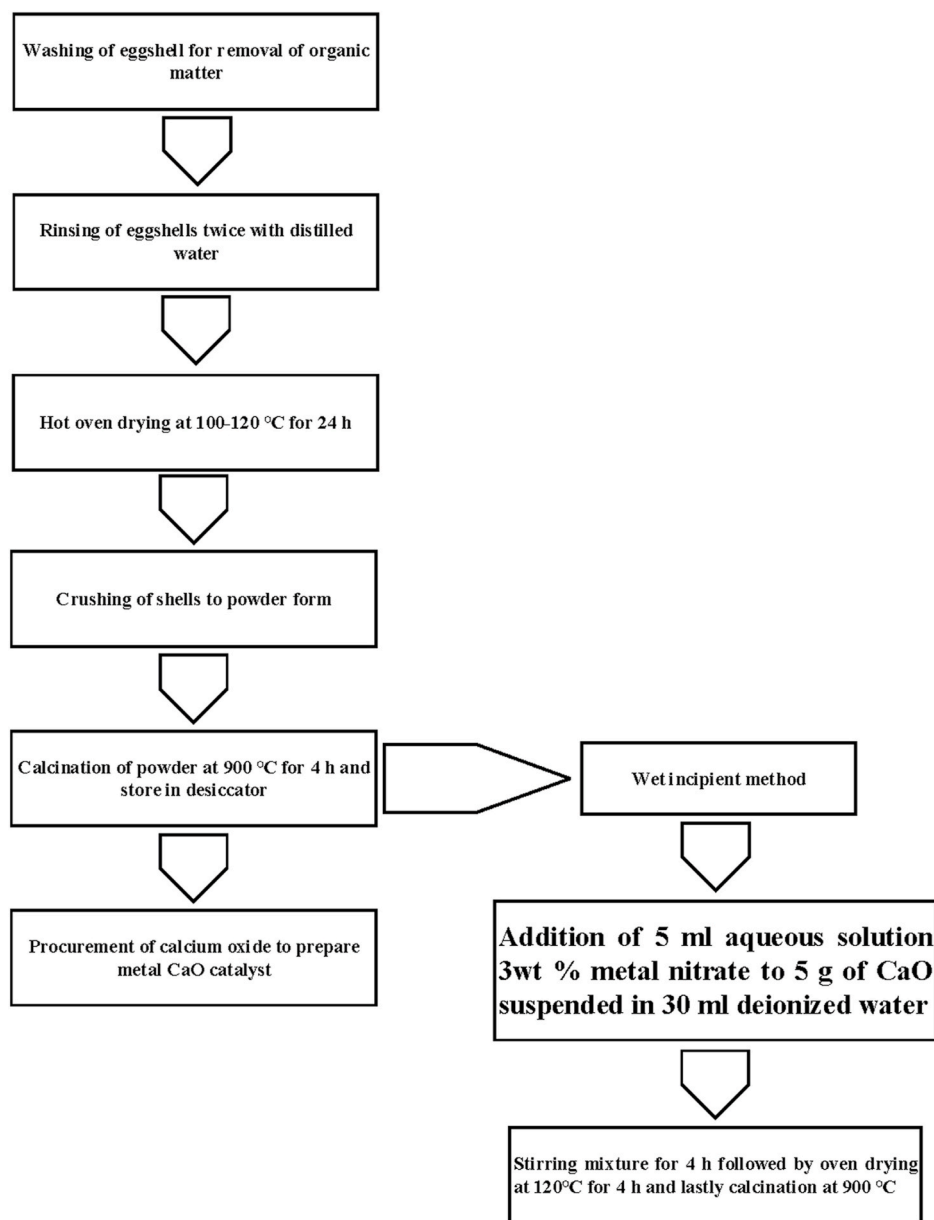


Fig. 6. Flowchart for the conversion of waste eggshell into solid catalyst [113].

