catalysts

Review

Application of Agricultural Waste as Heterogeneous Catalysts for Biodiesel Production

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Abstract: In this modern era, it has become essential to transform waste materials into valuables because of their excessive availability, along with achieving the targets of environmental protocols and waste management policies. With a growing population, the utilization and consumption of agricultural products have been increased extensively. In addition, it has increased the probability of agricultural waste generation. Waste produced from agricultural sources is considered as a viable source for synthesizing economical and ecofriendly catalysts and suitable ways for its disposal are sought. This study is targeted at agricultural waste-derived heterogeneous catalysts, which have been effectively employed for biodiesel generation. The types of agricultural waste, catalyst synthesis techniques, recent literature stated for agricultural waste-derived catalysts to produce biodiesel, the elemental composition and catalytic activity of agricultural waste ashes, the effect of reaction parameters to maximize biodiesel yield and catalyst reusability have been discussed. This work concludes that catalysts derived from agricultural waste are efficient in transesterification reaction, and they are easy to produce, and are cheap and ecofriendly. Moreover, this study encourages researchers to see the options for unexplored agricultural waste, which can be potentially converted into useful materials

Keywords: agricultural waste; heterogeneous catalysts; biodiesel; yield

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1. Introduction

Global energy consumption, particularly, from petroleum sources has increased owing to the fast growth in the worldwide population, urbanization, and industrialization; hence, it has triggered to a raise in emissions levels causing global warming and antagonistic medical issues. The threat of fossil fuel depletion in the upcoming years has motivated the scientific community to explore alternative renewable energy resources to avoid a situation of extreme energy crisis, along with environmental protection purposes. Therefore, the quest for renewable and ecofriendly fuels has become mandatory and is the need of the hour. In the past two decades, vegetable oil-derived methyl esters have gained popularity as a promising substitute for conventional diesel and is termed biodiesel [1–4].

Biodiesel is a renewable fuel possessing similar properties to diesel fuel, such as combustion, flow, chemical composition, etc., and therefore, its combination with mineral diesel can be effectively utilized in diesel engines, directly or with some modifications [5,6].

In addition, the absence of sulfur and aromatic components in biodiesel contributes to a higher burning efficiency, higher cetane number, and better lubricity characteristics, along with a reduction in emissions of particulate matter (NO_x, CO, etc.) [7]. Therefore, biodiesel combustion could be more environmentally friendly compared to conventional diesel. Regrettably, there exists extensive complications associated with the commercial viability of biodiesel owing to food vs. fuel competition and its high price. The utilization of inedible oils, waste oils, and cost-effective catalysts would facilitate reducing biodiesel production costs [8,9]. Numerous efforts have been made to generate biodiesel from variety of feedstocks [10], while the exploration of cost-effective efficient catalysts is being examined for upscaled biodiesel production.

Transesterification is considered to be an effective technique for transforming oils or fats into biodiesel using homogeneous catalysts [11]. Despite displaying a good catalytic performance in transesterification reactions, homogeneous catalysts are naturally corrosive for equipment and their difficult removal from the mixture implies further operational expenses. In addition, purification and water washing stages are required to achieve standard quality fuel, and results in high production costs [10,12]. Quite the opposite, the usage of solid/heterogeneous catalysts to produce biodiesel has been shown to be feasible and effective due to their simple separation, being less corrosive and their environmentally friendly nature [13]. These catalysts are effectively reusable and therefore, enhance production outcomes. There exists an extensive number of applications of heterogeneous (acid/base) catalysts in the literature. The utilization of a base catalyst in transesterification has been evaluated as being relatively noticeable owing to the issues of the high temperature and prolonged reaction times required for the acid catalyzed process of transesterification [14]. Consequently, the situation caused researchers to explore other types of heterogeneous base catalysts, such as calcined hydrotalcite, metal oxides, anion exchange resins, and supported alkali metals [15–18].

It would be a excellent opportunity if heterogeneous catalysts could be synthesized from abundantly available waste materials, such as agricultural waste, to cut down on the catalyst costs associated with biodiesel production. Therefore, the usage of waste materials for catalyst generation could make the system more economical and more eco-friendly, in addition to producing the aimed product. Catalyst synthesis from waste materials has been increasingly reported recently because of the excessive availability of waste resources, as well as their disposal issues. The characteristics of the obtained catalysts is notably affected by the type of waste origin, and consequently the catalytic products for a particular use are often made from an analogous category of materials [16].

The expansion of soil for agricultural production and technological development for the green revolution are major aspects responsible for increased agricultural production [19,20]. Twenty-four million tons of food are produced by the agricultural sector around the globe, which also causes about health-related issues for the environment if their waste disposal is not appropriate [19]. Although food is a necessity obtained from agriculture, its environmental effects are also obvious. The effective ways of tackling agricultural solid wastes are needed to avoid the ill effects of agriculture on marine life, human health, and overall ecosystems [21]. For instance, if this waste is left unhandled or burnt directly, it may create air, water, and land pollution.

