Brazilian Journal of Chemical Engineering (2024) 41:23–48
https://doi.org/10.1007/s43153-023-00371-6

REVIEW

Biomass derived heterogeneous catalysts used for sustainable biodiesel production: a systematic review

Gobinda Prasad Chutia[1] · **Kandarpa Phukan**[1]

Received: 6 March 2023 / Revised: 16 June 2023 / Accepted: 28 June 2023 / Published online: 1 August 2023

Abstract

Biodiesel is one of the most efficient and effective potential solutions to current environmental problems because of its renewable and eco-friendly nature. Out of several possible methods and techniques for biodiesel production from natural feedstock, transesterification reaction in presence of catalyst and an alcohol is consider to be the most suitable method. The application of modified heterogeneous catalysts offers several advantages, including renewable resources, non-toxic, reusable, high catalytic activity, and stability in both acidic and basic conditions. This paper, reviews the development and utilization of the bio-based heterogeneous catalyst for sustainable biodiesel production and their suitability for industrial application. Catalyst generated from various bio wastes such as waste shells, animal bones and biomass ash derived from natural resources being utilized and provides a greener synthesis route for biodiesel production. This review article is focused on the critical evaluation of different biomass based catalysts in terms of their efficiency in biodiesel synthesis from various biomass feedstocks under varying process conditions.

Keywords Biodiesel · Biomass · Transesterification · Heterogeneous catalyst

Introduction

The importance of alternative sources of energy has been driven by the increased globalization as well as the depletion of the supply of fossil fuels. The alternatives energy source produced from a wild or non-edible oil feedstock can be used in diesel engines for its fuel properties which are comparable with diesel. Biodiesel is considered as a potential replacement for petroleum-based diesel which can be prepared from vegetable oil or animal fats by a chemical process called transesterification, which involves a reaction with methanol, using acid or base as a catalyst. Biodiesel is most often used as bland with petroleum diesel and referred to as B2 (for the ratios of 2%), B5 (5%), or B20 (20%). According to U. S. Energy Information Administration (EIA), in 2020, the United States produced about 43.04 million barrels (1.81 billion gallons) of biodiesel, imported about 1.30 million barrels, and consumed about 44.38 million barrels (1.86 billion gallons) nearly 0.12 million barrels per day (Capuano 2020). International Energy Statistics of EIA demonstrate that the global biodiesel production about 293.83 million barrels (12.34 billion gallons) and consumed about 255.50 million barrels (10.73 billion gallons) in the year 2019. According to the Environmental protection agency (EPA), the application of biodiesel decreases greenhouse gas emissions by 57–86%. The increased consumption of non-renewable fossil fuels generates several greenhouse gases to the environment and acts as a significant contributor to global warming. Moreover, the absence of sulfur and aromatic compounds in biodiesel contributes to higher combustion efficiency, and superior lubricity which in turn increases the durability of the engine, and also reduces hazardous emissions such as CO, CO_2, and NO_x (Abdullah et al. 2017; Basumatary et al. 2018). The application of biodiesel reduces the emission of net carbon dioxide, carbon monoxide, other particulate matter, and unburned hydrocarbons by 78%, 46.7%, 66.7%, and 45.2%, respectively (Changmai et al. 2020).

Chemically, biodiesel is monoalkyl-esters of long-chain fatty acids and is often known as the fatty acid methyl esters (FAME) of a vegetable oil or animal fat as methanol

✉ Kandarpa Phukan
kandarpaphukan@gmail.com

Gobinda Prasad Chutia
prasadgobinda06@gmail.com

[1] Department of Chemistry, Handique Girls' College, Guwahati 781001, Assam, India

is commonly used in its production. Out of several types of alcohol methanol is commonly used due to its cheapest, short-chain alcohol, quickly reacted and easily dissolved properties into the reaction medium (Basumatary et al. 2018). Transesterification is the easiest and most cost-effective approach to produce biodiesel as compared to other methods including direct use and blending of raw oils, dilution, microemulsion, and thermal cracking or pyrolysis (Ezebor et al. 2014; Mohammed et al. 2017). The different techniques used for biodiesel production is showed in Fig. 1. Biodiesel synthesis through transesterification reaction can be catalyzed either alkali or acid or enzyme. In addition to being corrosive, homogeneous acid-catalyzed reactions require high methanol to oil ratio as well as longer reaction times for conversion. It has been reported that the conversion rate of acid-catalyzed transesterification is about 4000 times slower than that of a base catalyst. Although, homogeneous base (such as NaOH, KOH) catalyzed reactions require milder conditions and shorter reaction times with high catalytic activities, it associated with several drawbacks like highly sensitive to the presence of free fatty acids (FFA) and as a result formation of soap and saponification will cause complications in the separation and purification process of the product mixtures for which catalysts could not be recycled as these are consumed during reactions (Mohammed et al. 2017). Enzyme catalyzed transesterification is not feasible for cost-effective biodiesel production since the high price of the enzyme and extremely slow reaction rate make it limited. The application of heterogeneous or solid catalyst offers numerous advantages as it is not dissolved in the reaction mixture and can easily recovered and reused back in the reaction (Thangaraj et al. 2019; Atabani et al. 2014). Besides that, the required amount of heterogeneous catalyst is significantly lower than that of homogeneous one. For example, 88 tons of NaOH is required to produce 8000 tons of biodiesel while only 5.7 tons of solid-supported MgO catalyst can produce 100,000 tons of biodiesel (Bohlouli and Mahdavian 2019; Azad and Ameer Uddin 2013; Zabeti et al. 2009). However, chemical sources based on heterogeneous catalysts are highly toxic and associated with several complexities in the production processes found to be unsuitable for clean and green biodiesel. Biomass-based heterogeneous catalyst presents an environmentally friendly solution since it is non-toxic, non-corrosive, and reduces the associated production cost.