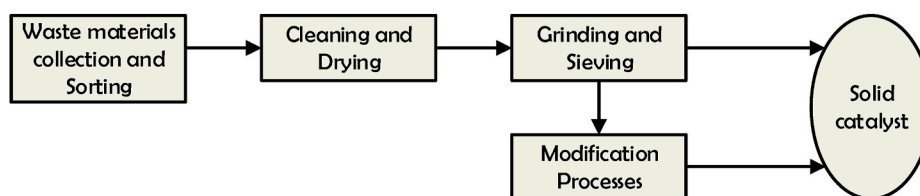


Fig. 7. Preparation methods for converting agricultural wastes to the solid catalyst.

they used eggshells, river snail shells, and golden apple snail shells as a green catalyst for the transesterification of palm olein oil into FAME. The powder derived from the waste shells was first subjected to high-temperature calcination at 800 °C in the air for 3 h with a heating rate of 10 °C/min. The calcined powder obtained was refluxed at 60 °C for 6 h, filtered and dried overnight at 100 °C and later dehydrated at 650 °C for 3 h. They reported an improved FAME yield of 94%, a better quality of fuel, and high catalyst reusability as a result of the

modification technique.

In another research, Harreh et al. [134], synthesized catalyst from *M. Lyrata* shells from the transesterification of crude *karanja* oil to *karanja* methyl ester. The catalyst modification processes include calcination at 900 °C for 2 h, refluxing in distilled water at 60 °C for 6 h, and dehydration at 600 °C for 3 h. The was found to display higher catalytic activity, specific surface area, pore diameter, and total pore volume, better reusability, and improved FAME yield of 97.3% compared with

Table 4

Process and effects of various modification techniques on agricultural waste-derived catalysts.