The prioritization of food and energy production for the increasing population has been mandated by global leaders and the population is expected to increase to about 10 billion by 2050. However, this target should be accomplished with zero solid waste, lower emissions, along with minimum fossil fuel consumption [22,23]. Moreover, food generation for an increasing population, industrial requirements, and animal feed are predicted to be included in the increased agricultural production. Agricultural activities involve the generation of solid waste at each step, depending on the category of product required, processing methods, and purpose of usage. The major producer of agricultural solid waste is farming activities, and may also encompass other activities that are connected with farming and the food chain. The purpose of this study was to focus on the literature reported on agricultural waste-based heterogeneous catalysts that are effectively used for biodiesel generation. The types of agricultural waste, catalyst synthesis techniques, recent literature on agricultural waste-derived catalysts to produce biodiesel, the elemental composition of agricultural waste ashes, the effect of reaction parameters in maximizing biodiesel yield, as well as catalyst reusability have been elaborated. The work concludes that catalysts derived from agricultural waste are efficient in transesterification reactions, easy to produce, cheap, and ecofriendly. Moreover, this study can encourage researchers to see the possible uses of unexplored agricultural waste, which can be potentially transformed into valuable materials. With respect to future prospects, alternate applications of these agricultural waste-based catalysts can also be explored based on the data reviewed in this article.

2. Types of Agro-Industrial Wastes

2.1. Agricultural Residues

Agro-industrial waste is categorized into two types, agricultural residues and industrial residues, as indicated in Figure 1 [24].

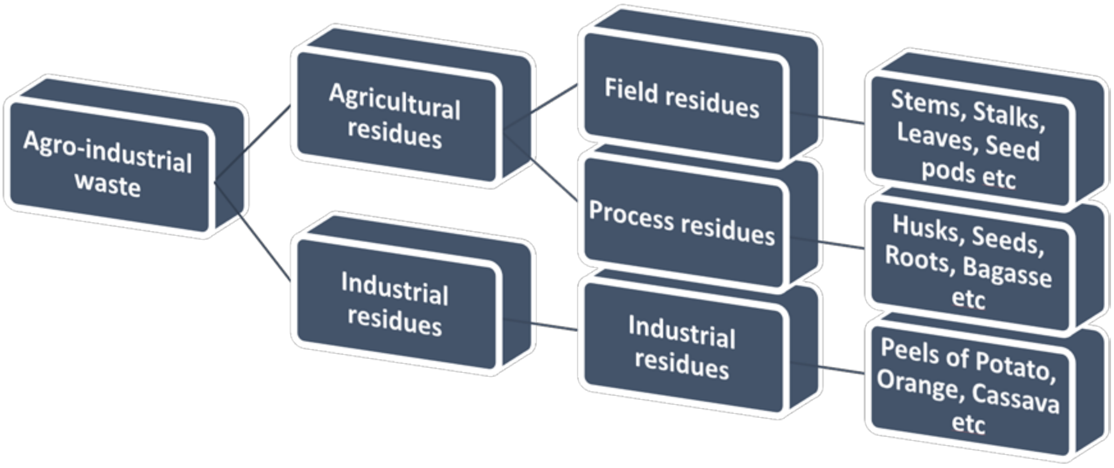


Figure 1. Categorization of agro-industrial waste.

Agriculture residues are written off as field residues and process residues; after harvesting, the waste that remains in the field are termed field residues, which consists of stalks, leaf stems, and seed pods etc whereas, the process residues are the remains up to the point where the crop is transformed into another valued resource. These remains are comprised of leaf straw, stem, husks, bagasse, stalk shell peels, roots, etc.

2.2. Industrial Wastes

Food processing manufacturers, such as potato chip, juice, sweets, and fruit industries, generate huge quantities of organic residues each year that can be used as diverse energy sources. For instance, fruit peels, coffee pulp, and husks are generated as waste by the juice industry, the coffee industry, and cereal industry, respectively. Each year, billions of tons of food industry waste are generated globally, such as peels from different fruits, sugarcane bagasse, wheat straw residues, rice straw remains, etc. For instance, in the 1990s, rice straw and wheat straw residues were estimated to have values of 673.3 and 709.2 million metric tons globally [25]. These huge quantities of waste, generated each year, require legal methods for proper management and potential utilization to lessen the ecological burden.