In recent times, much research and development of nanostructured based catalysts have been gaining attention to natural renewable resources. Considering the cost and efficiency, several reports have been successfully published on bio-based solid nanocatalysts from renewable biomasses resources. Some effective natural sources for CaO based catalyst preparation are eggshell, ostrich eggshell, chicken eggshells, crab shell, chicken bone, snail shell, animal bones, oyster shell, guinea fowl bone, clamshell, obtuse horn shell, etc. Moreover, numerous agricultural or forestry wastes have been effectively utilized for green catalyst synthesis

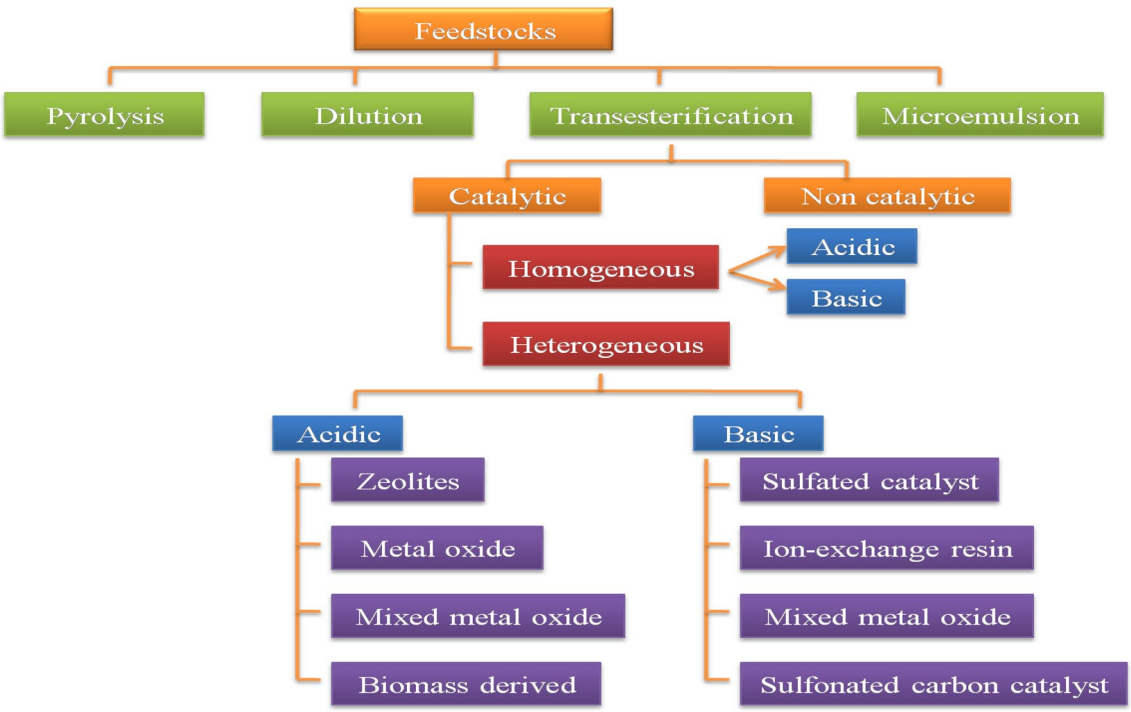

Fig. 1 Different techniques use for biodiesel production

such as dry leaves, fruit peels, rice husk, etc. The utilization of bio-based catalysts will make biodiesel production cost-effective as the raw materials are natural waste that is abundantly available without any cost. Besides that, the large-scale consumption of these catalysts will also help to maintain the waste minimization and disposal problem due to its biodegradable, non-toxic, easy to operate, and environmentally friendly nature. The utilization of biomass-derived activated carbon as a catalyst or catalyst support in transesterification reactions has been widely popularized in recent times (Konwar et al. 2014a, b; Faruque et al. 2020). Activated carbon is amorphous carbon that has composed of extremely porous structures and provides a large surface area available for adsorption or chemical reactions. Despite that, carbonaceous catalyst support offers multiple benefits including high stability in both acidic and basic media, high electron conductivity, high mechanical strength, and easy separation or recovery apart from its tunable textural and surface chemical properties (Dossin et al. 2006; Mbaraka and Shanks (2006);. In the last decades, the application of active metal ion impregnated or magnetic biochar catalysts has garnered considerable interest in biodiesel production. These types of modified catalysts show a high reaction rate as well as high recovery rate from products as compared to conventional ways such as filtration or centrifugation (Mbaraka and Shanks (2006). Likewise, concentrated H_2SO_4 acid solution is commonly used to sulfonate the biochar to develop the porosity and increase the surface area. In this review, the various natural sources of catalyst, method of synthesis, and their catalytic performance on sustainable biodiesel production are distinctly summarized. The present study includes several useful and innovative pieces of research on the biomass-derived heterogeneous catalyst for future development in the field of the biodiesel production industry.