Catalyst source	Modification method	Process	Feedstock	Effect	Ref
Waste eggshell	Physical mixing	Commercial CaO was physically mixed with CaO derived from waste eggshell	Waste cooking oil	- Improved conversion efficiency - Easier separation - Lower catalyst cost	[114]
Waste eggshell	Physical mixing	Iodized water was added to the mixture of ZnO and CaO derived from the waste eggshell. The resulting slurry was later dried in a furnace.	Jatropha and Karanja oils	- High conversion efficiency - Better integrity and physicochemical properties of the biodiesel produced	[113]
waste T striatula shells	Physical mixing	Ba was thoroughly mixed with waste T striatula shells-derived CaO	Waste cooking oil	- High catalytic activity - Better conversion efficiency - More reusability	[118]
Cocoa pod husks	Physical mixing	MgO was mixed with potash derived from cocoa pod husks	Soybean oil	- Improved biodiesel yields - Better purity and integrity of the product - Improved engine performance of the biodiesel generated	[119]
Cuttlebone	Physical mixing	Sr was mixed with CaO derived from cuttlebone	Waste palm olein oil	- Improved conversion efficiency - Better surface area and thermal stability	[156]
Waste oyster shells	Calcination	CaO derived from the waste oyster shell was calcined at 1000 °C for 2 h	Waste cooking oil	- Reaction time reduced from 3 h to 2 h - Reaction temperature dropped from 75 °C to 65 °C. - Improved biodiesel yield from 80% to 94.5%.	[124]
Waste chicken eggshell	Calcination and physical mixing	CaO derived from eggshell was mixed with MgO and calcined at 900 °C for 4 h	Waste cooking oil	- The activation energy of 9.56 kJ/mol - Biodiesel yield of 98.37% achieved. - Catalyst reused for 6 cycles - conversion yield (98.37%) was achieved in a reaction time of 7.08 h, reaction temperature of 69.37 °C,	[125]
Waste mussel shell	Calcination	Waste shells were calcined at 700–1000 °C for 4 h, at a heating rate of 10 °C/min	Waste pal oil	- CaO content increased to 98.367% - The surface area increased to 89.91 m²/g - Improved product yield - Higher activity - Enhanced reusability	[126]
Waste cockleshell	Calcination	Waste shells were calcined at 700–1000 °C for 4 h, at a heating rate of 10 °C/min	Waste palm oil	- CaO concentration increased to 99.17% - Surface area increased to 59.87 m²/g - Improved product yield - Higher catalytic activity - High reusability	[126]
Waste scallop shell	Calcination	Waste shells were calcined at 700–1000 °C for 4 h, at a heating rate of 10 °C/min	Waste palm oil	- CaO content increased to 97.529% - The surface area increased to 74.96 m²/g - Improved biodiesel yield - Higher activity and selectivity - Enhanced reusability	[126]
Coconut husk	Calcination	Coconut waste was calcined at 250–500 °C for 1 h	Jatropha oil	- Biodiesel yield of 97% - Shorter reacting time	[127]
Waste clamshell (Meretrix)	Calcination-hydration-dehydration	Calcination at 900 °C for 4 h, hydration at 100 °C for 24 h, and dehydration at 600 °C for 3 h.	Refined palm olein cooking oil	- Formation of strong basic sites for higher basicity - Improved surface area, pore volume, and pore size distribution - The conversion efficiency of 98%	[131]
Waste eggshells	Calcination-hydration-dehydration	Calcination at 900 °C for 2.5 h, hydration at 60 °C for 6 h, and dehydration at 600 °C for 3 h.	Waste frying oil	- Improved catalytic activity - Enhanced conversion efficiency - Better surface area - Higher basic strength - High reusability	[132]
Waste shells	Calcination-hydration-dehydration	Calcination at 800 °C in the air for 3 h, hydration at 60 °C for 6 h, and dehydration at 650 °C for 3 h.	Palm olein oil	- Improved FAME yield of 94% - Better quality of fuel - High catalyst reusability.	[133]
M. Lyrata shells	Calcination-hydration-dehydration	Calcination at 900 °C for 2 h, hydration at 60 °C for 6 h, and dehydration at 600 °C for 3 h.	Crude karanja oil	- Higher catalytic activity - Higher specific surface area, pore diameter, and total pore volume - Better reusability - Improved FAME yield of 97.3%	[134]
Waste animal bones	Wet Impregnation	Calcination at 900 °C of waste animal bones powder, the addition of KOH solution to the powder, stirring, and heating at 120 °C for 12 h.	Jatropha oil	- Better catalytic activity - High FAME yield of 96.1% - Improved reusability for four times	[138]
Waste chicken eggshell	Wet Impregnation	CaO derived from waste chicken eggshell was calcined at 900 °C for 2.5 h, hydrated, and mixed with Fe ₃ O ₄ dehydrated at 105 °C for 24 h.	Palm oil off-grade	- High catalytic activity - Improved mechanical strength - High reusability up to ten times - FAME yield of 93.4%.	[139]
Waste eggshell	Bifunctional	CaO was derived from calcined waste eggshell powder. WO ₃ -Zr ₂ O ₃ was generated from the impregnation of H ₃ PO ₄ 12WO ₃ .XH ₂ O and ZrO ₄ H ₄ were mixed at 80 °C for 1 h and dehydrated at 120 °C. The mixture of CaO and	Waste palm oil	- Better surface area, pore volume, pore size, and crystalline size - Biodiesel yield of 94.1%.	[146]

(continued on next page)

Table 4 (continued)