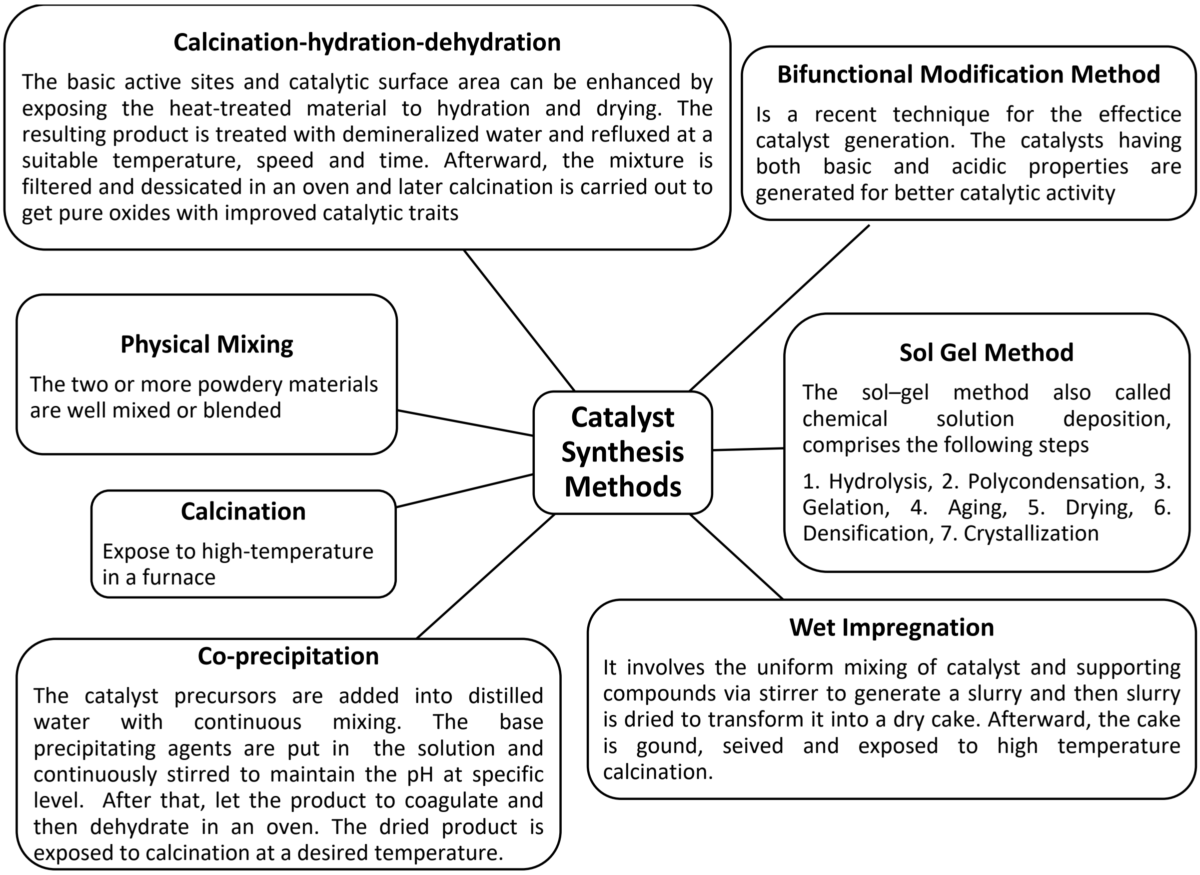
3. Waste to Valuables

The global trend of transforming waste into valuable materials for various applications is gaining popularity owing to environmental concerns. Recently, the literature has reported various commercial heterogeneous catalysts for transforming different feedstocks into biodiesel, including calcium, magnesium, and aluminum-based catalysts. Although some of these heterogeneous catalysts are found to be highly effective, they are still considered unsustainable for producing biodiesel owing to the labor-intensive methods involved in their synthesis. In addition, these catalysts are non-renewable, sourced commercial catalysts and therefore their usage creates disposal issues and ecological concerns. On the other hand, agricultural waste-based catalysts, such as banana and orange peels, cocoa pod husk ash, Musa balbisiana peel ash, leave ash, banana trunk ash, coconut husk and ash, are non-toxic, cheap, non-corrosive, and are readily available. These catalysts are shown to be effective, biodegradable, and a feasible way of managing agricultural waste by means of biodiesel production. In addition, agricultural waste shows diverse uses and applications, particularly in the production of biogas, biofuels, animal feed, mushroom, biofertilizers, and for other chemicals [26].

Synthesis Techniques for Catalysts Produced from Agricultural Wastes

Numerous methods have been utilized in the published works for the alteration of agricultural waste into catalysts. These techniques require careful selection to attain desired catalytic potentials. The synthesis methodology for transforming agricultural waste into catalysts entails the collection and sorting of different agricultural wastes from different places, and their delivery to scientific laboratories for further processing. After collection and sorting, waste is cleaned to detach impurities and then dried in an oven or in sunlight. Oven drying is quicker and has a controlled drying rate, but it is energy intensive. Sun-drying is inexpensive but time-consuming and the solid waste is vulnerable to impurities. After completion of the drying process, the material is milled to an appropriate size using meshes. Figure 2 shows the general procedure for the extraction of solid catalysts from waste resources. After that, the powdered material is exposed to a high-temperature heat treatment (calcination) for a specific time. The performance of the catalyst is greatly controlled by the temperature and time of calcination; therefore, this requires careful selection of both parameters. In addition to calcination, other modification techniques exist to upgrade the catalytic properties and these are indicated in Figure 3. Catalysts can either be directly utilized after milling and sieving or some modification methods, such as calcination, wet impregnation, physical mixing, co-precipitation, hydration, can be applied for the improvement of catalytic properties [27].

Figure 2. Generic synthesis method for transforming agricultural wastes into a solid catalysts.



Calcination-hydration-dehydration

The basic active sites and catalytic surface area can be enhanced by exposing the heat-treated material to hydration and drying. The resulting product is treated with demineralized water and refluxed at a suitable temperature, speed and time. Afterward, the mixture is filtered and dessicated in an oven and later calcination is carried out to get pure oxides with improved catalytic traits

Bifunctional Modification Method

Is a recent technique for the effectice catalyst generation. The catalysts having both basic and acidic properties are generated for better catalytic activity

Physical Mixing

The two or more powdery materials are well mixed or blended

Sol Gel Method

The sol–gel method also called chemical solution deposition, comprises the following steps

1. Hydrolysis, 2. Polycondensation, 3. Gelation, 4. Aging, 5. Drying, 6. Densification, 7. Crystallization

Calcination

Expose to high-temperature in a furnace

Wet Impregnation

It involves the uniform mixing of catalyst and supporting compounds via stirrer to generate a slurry and then slurry is dried to transform it into a dry cake. Afterward, the cake is gound, seived and exposed to high temperature calcination.