In addition, biochar materials loaded with magnetic property gain more attention as effective heterogeneous catalysts due to their unique identity. Magnetic biochar catalyst prepared through the impregnation of a ferrite ion which can be done either simple one step or multiple step reactions. Magnetic biochar based heterogeneous catalyst offers simple, rapid and effective separation of reactions products even from high viscosity reaction mixture as compared to other conventional process like filtration or centrifugation. The trends on the application of heterogeneous catalyst with magnetic properties in biodiesel production are gradually increasing as it minimize the dependence on time-consuming mechanical work and electrical instruments like centrifuge for the recovery of solid catalyst. The main objective of this paper is to explore the recent developments and advanced utilization of biomass substances in the synthesis of heterogeneous catalyst for sustainable biodiesel production. This review summarizes the effective utilization of different biowaste materials for the development of novel heterogeneous catalysts throughout the different synthetic methods and the fundamental characteristics of the catalyst which affect their catalytic performance and other process parameters. The catalytic activity and the leading features of the catalysts along with the entire process of biodiesel synthesis are compared thoroughly to provide better insights in this field.

Heterogeneous catalysts for biodiesel production

The application of heterogeneous or solid catalysts for biodiesel synthesis has gained increasing attraction worldwide as they are neither consumed nor dissolved in the reaction mixture which made it easier to be separated from the product. Moreover, recovered catalyst can be reusable several times in the reaction, hence reducing the catalyst consumption as well as provide quality products as the catalyst does not allow the formation of soaps during the reaction, and the whole process occurs in a eco-friendly manner. Numbers of catalysts have been reported and investigated in various literature studies for biodiesel production, which includes metal oxide, mixed metal oxides, transition metal oxide, ion exchange resin, carbon-based catalyst, zeolites, etc. In view of cost and efficiency of biodiesel production, researcher shows interest towards bio-based heterogeneous green catalyst derived from natural renewable resources such as biomass. Many researchers reported that application of the natural biological source of calcium and carbon becomes a potential heterogeneous catalyst for transesterification of vegetable oil. Some biomass materials utilized for catalyst preparation are the mussel shell, cockle shell, biont shell, egg shell, chicken egg shells, ostrich egg shell, crab shell, snail shell, turbonilla striatula shell, shrimp shell, clam shell, animal bones, chicken bone, etc. (Ooi et al. 2021; Catarino et al. 2017; Risso et al. 2018; Sai et al. 2020; Wei et al. 2009; Singh and Sharma (2017); Lee et al. 2015; Corro et al. 2016). Besides that, several metal oxides or mixed metal oxides modified or functionalized biomass derived materials have been effectively utilized for biodiesel production (Demirbaş et al. 2006; Dhawane et al. 2018; Balajii and Niju (2019a, b); Quah et al. 2019). Figure 2 shows the different process employed for biochar based heterogeneous catalysts synthesis.

Sources of biomass-derived heterogeneous catalyst

Utilization of solid heterogeneous catalyst derived from the waste shell in biodiesel production is advantageous which is both cost-effective and eco-friendly. In the last decades, several waste shell derived heterogeneous catalyst such as

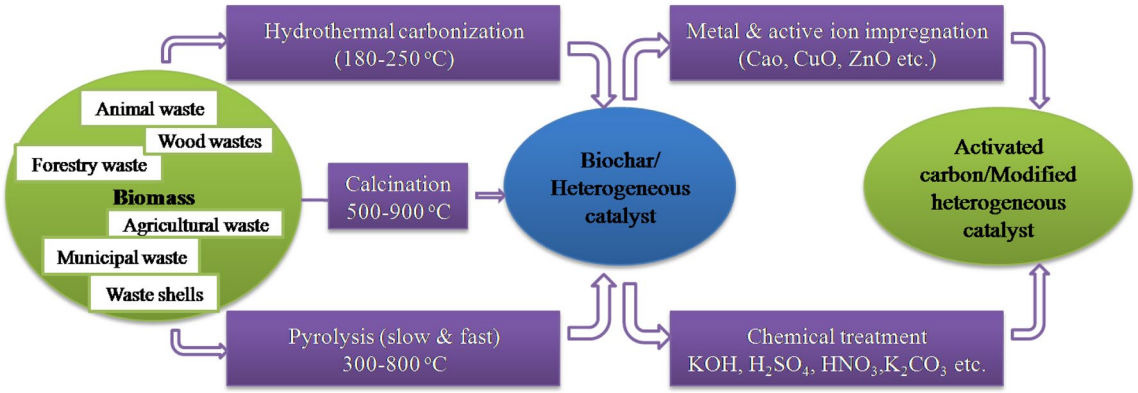

Fig. 2 Different process employed for heterogeneous catalysts synthesis from biomass

chicken eggshell, crab shell, ostrich eggshell, coconut shell, peanut shell, walnut shell, empty fruit bunch, etc. has gained more attention to reduce the overall biodiesel production cost (Balajii and Niju 2019a, b). Waste shells are mainly composed of $CaCO_3$ (96–98%) with a trace amount of magnesium carbonate ($MgCO_3$), strontium carbonate ($SrCO_3$), calcium phosphate, metal oxides (K_2O, Fe_2O_3, SiO_2, etc.), and water. Performing high-temperature combustion of waste shells formation of metal oxides occurs from metal carbonates which is a highly active base catalyst for biodiesel production. CaO has been frequently used for biodiesel production from various types of feedstock as it provides low toxicity, low solubility in methanol, high catalytic activity, cost efficiency, simply natural and waste sources, and mild reaction conditions. Waste shells are the cheapest raw materials for the synthesis of CaO and have been significantly utilized as a heterogeneous catalyst in transesterification reactions to produce biodiesel. The composition of some bio-waste materials before and after calcination process is summarized in Tables 1 and 2.