Catalyst source	Modification method	Process	Feedstock	Effect	Ref
Waste Angel Wing Shells	Bifunctional	WO ₃ –Zr ₂ O ₃ was calcined at 650 °C for 5 h to produce WO ₃ –Zr ₂ O ₃ /CaO catalyst. Powder derived from waste angel wing was calcined at 900 °C for 2 h. CaO was dissolved into a dilute sulphuric acid solution to form a slurry. The slurry was filtered and calcined at 150 °C overnight to form sulphated CaO catalyst.	Palm fatty acid distillate	• Biodiesel yield of 98% • Increased specific surface area, pore volume, and pore size • High selectivity • High reusability • High stability	[147]
Waste chicken eggshell	Co-precipitation	Waste chicken eggshell powder mixed with nickel nitrate, cobalt nitrate, and anthill powder was dissolved in deionized water maintained at 80 °C and stirred for 5 h. Na ₂ CO ₃ was added to the resultant slurry and stirred at 80 °C for 2 h. The mixture was allowed to coagulate, filtered, and dehydrated at 110 °C for 12 h followed by calcination at 1000 °C for 4 h. CaO is generated from waste chicken eggshell and dispersed in deionized water, HCl, and tetraethyl orthosilicate. The obtained blend was refluxed at 65 °C for 2 h and 400 rpm, NH ₄ OH added and heated at 75 °C for 5 h until a gel is formed. The gel is dehydrated, at 110 °C for 20 h, crushed, sieved, and calcined at 850 °C for 3 h.	Waste frying oil	• Biodiesel yield of 90.23% • Reusable in four cycles	[148]
Waste chicken eggshell	Sol gel		Corn oil	• Product purity of 98.5% • FAME yield of 85.6% • Five cycles reusability	[152]

commercial CaO. Several other researchers including Erchamo et al. [135], Risso et al. [136], and Gupta & Rathod [137], among others, have demonstrated the application of calcination-hydration-dehydration modification techniques to improve the catalytic activity of the agricultural waste-derived heterogeneous catalyst for the transesterification of various oil feedstocks.

1.10. Wet impregnation method

The purpose of this modification is to improve the catalytic activity of the agricultural waste-derived solid catalysts for better yield, improved quality and purity of the product. In this method, the catalyst is thoroughly mixed with supporting compounds using a stirrer until a slurry is formed. The generated slurry is dried in the oven at an appropriate temperature for a given length of time until the slurry turns into a dry cake. The dried cake is thereafter pulverized, sieved using appropriate mesh, and subjected to high-temperature calcination. Etim et al. [117] enumerated the supporting compounds to include potassium hydroxide (KOH), sodium hydroxide (NaOH) or sodium sulphate (Na₂SO₄), and the preparation technique to involve refluxing and stirring time of 4–6 h, hydration in the oven at 100–120 °C at 12–24 h, and calcination temperature of 250–600 °C for a duration of 2–3 h. Nisar et al. [138] adopted the wet impregnation method to improve the surface area, chemical properties, catalytic activity, biodiesel yield, and reusability of waste-derived catalysts. In an experiment, waste animal bone was impregnated by KOH for the transesterification of *Jatropha oil* into FAME. The clean waste animal bones were dried, crushed into a fine powder, and the powder calcined at 900 °C. The calcined powder was soaked into a beaker containing KOH solution and stirred in a shaker maintained at 200 rpm to form slurry. The slurry was subjected to slow heating to produce dry cake. The dry cake was pulverized, sieved, and heated at 120 °C for 12 h to produce the catalyst. On application, the KOH-supported catalyst exhibited better catalytic activity, FAME yield of 96.1%, and reused four times.

The same method was adopted by Helwani et al. [139] when the waste chicken eggshell powder was impregnated by magnetite (Fe₃O₄) for the conversion of palm oil off-grade into FAME. The CaO generated from waste chicken eggshell was subjected to calcination at 900 °C for 2.5 h. An aqueous solution of Ca(OH)₂ was formed from the calcined CaO powder by dissolving the powder in water maintained at 70 °C and stirred vigorously. The aqueous solution of Ca(OH)₂ is mixed with Fe₃O₄ using a stirrer maintained at 700 rpm for 4 h to form a slurry. The slurry was dried in an oven maintained at 105 °C for 24 h to remove excess water in the mixture. The dried mixture was later subjected to high-temperature calcination for 4 h. The modified catalyst showed high

catalytic activity, improved mechanical strength, reused ten times, and the transesterification reaction yielded 93.4%. The effectiveness of the wet impregnation method of modification of CaO derived from agricultural wastes has been well reported in the literature by Kesica et al. [140] with CaO–ZnO, Liu et al. [141] with MgFe₂O₄–CaO, and Istadi et al. [142] with, K₂O/CaO–ZnO.