Co-precipitation

The catalyst precursors are added into distilled water with continuous mixing. The base precipitating agents are put in the solution and continuously stirred to maintain the pH at specific level. After that, let the product to coagulate and then dehydrate in an oven. The dried product is exposed to calcination at a desired temperature.

Figure 3. Catalyst synthesis methods for biodiesel production using agri-waste [27–30].

4. Evolution and Development of Agricultural Wastes-Derived Catalyst

Owing to environmental concerns and waste management policies, several investigators have started to make efforts to transform different types of agricultural waste into green catalysts to attain cost-effective production processes and other ecological benefits. The various important factors, such as types of agricultural waste, catalyst preparation techniques, particle size, morphology, active site density, catalyst basicity, and reusability, have been considered as key research points to attain the benefits of agricultural waste-derived catalysts. Moreover, reaction constraints, such as alcohol/oil molar ratio, catalyst percentage, temperature, and reaction time are required for optimization to get a maximum biodiesel yield.

For instance, waste tucuma peels, heat-treated at 800 °C for 4 h, were applied as an effective solid catalyst in transforming soybean oil into biodiesel, displaying 97.3% yield, under specific reaction conditions [31]. Similarly, in two different places, banana peels (Musa acuminata) and wild banana peels (Musa balbisiana Colla) after open-air burning and calcination (700 °C for 4 h), respectively, were utilized as solid catalysts for biodiesel production with yields greater than 98% in both cases [32,33]. In another study, banana peduncle upon calcination at 700 °C for 4 h (ramping rate: 5 °C/min) demonstrated excellent catalytic effectiveness with more than 98% biodiesel conversion [34]. The discussed cases indicate that agricultural waste, after calcination, or open-air burning in some cases, showed good catalytic properties for getting biodiesel from different sources of oil.

In another investigation, the waste plant Sesamum indicum (burnt and further heat-treated at 550 °C for 2 h) demonstrated an excellent catalytic performance in transformation of sunflower oil into biodiesel with a biodiesel yield of 97.9% [35]. In another study, waste peanut husk calcined at the temperature of 900 °C for 2 h and further modified with Li_2CO_3 was effectively employed as a solid catalyst for transforming soybean oil into biodiesel [36]. Even pineapple leaf ash has been used for heterogeneous catalyst development after simple calcination and was employed for converting soybean oil into biodiesel, achieving a 98% yield [37]. In another report, Tectona grandis leaves were calcined at 700 °C to synthesize a solid catalyst and this was applied in the transformation of waste cooking oil into biodiesel with a 100% yield [38]. The major ingredients found in leaf ash are oxides of calcium, potassium, and magnesium, which are responsible for the catalytic activity. Moreover, seed ashes have also been applied as a catalyst for transesterification reactions. In other research, Acai seed ash was heat-treated at the temperature of 800 °C for 4 h to transform it into a catalyst carrying the main elements of metal oxides and carbonates. The synthesized catalyst was employed in soybean oil based biodiesel generation. The highest biodiesel yield of 98.5% was achieved after 100 min maintaining M/O:18:1, temperature: 60 °C, and a catalyst amount of 12 wt.% [39]. Again, the oxides and carbonates of different metals play important roles in providing active sites for reaction. Therefore, it can be deduced that high temperature heat treatment, in most cases, is sufficient to convert agricultural waste into catalytic products. Similarly, different types of agricultural waste shells, plants, and leaves upon burning and after application of some modification methods, such as calcination, co-precipitation, and bifunctional modification, have been successfully converted into efficient heterogeneous catalysts to produce biodiesel from different oil sources, as presented in Table 1. In addition, ecofriendly methods must be chosen for catalyst synthesis, keeping in mind the sustainability issues when large-scale production is needed. However, most of these catalysts have been evaluated in laboratory scale experiments. Pilot plant studies and their application in large-scale biodiesel production should also be considered to justify their commercial suitability.

4.1. Elemental Composition and Catalytic Activity of Agricultural Waste Ashes

As discussed earlier, different types of agricultural waste, upon treatment, such as calcination, burning, etc., are found to be efficient and effective heterogeneous catalysts in transforming a variety of oil sources into biodiesel. The elemental compositions of some of the agricultural waste ashes in their calcined forms are provided in Table 2. This indicates that most of the agri-waste ashes, such as tacuma peels, orange peels, walnut shells, and Musa balbisiana peels contain potassium and calcium as major components, which demonstrate catalytic activity in the trans-esterification reaction, either in oxide or carbonate forms. It has been reported that mixed metal oxides displayed better catalytic activity in transesterification reactions in comparison with pure metal oxides [69]. The presence of numerous materials as catalytic components in the transesterification reaction demonstrate a synergistic effect that increases the overall catalytic performance. For instance, the presence of K_2O as a prime component in Mangifera indica peel ash, which is predominantly accountable for the basic strength of catalysts. Moreover, the existence of CaO and MgO in Mangifera peel ash could additionally increase the catalytic performance in reactions while other amphoteric metal oxides may assist both acid-catalyzed transesterification of oil and esterification of FFAs of vegetable oil to biodiesel [70]. In addition, the variation in the elemental composition of different waste ashes may vary the catalytic activity in terms of biodiesel yield. Therefore, such waste resources, which are otherwise an ecological burden, can be easily converted into valuable materials, such as catalysts that facilitate renewable energy production outcomes. Here, in this review, elemental composition analysis of heterogeneous catalysts made from various agricultural waste materials has been analyzed, in particular, for converting oil into biodiesel. The application of these waste ashes as catalysts is not limited to biodiesel generation. The effectiveness of these catalysts may also be tested for other applications, such as wastewater treatment and chemical transformations.