Suryaputra et al. (2013) utilized waste capiz shell as raw material for the production of CaO catalyst from calcium carbonate through the calcination process. In a study, Laskar et al. (2018) utilized waste snail shells (Pila spp.) as a source of CaO to produce biodiesel from soybean oil at room temperature. The catalyst was prepared via calcination in a muffle furnace at various temperatures (400–1000 °C) for 4 h. It was found that at calcination temperature more than 700 °C, the decomposition of calcium carbonate was initiated and completely converted to CaO at 900 °C as shown in the XRD pattern (Fig. 3). The EDS analysis also showed that the percentage of carbon decreases and the percentage of calcium increases gradually with an increase in the calcination temperature. It was found that a very small carbon (4.6%) was remained after the calcination at 900 °C. Following that a biodiesel yield of 98% was reported under optimized reaction conditions and the derived catalyst exhibits high catalytic activity up to eight times with significant results. Roschat et al. (2016) developed river snail shells-based CaO heterogeneous catalyst for economical and green biodiesel production processes. The results displayed a significant increase of FAME% with calcination temperature of the shells from 600 to 800 °C due to the increasing CaO formation from $CaCO_3$. Moreover, they also reported that at calcination temperature 900 and 1000 °C catalytic activity gradually decreases and gave lower FAME yield under the same reaction condition. The study concluded that higher than 800 °C results in CaO with lower BET surface area, total pore volume, and mean pore diameter due to the severe sintering of particles which significantly reduced total basic sites and basic site density of the sample. In another study, Sirisomboonchai et al. (2015) reported calcined scallop shell (CSS) as a catalyst in the transesterification of waste cooking oil (WCO) and methanol. The study suggested that the calcined scallop shell-based catalyst showed higher catalytic activity as compared with the commercial CaO. Experimental results found that CaO of the derived catalyst transferred to calcium glyceroxide upon transesterification reaction, and calcium glyceroxide also provides good catalytic activity in reutilization.

Eggshells are one of the widely used raw materials for the synthesis of CaO based catalysts. Much research work has been reported successful utilization of waste eggshell to develop a metal oxide or bimetallic mixed oxide catalyst for transesterification as it provides high natural abundance, low cost, eco-friendly sustainable route. Mansir et al. (2018) developed a bimetallic mixed oxide catalyst from waste eggshells to produce biodiesel from high free fatty acid content waste cooking oil. The prepared catalyst showed a high biodiesel yield of 92.1% under the optimized reaction conditions and can be reused in five cycles without any significant loss activity. In a study, Chowdhury and his team investigated the biodiesel synthesis from Madhuca indica oil with waste egg shell-derived heterogeneous catalyst. The

Table 1 Elemental composition of some biomass resources used for catalyst synthesis

Catalyst source	Composition %											Yield%	References
Snail shell	$CaCO_3$ 97.14	SiO_2 0.628	Fe_2O_3 0.409	SrO 0.457	Na_2O 0.336	K_2O 0.212	MnO 0.308	Al_2O_3 0.18	MgO 0.152	Cr_2O_3 0.083	SO_3 0.073	–	Laskar et al. (2018)
Cow bone	CaO 70.10	SiO_2 1.00	Fe_2O_3 0.50	SrO 0.30	Na_2O 0.60	K_2O 0.10	MnO_2 0.10	Al_2O_3 0.40	MgO 1.10	PbO 0.40	SO_3 < 0.01	–	Mohadesi et al. (2021)
Jatropha hulls	C 48.6	H 7.23	O 41.1	N 2.67	S 0.173	Fe 0.227						–	Zhang et al. (2017)
Palm empty fruit bunch	C 14.24	O 54.21	Mg 12.56	Ca 18.99								–	Lim et al. (2020)
Waste tires	C 85.88	H 10.01	N 0.39	S 0.810								–	Ayoob and Fadhil (2020)
Kenaf seed cake	C 67.51	O 32.29	P 0.1	S 0.08								–	Akinfalabi et al. (2019)
Palm kernel shell	C 45.86	H 6.09	N 0.11	S 0.04	0 44.26							–	Abdullah et al. (2021)
Orange peel	C 39.61	O 53.60	Mg 0.41	Al 0.08	Si 0.24	S 0.32	K 2.53	Ca 3.22				91.6	Lathiya et al. (2018)
Moringa leaves	C 62.62	O 36.06	Mg 0.36	K 0.31	Ca 0.38	P 0.18						–	Aleman-Ramirez et al. (2021)
Sawdust	C 47.85	H 6.55	N 0.41	S 0.06	O 45.13							–	Chellappan et al. (2018)
Heteropanax fragrans	C 38.95	O 36.37	K 14.69	Ca 3.05	Mg 1.31	Al 0.50	Si 2.99	P 0.80	Cl 1.32			96.61	Basumatary et al. (2021)
Banana peduncle	Mg 7.74	K 63.64	Ca 7.51	O 21.11								–	Balajii and Niju (2020)
Coconut coir Husk	C 45.91	H 5.08	N 0.58	O 35.06	S 0.06							–	Thushari et al. (2019
Rice husk ash	C 4.34	O 56.55	Si 38.21	K 0.90								–	Chen et al. (2013)
Wood ash	Si 17.6	Ca 14.7	Mg 2.9	Na 0.6	K 7.3	Al 9	P 1.15					–	Sharma et al. (2012)
Woody biomass	C 32.4	Ca 62.44	Na 1.19	Mg 1.14	Mn 0.12	K 0.45	Fe 2.10	Zr 0.16				–	Maneerung et al. (2015)
Eggshells	CaO 96.131	MgO 0.531	Al_2O_3 0.353	SiO_2 1.504	P_2O_5 0.283	SO_3 0.559	K_2O 0.118	Fe_2O_3 0.017	SrO 0.305	Mn_2O_3 0.003		91	Ayodeji et al. (2018)
Waste turkey bones	CaO 62.335	P_2O_5 30.084	SiO_2 2.882	MgO 0.640	Al_2O_3 0.647	SO_3 0.454	K_2O 0.103	Fe_2O_3 0.158	ZnO 0.047	SrO 0.025	Mn_2O_3 0.004	93.3	Ayoola et al. (2018)
Chicken manure	C 55.3	H 8.9	N 6.6	S 0.1	K 3.2	P 3.5	Ca 14.9	Mg 1.8	Zn 4.0	Si 1.7		–	Maneerung et al. (2016)