1.11. Bifunctional modification method

This is a recent methodology of catalyst modification of heterogeneous catalysts due to breakthroughs in technological techniques to the development of effective green catalysts. This approach generates catalysts that are amphoteric in nature, having both acidic and basic properties, and consequently improve acidic and basic sites for better performance [143,144]. This method allows for the combination of the physicochemical properties lacking in each catalyst to save cost, overcome the problems associated with the transesterification of feedstock with high free fatty acid (FFA), the water content of low-grade feedstocks like WCO, and improve product yield. For example, rather than using a two-step conversion process for feedstocks with high FFA value, a catalyst can be modified to become bifunctional and simultaneously perform both esterification and transesterification in a single step reaction under moderate reaction parameters [114,145].

Mansir et al. [146] applied a bifunctional modification method on CaO derived from the waste shell into a bifunctional catalyst for the conversion of unrefined waste palm oil into biodiesel. Tungsten-zirconia (WO₃–Zr₂O₃) was used to modify CaO to simultaneously perform esterification and transesterification of high FFA waste palm oil in a single-stage reaction. The waste eggshell powder was converted into CaO by calcination at 900 °C for 3 h while WO₃–Zr₂O₃ was synthesized through the impregnation of H₃PO₄12WO₃.XH₂O and ZrO₄H₄ at 80 °C for 1 h under intense stirring. The resulting solution was mixed with CaO by stirring for 3 h, followed by overnight dehydration in a clean furnace at 120 °C. The outcome was subjected to calcination at 650 °C for 5 h and thereafter used for the transesterification of low-grade waste palm oil into biodiesel. The developed WO₃–Zr₂O₃/CaO exhibited surface area, pore volume, pore size, and crystallite size of 13.8 m²/g, 0.20 cm³/g, 568.3 Å, and 47.5 nm respectively, and was able to transesterify a high FFA low-grade feedstock in a one-stage reaction with a biodiesel yield of 94.1%.

The same method was adopted in the production of bifunctional catalyst from CaO-based calcined angel wing shell sulphated catalyst for the synthesis of FAME from high FFA palm fatty acid distillate. Waste angel wing shells were cleaned, dried in the oven at 150 °C for 24 h, pulverized, and filtered with 250 mm sieve mesh. The CaO powder was

subjected to calcination at 900 °C for 2 h. The CaO was thereafter immersed in dilute sulphuric acid for 2 h at the prevailing temperature to form slurry. The slurry was filtered and rinsed with distilled water to eliminate any extra sulphate. The resultant compound was subjected to calcination at 150 °C overnight to form the bifunctional catalyst. The specific surface area, pore volume, and pore size of the sulphated CaO were found to be significantly higher than the unsulphated CaO. The use of sulphated CaO bifunctional catalyst possesses high catalytic activity, selectivity, and physicochemical properties potent enough to convert feedstock with an acid value of 127.21 mgKOH/g to biodiesel with a yield of 98% [147]. Generally, heterogeneous bifunctional catalysts exhibit encouraging properties like environmental compatibility, superior selectivity, thermal stability, and high degree of reusability.