Table 1. Agri-waste-derived catalysts for biodiesel generation.

Agri-Waste	Catalyst Preparation	Catalyst	Oil Used	Reaction Parameters (A/O, Catalyst wt.%, Time, Temperature)	Yield	References
Waste tucuma peels (Astrocaryum aculeatum Meyer)	Calcination for 4 h at 800 °C	Components involved (K, P, Ca, Mg)	Soybean oil	15, 1, 240, 80	97.3	[31]
Banana peels (Musa acuminata)	Completely burned in air to produce ash.	K_2O	Soybean oil	6, 0.7, 240, 25	Y = 98.95	[33]
Pomelo peels	Calcined for 2 h at 600 °C in nitrogen environment, the specific amount of pomelo peel ash was mixed with KOH solution for 2 h and filtered and then washed with demineralized water before final drying. After that, the ash powder was mixed with the K_2CO_3 impregnating solution to synthesize catalyst.	K_2O and K_2CO_3	Palm oil	8, 6, 150, 65	Y > 98	[40]
Wild banana peels (Musa balbisiana Colla)	Calcination for 4 h at 700 °C.	High percentage of potassium	WCO	6, 2, 180, 60	Y = 100	[32]
Pineapple (Ananás comosus) leaves ash	Calcination for 2 h at 600 °C and for 1 h at 900 °C.	Catalytic performance may be owing to the reasonable proportion of K, Ca and Mg	Soybean oil	40, 4, 30, 60	Y = 98	[37]
Waste Brassica nigra plant	Burnt and heat-treated at 550 °C for 2 h.	K_2O, K_2CO_3 and KCl	Soybean oil	12, 7, 25, 65	Y = 98.79	[41]
Waste Sesamum indicum plant	Burnt and calcined at 550 °C for 2 h.	Due to K and Ca components	Sunflower oil	12, 7, 40, 65	Y = 97.9	[35]
Banana peduncle	Calcination for 4 h at 700 °C.	The presence of metallic components such as K, Ca, and Mg	Ceiba pentandra oil	9.2, 1.978, 60, 70	C = 98.69 ± 0.18%	[34]
Musa paradisiacal (plantain) peels	Calcined at 500 °C for 3.5 h.	The catalytic activity may be owing to high proportion of potassium	Thevetia peruviana oil	0.3 (v/v), 3.0% (w/v), 90, 60	Y = 94.87	[42]
Acai seed ash	Calcination for 4 h at 800 °C.	The major components are metal oxides and carbonates	Soybean oil	18, 12, 60, 100	Y = 98.5	[39]
Walnut shell ash	Burnt and calcined at 800 °C.	Ca, K, Mg, Si	Sunflower oil	12, 5, 10, 60	Y = 98	[43]
Waste cupuaçu (Theobroma grandiflorum) seeds	Calcined for 4 h at 800 °C.	The catalytic activity mainly attributed to potassium	Soybean oil	10, 10, 480, 80	Y = 98.36	[44]

Table 1. *Cont.*

Agri-Waste	Catalyst Preparation	Catalyst	Oil Used	Reaction Parameters (A/O, Catalyst wt.%, Time, Temperature)	Yield	References
Tectona grandis leaves	Calcination at 700 °C for 4 h.	Heterogeneous base catalyst having CaO, K_2O, MgO, K_2CO_3, SiO_2	Waste cooking oil	6, 2.5, 180, 25	Y = 100	[38]
Waste rice-straw	First, heat treated for 5 h at 700 °C. The specific calcined amount was mixed with 1 M NaOH solution and performed boiling for 2 h in a flask and dried. After drying, again calcined at various temperatures between 350 °C and 500 °C.	Sodium silicate (Na_2SiO_3)	Waste cooking oil	15, 3.5, 150, 65	Y = 93.7	[45]
Waste rubber seed shell	Calcined at 800 °C	CaO generated from rubber seed shells, upon calcination indicated basic catalytic properties	Rubber seed oil	0.2 v/v, 2.5 g, 60, 60	Y = 83.06 ± 0.013%	[46]
Musa acuminata banana trunk ash	The trunk was burnt and ground to a fine ash catalyst.	Oxides of potassium, calcium and magnesium deliver strong basic sites on catalytic surface	Soybean oil	6, 0.5 g, /, 25	Y = 98.39	[47]
Cocoa pod husk-plantain peel blend	Calcined at 500 °C for 4 h.	K, Mg and Ca	Honne seed oil	15, 4.5, 150, 65	Y = 98.98	[48]
Wheat bran ash	Calcined at 700 °C for 4 h and CaO was obtained from the water scale taken from the distillation assembly. After washing with demineralized water, precipitated were dried at 120 °C for 24 h. Next, the temperature was elevated to 900 °C and the precipitates were calcined for 2 h at 900 °C. The blend of precipitate (40 wt.%) and wheat bran (60 wt.%) ash was synthesized as catalyst.	Wheat ran ash/CaO	Waste cooking oil	12, 11.66, 114.21, 54.6	Y = 93.6	[49]