Table 2 Elemental composition of some biomass resources after calcination process

Catalyst source	Calcination		Composition%										Yield%	References
	T	*t*												
Snail shell	900	4	CaO 98.017	SiO_2 0.467	Fe_2O_3 0.357	MnO 0.24	MgO 0.182	Na_2O 0.17	SrO 0.16	K_2O 0.07	SO_3 0.06		98	Laskar et al. (2018)
Egg shell	850	4	CaO 97.08	SiO_2 1.26	Fe_2O_3 0.01	MgO 0.54	Al_2O_3 0.25	P_2O_5 0.31	SO_3 0.12	K_2O 0.10	SrO 0.26		91	Ayodeji et al. (2018)
Ostrich bone	900	–	CaO 66.4	SiO_2 0.02	Fe_2O_3 0.04	MgO 1.4	Na_2O 0.6	SrO 0.09	K_2O 0.01	SO_3 0.5			90.56	Khan et al. (2020)
Cow bone	800	5	CaO 74.50	SiO_2 0.20	Fe_2O_3 0.01	Na_2O 1.10	SrO 0.3	K_2O 0.1	SO3 0.4				99.24	Mohadesi et al. (2021)
Chicken bone	900	–	C 17.51	O 39.3	Mg 0.91	P 13.60	Ca 28.69						89.33	Farooq et al. (2015)
Walnut shell	800	–	O 56	K 24	Ca 17	Na 0.9	Mg 1.0	Al 1.1					98	Miladinović et al. (2020)
Turbonilla striatula	600	–	O 58.77	Ca 21.22	Sc 3.07	Si 1.78	Mg 1.02	Na 0.37					93.3	Boro et al. (2011)
Jatropha hulls	600	–	C 35.1	H 3.88	O 16.2	N 1.67	S 0.250						95.9	Zhang et al. (2017)
Turkey bones	800	–	CaO 65.55	P_2O5 32.11	SiO_2 1.76	MgO 0.29	Al_2O_3 0.46	SO_3 0.12	Na_2O 0.35	K_2O 0.12	TiO_2 0.06	Fe_2O_3 0.18	93.3	Ayoola et al. (2018)
Moringa leaves	500	2	C 12.19	O 59.57	Mg 5.92	K 9.87	Ca 10.09	P 1.19	S 1.05				86.7	Aleman-Ramirez et al. (2021)
Sawdust	400	1	C 28.98	H 2.71	N 0.22	S 6.62	O 61.47						95.1	Chellappan et al. (2018)
Banana ash	650	3	K 74.41	Cl 10.88	Si 5.22	Na 2.88	Li 2.96	Al 0.21	Mg 1.19	Ca 1.62	Fe 0.25		99.8	Madai et al. (2020)
Heteropanax fragrans	550	2	C 16.71	O 46.74	K 19.05	Ca 5.31	Mg 0.86	Al 0.44	Si 8.51	P 0.64	Cl 1.92		97.75	Basumatary et al. (2021)
Banana peduncle	700	4	CaO 9.92	MgO 7.73	K_2O 82.35								98.69	Balajii and Niju (2020)
Coconut husk ash	350	1	C 1.29	O 4.44	Na 2.92	Mg 1.21	Si 3.25	Cl 43.57	K 42.9				97	Vadery et al. (2014)
Tea waste char	700	2	C 64.65	H 3.94	N 2.69	S 0.28	O 28.19						–	Rashid et al. (2019)
Brassica nigra	550	2	Na 0.94	Mg 2.86	Si 5.37	K 56.13	Ca 26.04	Mn 0.05	Fe 1.26	Zn 1.63	Sr 5.72		98.79	Nath et al. (2019)
power plant's fly ash	550	1	CaO 30.74	SiO_2 27.87	K_2O 13.96	MgO 6.67	SO_3 4.83	Al_2O_3 2.83	Fe_2O_3 2.36	P_2O_5 1.34	Na_2O 1.14	Cl 3.36	93.9	Kumar et al. (2015)
Wood ash	800	–	Si 21.5	Ca 17.8	Mg 4.5	Na 5.7	K 5.7	Al 1.2	P 0.50				97	Sharma et al. (2012)