1.12. Co-precipitation method

The co-precipitation technique of catalyst modification involves the dissolution of catalyst precursors into distilled water and mixed vigorously at high speed. Drops of base precipitating agents like potassium carbonate (K_2CO_3), ammonium hydroxide (NH_4OH), KOH, and NaOH are thereafter added to the solution and stirred for 3 h to maintain the pH at 10. The resultant mixture is allowed to coagulate and then dehydrated in an oven maintained at 100–120 °C for 24 h [114]. The dried sample is subjected to calcination in a furnace at an appropriate temperature and the resultant powder is deployed as a catalyst for biodiesel synthesis. This technique was adopted by Yusuff et al. [148] in their work to generate mixed oxides catalyst for the conversion of waste frying oil to biodiesel. Fine powder derived from waste chicken eggshell was mixed with nickel nitrate, cobalt nitrate, and anthill powder and dissolved in deionized water at 80 °C and stirred for 5 h. Na_2CO_3 was added to the resultant slurry to regulate the pH and kept in a fume hood with continuous stirring for 2 h and temperature of 80 °C. The slurry was allowed to coagulate and was filtered. The residue was dehydrated in an oven maintained at 110 °C for 12 h followed by calcination at 1000 °C for 4 h. The generated catalyst was found to exhibit high stability, caused a biodiesel yield of 90.23%, and reused in four cycles. The effectiveness of the coprecipitation method of catalyst modification has also been investigated and proven by other researchers including Gardy et al. [149], Pathak et al. [150], and Lee et al. [151].

1.13. Sol gel method

In this method, drops of butyl titanate and anhydrous ethanol are added and mixed with a solution of deionized water anhydrous ethanol, HNO_3 , and nitrate precursor at room temperature. After sustained stirring for 3 h, 200–600 rpm, and at room temperature, a yellowish viscose sol will be formed, congealed, and dehydrated at 80 °C for 24 h. The gel is pulverized, sieved, and subjected to high-temperature calcination [114]. In an experiment, Moradi et al. [152] generated CaO/SiO₂ for the transesterification of corn oil into FAME. The CaO was synthesized from waste chicken eggshell and dispersed in de-ionized water, HCl, while tetraethyl orthosilicate was later added. The resultant blend was refluxed at 65 °C for 2 h and a stirring speed of 400 rpm. An appropriate quantity of NH_4OH was added and heated at 75 °C for 5 h to allow extra moisture in the mixture to gradually evaporate and a viscose gel formed. The resultant gel is dehydrated, at 110 °C for 20 h, crushed, and sieved using an appropriate mesh. The obtained powder is subjected to calcination at 850 °C for 3 h in a clean furnace. The catalyst was effective in the production of FAME of 98.5% purity, a yield of 85.6%, and reusability of five cycles. Similar results were obtained by Habte et al. [153], Chen et al. [154], and Afsharizadeh and Mohsenna [155].

1.14. Characterization techniques for catalyst derived from agricultural wastes

Various techniques have been identified and used to investigate

materials with a view to understanding and measuring their properties and structures. Materials are subjected to mechanical, structural, thermal, optical analysis, electron microscope, and various mass spectrometry testing using photons, electrons, ions, etc to gather the necessary information for identification and groupings with a view to predicting their performance and behaviour. These techniques may be grouped as macroscopic, microscopy, spectroscopy, etc. Microscopy techniques use photons, ions, electrons, etc to carry out the surface and sub-surface structure mapping of the samples [157]. The spectroscopy techniques are to determine the chemical composition, composition variation, crystal structure, and photoelectric properties of the samples [158]. The macroscopic testing techniques apply the mechanical, thermal, density of a sample to determine its properties. Table 5 shows the major catalyst characterization techniques.

Over the years, researchers have used some of these characterization techniques to predict the suitability or otherwise of a particular material as a potential catalyst. The performance of a given material as a potential catalyst can be predicted by the outcomes of the characterization techniques. For example, information on the characteristics and properties such as pore size, surface area, elemental composition, molecular composition, etc can be obtained through the characterization techniques by both Brunauer–Emmett–Teller (BET) and X-Ray Diffraction (XRD) [109]. By characterization, it was discovered that the composition of CaO in an uncalcined chicken eggshell waste is 97.86%, while the 37.9% weight loss during thermogravimetric analysis (TGA) was due to the loss of moisture and CO₂ contained in the eggshell powder between 700 °C and 800 °C [159]. The type and nature of bonds between the

Table 5
Characterization techniques and their purpose [161–163].