Table 1. *Cont.*

Agri-Waste	Catalyst Preparation	Catalyst	Oil Used	Reaction Parameters (A/O, Catalyst wt.%, Time, Temperature)	Yield	References
Waste orange peel	Dried peels were ground and blended with KOH in a specific ratio for carbonization and activation under hydrothermal conditions. The potassium from KOH impregnated activated carbon was removed using deionized water to the point where the pH of the filtrate comes to neutral. Lastly, the activated carbon obtained from peels was exposed to drying and sulfonated using concentrated H_2SO_4 to generate covalent bonding of sulfonic groups against the support surface.	-SO_3H functionalization orange peels	Corn acid oil	19.95, 5, 274, 65	Y = 91.68	[50]
Waste mango (Mangifera indica) peels	The desiccated peel waste was burnt and ground to a fine powder to get the catalyst	K_2O, SiO_2, CaO, MgO, MnO, CuO, SrO	Soybean oil	6, 4, 340, 28	Y = 98	[38]
Carica papaya stem	Calcined at 700 °C for 4 h.	K_2O and K_2CO_3	Waste cooking oil and Scenedesmus obliquus	9, 2, 180, 60	Y = 95.23 Y = 93.33	[51]
Banana peels	The peels were burnt, ground and sieved to get fine ash. The product was heat-treated at 700 °C in furnace for 4 h.	Effectiveness is ascribed to potassium content	Napoleon's plume (Bauhinia monandra) seed oil	7.6, 2.75, 69.02, 65	Y = 98.5 ± 0.18	[52]
Heteropanax fragrans (Kesseru) plant	The waste plant was gathered, cut and left for drying under sunlight. The dried material was burnt to ash. The obtained ash was then heat treated at 550 and 850 °C for 2 h in a furnace. The burnt and calcined ashes were ground discretely using a grinder and placed individually in a dry place.	Carbonate and oxide of potassium demonstrated catalytic activity	Jatropha curcas oil	(CC-550) 12, 7, 65, 65	Y = 97.75	[53]
Birch Bark ash	Birch bark was cleaned and dried in an oven. The desiccated material was burnt to get ash which was calcined at 800 °C for 4 h.	CaO	Refined palm oil	12, 3, 180, 60	C = 69.70 ± 0.83	[54]
Fly-ash from wood pellet	The ash powder was calcined at 800 °C for 4 h.	CaO	Refined palm oil	12, 9, 180, 60	C = 87.76 ± 1.14	[54]
Lemna perpusilla Torrey ash	It was burnt in the open air to get ash and then further heat-treated in a furnace at 550 °C temperature for 2 h.	The residue holds 11.3% potassium which is ascribed to its catalytic activity	Jatropha oil	9, 5, 300, 65	Y = 89.43	[55]

Table 1. *Cont.*

Agri-Waste	**Catalyst Preparation**	**Catalyst**	**Oil Used**	**Reaction Parameters (A/O, Catalyst wt.%, Time, Temperature)**	**Yield**	**References**
Orange peel ash	The peels were washed, cut and dried for 3 days. The dried material was burnt for 30 min and milled to produce ash.	The availability of basic sites such as K and Ca	Soybean oil	6, 7, 420, 25	C = 98	[56]
Raw sugar beet agro-industrial waste	Raw sugar beet industrial waste was dried, milled and calcined for 2 h at various temperatures varying from 600 °C to 1000 °C.	CaO	Sunflower oil	4.5, 1, 60, 75	C = 93	[57]
Murumuru kernel shell biochar	The crushed shell of specific particle size was charred in a tubular furnace for 1 h at 600 °C. After that the product was further marinated to reduce the particle size. After that the sulfonation procedure was carried out for biochar functionalization.	MKSB–SO_3H	Jupati oil	30, 6, 240, 135	Y = 91.8	[58]
Waste ginger straw	The ginger straw was crushed and sieved. After that the obtained powder was charred under N_2 atmosphere at the specified temperature and for the specified time. Later, the sulfonation was carried out. The resulting ppt was then cleaned with hot distilled water and dried.	The catalyst synthesized via carbonization holding an amorphous carbon structure with a sulfonic group density of 1.05 mmol/g	Oleic acid	9, 7, 210, 64	Y = 93.2	[59]
Waste Musa paradisiaca trunk	After harvesting, M. paradisiaca trunk was pieced and dried in sunlight and then burnt to get ash. The ash is further calcined for 2 h at 550 °C and crushed to a fine powder.	Potassium as K_2CO_3, KCl and K_2O,	Jatropha oil	9, 5, 9, 65	Y = 97.65	[53]
Tamarindus Indica fruit shell ash	The crushed catalyst precursor was heat-treated in furnace at 800 °C for 3 h with an increment of 5 °C/ min to obtain shell ash.	CaO	P. curatellifolia seeds oil	9, 5, 120, 60	Y = 96.2	[60]
Waste peanut husk	Calcined at 900.5 °C for 2 h, a highly active solid catalyst may be found by mixing and well- ground waste peanut husks with Li_2CO_3 calcined in air for 4 h.	Li_2CO_3-modified waste peanut husks	Soybean oil	12, 5, 240, 65	Y = 98.4	[36]