Table 2 (continued)

Catalyst source	Calcination		Composition%											Yield%	References
	T	*t*													
Musa balbisiana Colla peel	700	4	K 41.37	Ca 36.08	Mg 12.02	Na 10.41								–	Gohain et al. (2017)
Red banana peduncle	700	4	O 50.54	Mg 1.30	Si 1.54	P 1.91	S 0.03	K 42.23	Ca 1.20					98.7	Balajii and Niju (2019a, b)
Musa paradisiacal peel	500	3.5	Al 3.42	Si 33.01	P 1.99	S 0.67	Cl 4.89	K 54.73	Ca 1.13	Mn 0.05	Fe 0.04	Zn 0.01		94.9	Betiku and Ajala (2014)
Camphor tree ash	800	2	Na 0.23	K 1.22	Ca 12.05	Mg 1.82	Al 2.70							92.27	Li et al. (2018)
Carica Papaya stem	700	4	K 56.71	Na 14.78	Ca 21.08	Mg 4.41	Si 3.02							95.2	Gohain et al. (2020a, b)
Banana peel	700	4	K 99.73	Na 0.19	Mg 0.03	Ca 0.03	Mn 0.01	Fe 0.01						98.5	Betiku et al. (2016)

T Calcination temperature in °C; *t* calcination time in hour

synthetic process was optimized by the Taguchi approach (Chowdhury et al. 2019). In another study, Farooq et al. (2018) explained the preparation of a CaO based efficient catalyst from waste chicken eggshells for exploring environment-friendly and cost-effective biodiesel production process. The precalcined CaO powder at variable temperature (800–1000 °C) was dispersed in distilled water to form $Ca(OH)_2$ suspension after that the sample was placed in an autoclave for 24 h at 150 °C. Finally, the filtered sample was calcined at elevated temperature (800–1000 °C) for another 3 h. Similarly, the study found that calcination temperature lower than 800 °C could not lead to complete decomposition of $CaCO_3$ to CaO. However, at 800, 900, and 1000 °C the catalysts are mainly composed of CaO as a major phase. The BET analysis demonstrated that at 900 °C calcination temperature catalyst showed a maximum surface area however, beyond 900 °C the surface area was found to be significantly reduced. The experimental results showed that catalysts prepared at 900 °C possess the excellent activity and provided a high yield of biodiesel up to 93.5% at methanol to oil molar ratio of 12:1 with 5 wt% of catalyst in 90 min. Tan et al. (2015) developed a calcium oxide heterogeneous base catalyst by utilizing ostrich eggshell and chicken eggshell waste as the raw material. They investigate the performance of CaO catalysts derived from both waste ostrich eggshell and the conventional chicken-eggshell for biodiesel production from waste cooking oil and reported yield of biodiesel was 96% and 94% for calcined ostrich and calcined chicken eggshells respectively under the same optima reaction conditions. In another study, Correia et al. (2014) investigate the catalytic activities of calcium oxide obtained from crab shells and eggshells in the transesterification of vegetable oil. The study found that the prepared CaO catalyst converts triglycerides to methyl esters up to 84% (crab shell) and 94% (eggshell) under optimized reaction conditions.

Animal bone is one of the solid wastes that are cheap, easy, and abundantly available all over the world. In many studies, the waste bone-derived catalysts have been shown to be highly effective as a catalyst for biodiesel production. The X-ray diffraction analysis confirms that waste animal bones are composed of two different phases of $CaCO_3$, known as aragonite and calcite. These can be used as a potential source of CaO based basic catalysts for transesterification. Nisar et al. (2017) investigated the modified animal bones with KOH as a heterogeneous base catalyst for transesterification of non-edible Jatropha oil. The XRD diffractogram showed that the uncalcined bone mainly composed of $CaCO_3$ as aragonite and calcite and after calcination at 900 °C all the aragonite phase converted to CaO which acts as effective base catalyst for biodiesel production. The experimental results confirm a maximum biodiesel yield of 96.1% at optimal parametric conditions viz. methanol to oil molar ratio of 9:1, calcination temperature, 900 °C, and catalyst