Characterization techniques	Purpose
Microscopy	
Scanning Electron Microscopy (SEM)	Structural analysis
Brunauer–Emmett–Teller (BET)	Structural and specific surface area analysis
Transmission Electron Microscopy (TEM)	To study the morphological, compositional, and crystallographic data of samples
Field Ion Microscope (FIM)	Determination of the orientation atoms at the surface of a material
Scanning Tunneling Microscope (STM)	Apply electron beams or light to conduct mapping of the surface atom of material
Atomic Force Microscope (AFM)	Measurement of chemical, magnetic, mechanical, electrical properties of materials to generate 3D information of surface defects, scribes, and scratches.
X-ray diffraction topography (XRT)	Determination of the quality and defects in crystal materials.
Scanning probe microscopy (SPM)	Observation of surface quality of the sample.
Spectroscopy	
X-ray Photoelectron Spectroscopy (XPS)	Surface chemistry analysis
Fourier transform infrared spectroscopy (FTIR)	Determination of specific functional groups of materials
X-Ray Diffraction (XRD)	To identify and determine the sample's composition, phase, or structure
Energy-dispersive X-ray spectroscopy (EDX, EDS)	Elemental analysis
X-ray photoelectron spectroscopy (XPS)	Determination of the chemical, electronic, elemental composition of materials as well as nature, and relative content of each functional group in a material.
Nuclear magnetic resonance spectroscopy (NMR)	Provision of information on the molecular structure and dynamics of material using the spectra
Macroscopic	
Mechanical testing	Determination of mechanical properties of materials
Differential thermal analysis (DTA)	Measurement of the endothermic and exothermic phase transitions of material.
Thermogravimetric analysis (TGA)	Thermal stability analysis
Differential scanning calorimetry (DSC)	Determination of heat flow and heat capacity of materials

atoms, ions, or molecules in a given agricultural waste-derived potential catalyst can be determined by the fourier transform infrared spectroscopy (FTIR) technique [160].

1.15. Recent progress in the application of agricultural wastes-derived catalyst

Over the past decades, researchers have intensified efforts in converting various agricultural wastes into green heterogeneous catalysts in a bid to reduce the pump price of biodiesel and other environmental benefits. Many factors including the types of agricultural wastes, particle size, catalyst loading, synthesis and modification methods, characterization techniques, cycle of reusability, etc have continued to be the major research points towards maximizing the benefits of waste-derived catalysts. Since catalyst surface area influences the catalytic activity of solid catalysts, researchers have been tending towards minimizing the particle size of the catalyst with the adoption on nanoparticle size for better performance. Though modification techniques such as calcination, calcination-hydration-dehydration, wet impregnation, sol-gel, bifunctional, etc impose added cost and infrastructure demands on the catalyst generation, researchers are working towards optimizing these parameters for biodiesel production [11].

Concerning the production methods, the use of a three-neck-round bottom flask for the laboratory-conducted transesterification and esterification processes remained the simplest and most used. The round bottom flask is fitted with a reflux condenser, thermometer connected to the water-cooling condenser. The apparatus also contains a magnetic stirrer or an electric heater with a mechanical stirrer inserted into the flask. The use of a water bath maintained at an appropriate temperature has been preferred over putting the round bottom flask directly over an electric stove. This is to ensure uniform temperature and minimize heat loss in the flask. However, production parameters such as reaction temperature, reaction time, alcohol:oil ratio, stirring speed, etc are major contributing factors to biodiesel yield. Various authors have explored the use of experimental design software like response surface methodology (RSM) based on Box-Behnken design (BBD) and analysis of variance (ANOVA) statistical analysis Experimental design and data analysis to optimize the production [164,165]. This is towards reducing material quantity and cost of production.