Table 1. *Cont.*

Agri-Waste	Catalyst Preparation	Catalyst	Oil Used	Reaction Parameters (A/O, Catalyst wt.%, Time, Temperature)	Yield	References
Musa Balbisiana Colla Underground Stem (MBCUS)	The Stem was thermally treated using strontium. Then, the obtained product was calcined at 550 °C for 1 h.	MBCUS-SrO	Jatropha curcas L. oil	9, 5, 60, 200	Y = 96	[61]
Acacia nilotica (babul) tree stem	The material was dried and burnt to ash individually and heat-treated between 500 and 1200 °C	Calcium phosphate silicate $Ca_2SiO_4.0.05\text{-} Ca_3(PO_4)_2$	Jatropha oil	12, 5, 180, 65	C = 98.7	[62]
K_2CO_3-Camphor tree ash	The camphor tree leaves were burnt to generate ash and generated ash was first calcined for 2 h at high temperature. The calcined product was impregnated with potassium carbonate solution of specific concentration for 12 h. After that the mixture was again desiccated and calcined for 3 h.	K_2CO_3/camphor tree ash	Soybean oil	14, 5, 210, 65	Y = 92	[63]
Mixture of palm kernel shell husk (KSH) and fermented kola nut husk (FKNH)	First palm kola nut husk was washed and fermented for 10 days. The obtained product was dried and milled. After that the palm kernel shell husk powder was mixed with fermented kola nut husk in the ratio (1:1) and then the mixed product was calcined for 3 h at 800 °C.	CaO	Pig and neem seeds blend oil	5.9, 3.179 g, 57.45, 59.91	Y = 98.03	[64]
Cocoa pod husk	Calcined at 700 °C for 4 h.	The catalytic action was due to its K content	Azadirachta indica oil	3/2.2, 0.65, 57, 65	Y = 99	[65]
Lithium carbonate and rice husks as Li_4SiO_4 solid-base catalyst	Lithium silicates-based catalysts were synthesized via solid-state reaction, mixing, and grinding rice husk ash with lithium carbonate heat treated for 4 h at 800 °C	Li_4SiO_4 catalysts	Soybean oil	12, 1, 180, 65	Y = 96.8	[66]
Ficus carica leaves	The leaves were initially rinsed and dried followed by grinding and calcination at 800 °C for 2 h to prepare a catalyst.	-	Waste cooking oil	6, 1, 120, 60	Y = 90.75	[67]
Calcined jatropha cake	The cake was cleaned and dried at 70 °C followed by crushing, grinding and calcination at 450 °C for 3 h.	-	Jatropha curcas oil	6, 1, 60, 60	Y = 94	[68]

Table 2. Elemental composition of differently sourced agricultural waste.

Calcined Agricultural Waste Ash	**Major Elemental Composition (%)**					
	Ca	**K**	**P**	**Mg**	**Na**	**References**
Waste tucuma peels	12.28	63.81	12.67	6.69	traces	[31]
Banana peels	0.03	99.73	-	0.03	0.19	[52]
Brassica nigra plant	26.04	56.13	-	2.86	0.94	[41]
Sesamum indicum plant	33.80	29.64	-	9.68	1.42	[35]
Orange peel ash upon burning (in oxide form)	25.67	51.64	2.95	4.76	1.81	[56]
Mangifera indica peel (in oxide form)	4.20	59.14	3.92	8.08	1.58	[70]
Tectona grandis leaves	30.28	53.25	-	4.77	1.67	[38]
Cocoa pod husk-plantain peel blend	2.3	50.95	1.38	2.49	-	[48]
Walnut shell ash	17.67	23.55	-	traces	-	[43]
Musa balbisiana peels	36.08	41.37	-	12.02	10.41	[32]
Brassica nigra	26.04	56.13	-	2.86	0.94	[41]
Lemna perpusilla	-	11.32	-	-	0.53	[55]
Carica papaya stem	21.08	56.71	-	4.41	14.78	[51]
Banana peduncle	5.27	52.04	-	5.71	-	[34]

4.2. Parametric Optimization Study

In addition to the effectiveness of the catalyst in reaction, the biodiesel conversion/yield is significantly controlled by different reaction parameters, such as alcohol/oil (mole basis), catalyst weight %, reaction temperature and time, and mixing intensity. Owing to the reversible nature of the transesterification reaction, surplus methanol from its stoichiometric amount is desired to move the equilibrium forward and to enhance the biodiesel yield. This would assist in the generation of OCH_3- on the surface of the catalyst and, therefore, positively alter the biodiesel yield [71]. However, excessive methanol above the optimum value will not affect conversion and rather adds an extra cost for its recovery. It could be possible reason that too much methanol in the reaction mixture may dissolve in already generated glycerol, which obstructs the methanol reaction to the catalyst and oil [72]. Similarly, the quantity of catalyst present in the reaction mixture affects the biodiesel yield. The biodiesel yield increases upon addition of more catalyst, which indicates that a higher amount of catalyst may make more active sites available, which are directly related to conversion [73,74]. However, beyond the optimum quantity, the yield begins to decrease, which could be due to the rise in the viscosity of the mixture and probably some amount of catalyst might not be suitably exploited due to mass transfer resistance, therefore, decreasing the conversion [74]. Moreover, the reaction temperature also strongly affects the biodiesel yield. An optimal temperature is mandatory overcoming the resistance of diffusion generated among multiple phases of a heterogeneously catalyzed process to attain maximum conversion. High temperature generally favors collusion between molecules, thereby improving miscibility and mass transfer [75]. However, if the temperature is not maintained at an optimum value, the yield may decrease owing to methanol vaporization. The optimized reaction parameters with improved biodiesel yield described in the literature, using agricultural waste-based heterogeneous catalysts, are demonstrated in Table 1. It can be assumed that in addition to the catalytic activity and performance, it is necessary to tradeoff between the reaction parameters to get highest yield of biodiesel.