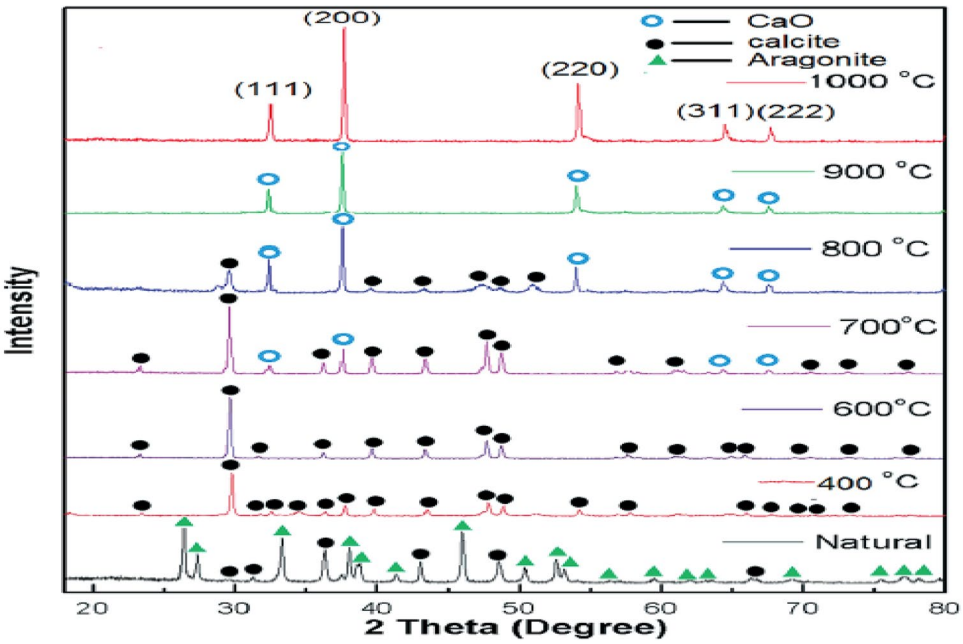

Fig. 3 XRD pattern of snail shell based catalyst (Reproduced from Laskar et al. 2018)

concentration 6 wt% of oil. The reusability of the catalyst was also investigated and results show that it could be recycled up to four times without losing any significant activity. In a study, Smith et al. (2013) employed bovine bone waste as an effective catalyst in the transesterification reaction between soybean oil and methanol. They perform the calcination process at temperature of 950 °C which implies the complete conversion of $CaCO_3$ to CaO. The XRF study also showed that the high concentration of Ca (81.02%) which provides crucial contribution toward the biodiesel synthesis. They reported that the maximum yield of methyl ester was about 97% obtained by performing the closed-system transesterification reaction with 8 wt% of catalyst and 6:1 methanol to oil ratio at 65 °C for 3 h.

In another study, Khan and his team investigated biodiesel production from waste cooking oils by utilizing cheap heterogeneous catalyst derived from waste Ostrich (Struthio camelus) bones (Khan et al. 2020). It was reported that after calcination at 900 °C for 4 h the sample displayed the hexagonal crystal structure due to the breakdown of carbonates and the formation of metal oxides. It is well known that the activity of the catalyst is directly related to the strength of basic sites. The basicity of catalysts could be considered as the prime parameter to enhance the transesterification process. The basicity of the obtained ostrich bone catalyst was found to be 13.6 mmol g^{-1} by using the acid titration method. The reaction parameters had been optimized to maximize biodiesel yield and the optimum yield of 90.56% was achieved at methanol to oil ratio of 15:1 and catalyst loading of 5 wt% within a reaction period of 4 h. The study concluded that the presence of hydroxyapatite in the derived ostrich bones catalyst showed the good catalytic performance to produce biodiesel from waste cooking oil. Farooq et al. (2015) also derived heterogeneous catalysts from chicken bones for the transesterification reaction of waste cooking oil for biodiesel production. The investigation showed that the heterogeneous catalyst calcined at 900 °C provides good catalytic activity in the transesterification of waste cooking oil and exhibiting a maximum biodiesel yield of 89.33% at optimum reaction conditions. The study found that the catalyst surface area increases from 5.25 to 120.02 $m^2\ g^{-1}$ as the calcination temperature increases from 800 to 1000 °C. The catalyst characterization confirmed the transformation of hydroxyapatite into β-$Ca_3(PO_4)_2$ that could act as a base catalyst for transesterification reaction. Besides that, it was also observed that at 900 °C calcination catalysts shows a greater number of basic sites on the surface as it shows greater uptake of CO_2 in comparison to catalysts prepared at 800 and 1000 °C. Moreover, the experimental results reported successful reutilization of derived catalyst up to four times for biodiesel production. Mohadesi et al. (2021) developed CaO based heterogeneous catalyst from cow bone to produce biodiesel from waste cooking oil. Transesterification reaction was carried out in a microreactor to reduce the residence time to 1 min and the maximum purity of biodiesel in presence of 8.5 wt% catalysts at 63.1 °C was 99.24%.

Kostić et al. (2016) experimented on biodiesel production via CaO-rich catalyst developed from palm kernel shell biochar (PKSB). The study reported that CaO based PKSB catalyst can be reused for three consecutive cycles without any significant loss of activity. The experiments found a high biodiesel content of about 99% in presence of 3 wt% catalyst concentration and a 9:1 molar ratio of methanol to oil.