In the future, more investigations are required on the potential of some readily available but underutilized agricultural wastes as potential catalysts. Wastes such as orange peel, maize cob, potato peel, sugarcane bagasse, etc should be explored and tested. An efficient preparation method involving the use of technological innovations should be employed in the conversion of the wastes particularly at a competitive industrial scale. The use of combinations or blends of two or more heterogeneous catalysts developed from agricultural wastes should be investigated to ensure better catalytic performance. More targeted investments in the amalgamation of modification techniques capable of ensuring high basic sites, better surface area, improved pore sizes, and increased acidic density should be encouraged. More investigations are needed on the novel method of feedstock hybridization to solve the problem of seasonal scarcity, availability, and unreliable supply chain. By employing hybridization or blending of feedstock, the advantages of a given feedstock can be explored to improve the other feedstock and improve the product yield and better biodiesel properties.

2. Conclusions

The present work has reviewed the potential of converting agricultural wastes to heterogeneous catalysts for biodiesel synthesis. The following conclusions are drawn from the study.

The abundant agricultural wastes which are constituting nuisance and increasing the cost of disposal can be converted to other uses including catalysts and other bioplastics. The sanitation problem created by inappropriate agricultural wastes disposal can be solved by waste

recycling.

The categorization of agricultural wastes is extended to include wastes generated from the consumption and utilization of agricultural products. These classifications will give room for a broader and more encompassing look at the menace created by these wastes.

A more inclusive preparation approach has been developed for the conversion of agricultural wastes to heterogeneous catalysts. The application of these waste-derived catalysts will not only reduce the cost of waste recycling but also ensure a reduction in the pump price of biodiesel.

Various preparation and modification techniques such as physical mixing, calcination, calcination-hydration-dehydration, wet impregnation, bifunctional, sol gel, co-precipitation are useful approaches in improving the activity of waste-derived heterogeneous catalysts. A combination of any of these modification techniques is proposed to further improve the performance of the catalysts.

The potential and performance of agricultural wastes-derived heterogeneous catalysts can be tested using various characterization techniques without necessarily using the catalysts in real biodiesel production. This will not only save materials but also give an insight into the suitability or otherwise of the agricultural wastes-derived solid catalyst for transesterification.

Overall, the various biocatalysts derived from agricultural wastes are highly active, reusable, and easy to synthesize. These waste-derived catalysts eliminated the use of costly commercial catalysts, reduction in the price of catalysts, and environmentally friendly. The use of agricultural wastes-derived heterogeneous catalysts not only ensures easier biodiesel purification but such discarded catalysts can be used as manures.

Going forward, the use of optimization and statistical tools are recommended in investigating the effects of the production parameters including catalyst particle size, catalysts loading, reaction time, reaction temperature, etc on the performance of the catalyst. This will not only save time and energy cost but also allow judicious use of materials and feedstocks thereby reducing the cost of production.

More agricultural wastes should be tested to determine their suitability as green catalysts. Agricultural wastes such as orange peels, sugarcane bagasse, maize cob, potato peels, groundnut shells, etc have not been adequately tested by researchers to determine their potentials as low-cost heterogeneous catalysts for biodiesel synthesis.

Statement of novelty

This work presents a novel classification of agricultural wastes that is inclusive and all-encompassing. An innovative preparation protocol for the conversion of agricultural wastes to catalysts was unearthed. After a comprehensive study of the effects of the various modification techniques on the performance of heterogeneous catalysts derived from agricultural wastes, the authors advanced the combination of two or more modification techniques for improved catalytic performance. The current effort is one of the few comprehensive interventions in the study of the generation of catalysts from agricultural wastes, and it is bound to increase the available knowledge in this field.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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