4.3. Agri-Waste Derived Catalyst Reusability

The catalysts derived from agricultural waste, such as peels of different fruits, stems, leaves, and husks, displayed excellent catalytic reusability in transesterification, which is an important parameter concerning the sustainability of catalysts. Various investigators have explored the reusability of agri-waste-derived catalysts for multiple runs. For example, Nath et al. [41] noted the reusability of waste Brassica nigra plant-derived catalyst for three successive runs with a biodiesel yield of 96%, indicating a minor loss in catalytic activity.

In another similar investigation, catalyst derived from the banana trunk showed a yield reduction to 91% in the third cycle from 96% in the first run [76]. Similarly, a 20 % yield reduction in third consecutive run was described by Sarma et al. [77]. Mendonça et al. [31] also described catalyst reusability gained from waste tucumã peels, up to 5 runs, with a 17.3% reduction in catalytic activity. The reason for this drop in catalytic activity could be leaching or a loss of active components during successive transesterification reactions. The reasonable reusability of agri-waste-based catalysts to generate biodiesel indicates the commercial viability of agricultural waste-derived catalysts for the sustainable production of biodiesel.

5. Biodiesel Production via Heterogeneously Catalyzed Technology

Presently, commercial-scale biodiesel generation mostly comprises homogeneous catalyzed process technology. Nevertheless, there are several leading technology companies that are making efforts to develop and operate heterogeneous catalyzed process technologies. For example, a biodiesel refinery based on a novel heterogeneous catalyst was established by Benefuel, Inc., in Seymour, U.S. [78]. A biodiesel industry with 0.16 million tons of capacity per year is located in Sete, France, and is operated using heterogeneous catalyzed process technology. Correspondingly, 8000 MT/annum of biodiesel was industrialized in Malaysia by Biofuel, Ltd., in cooperation with Incbio [79]. It seems that commercial scale biodiesel production using heterogeneous catalysts has been established. Most often, catalysts are synthesized from technical grade reagents to achieve a high performance and reliable results rather than being manufactured from waste resources. There could be possible drawbacks associated with waste-based catalyst synthesis, including sustainability and availability of same category of waste resources, their varied compositions and purity levels, selectivity, length of time, and cost evaluation of processing steps involved in waste-based catalyst synthesis. These factors may explicitly or implicitly link to the performance and reliability of a catalyst and, therefore, biodiesel yield and its quality parameters may be negatively influenced. Therefore, catalysts synthesized from synthetic chemicals/technical grade reagents are considered more reliable with respect to their design and performance. There are numerous researchers presently involved in evaluating the effectiveness of agricultural waste-based catalysts, but there still needs to be an extensive evaluation of these catalysts for large-scale production and their commercial utilization. Owing to the profits associated with heterogeneous-based catalyst systems, it has become essential to encourage its marketable development and applicability. It would be an excellent opportunity if heterogeneous catalysts were produced from waste materials, such as agricultural waste, which is amply generated each year across the world.

6. Conclusions

Although agricultural waste is considered as waste, it possesses vast potential to be transformed into valuable materials, such as catalysts, which facilitate the biodiesel production process in a feasible and sustainable way. If this waste is left unused, it would create disposal issues and sanitation problems owing to its inappropriate disposal. With a growing population, the intensity of agricultural waste generation is also continuously increasing because of growing consumption and utilization of agricultural products. This work focused on reviewing the transformation of different types of agricultural waste into valuable catalysts that have been efficiently and effectively utilized in the biodiesel production process. Waste-derived catalyst synthesis for biodiesel production would ultimately lessen biodiesel production costs and its pump price. Agricultural waste-derived catalysts can be manufactured using various methods, such as calcination, physical mixing, wet impregnation, sol-gel method, to improve the effectiveness of catalysts. These wastes-based heterogeneous catalysts are easy to fabricate, highly active, and reusable, along with providing options to get rid of homogeneous catalyzed process technologies and their associated drawbacks, which are presently commercially active. There is a need for extensive evaluation of these catalysts for large-scale production and their commercial utilization. In addition, a summary of agricultural waste-derived catalysts that are being utilized in biodiesel production processes might encourage researchers to explore various unexplored waste materials that can be potentially converted into valuable materials. Here, in this study, elemental composition analyses of heterogeneous catalysts made from various agricultural waste materials has been reviewed, particularly for transforming oil into biodiesel. The effectiveness of these catalysts may also be tested for other applications, such as wastewater treatment and chemical transformations.

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