Miladinović et al. (2020) investigated the catalytic activity of the walnut shell-derived catalyst in biodiesel production by the sunflower oil methanolysis. The prepared CaO based catalyst offered a very fast reaction and provides a high yield of biodiesel up to 98%. The study conducted successfully recycled the catalyst up to four times after the regeneration of the catalytic activity by recalcination at 800 °C. In a study, Boro et al. (2011) utilized solid oxide catalyst derived from the waste shell of turbonilla striatula for biodiesel production via transesterification of mustard oil. The experimental results confirmed the formation of solid oxide i.e. CaO at a calcination temperature of 800 °C. A maximum biodiesel yield of 93.3% was achieved at methanol to oil molar ratio of 9:1 and 3 wt% of catalyst loading. The study also investigated the reusability of the derived catalysts in different temperatures. Apart from that, various waste shells based biomass precursors such as peanut shell (Zeng et al. 2014), coconut shell (Endut et al. 2017), palm shell (Farabi et al. 2019), jatropha hulls (Zhang et al. 2017), empty fruit bunch (Lim et al. 2020), etc. have been investigated as an effective catalyst for biodiesel production. It is clearly observed that calcination temperatures play a vital role in the catalytic performance of the waste shell-derived heterogeneous catalyst. Although, there are no fixed relations between FAME yield and calcination temperatures, it is directly associated with the catalyst surface area and pore size distribution as well as the entire surface texture of the catalyst. Besides that, doped CaO based catalyst significantly affects the transesterification process that could alter the FAME yield. The selection of appropriate doping agents with optimal conditions leads to the formation of sufficient active sites and compatible surface properties that enhance the activity of catalyst.

High carbon content compounds such as coal, wood, and coconut shell are being utilized for the synthesis of activated carbon (AC). It provides a high surface area with a well-decorated porous structure in nature as illustrated in Fig. 4. AC possesses a high number of active sites that provide sufficient adsorptive sites for reaction to take place as a result the overall performance of the reaction significantly increased. Activated carbon-based materials developed from several biomass resources have been successfully utilized as an effective green heterogeneous catalyst for the sustainable production of biodiesel. The presence of highly active sites and different functional groups such as phenolic, carboxylic, etc. on their surface effectively contributes to enhancing the reaction rates. Farid et al. (2017) investigated the fatty acid

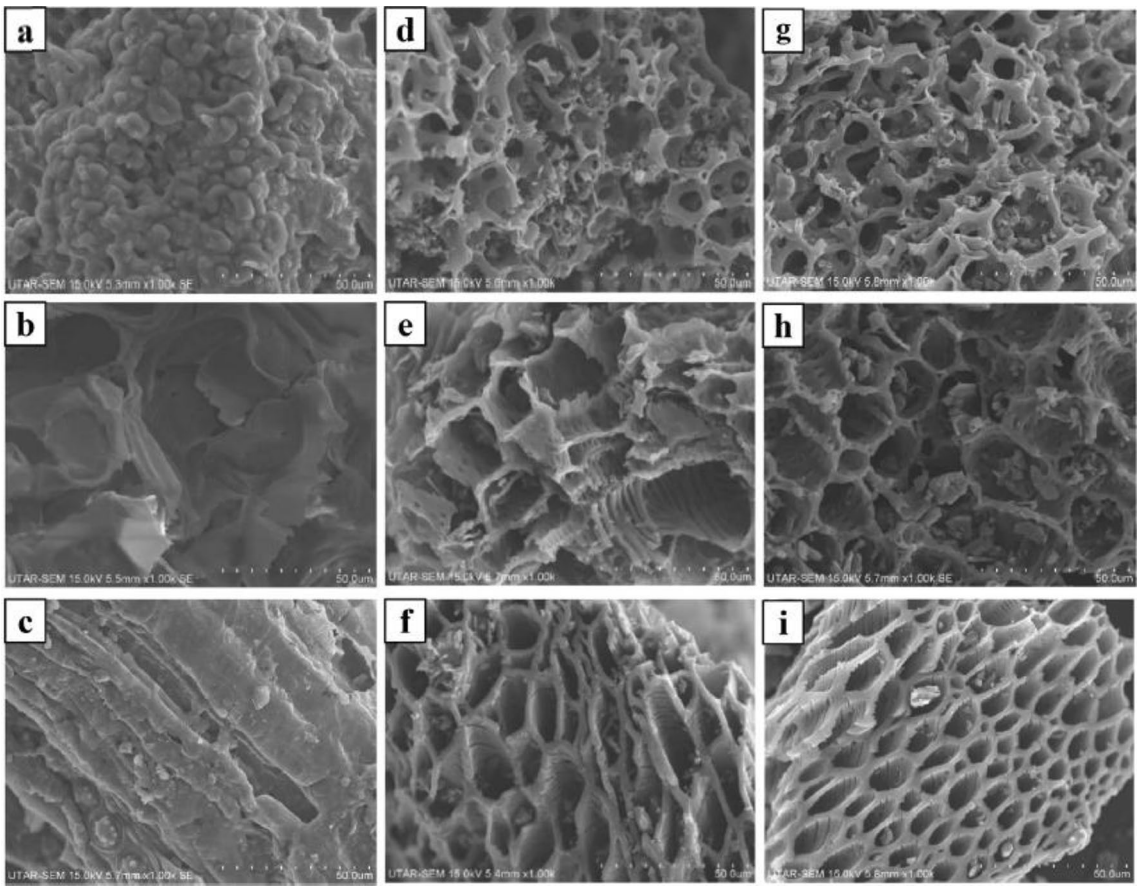

Fig. 4 Porous network of activated carbon derived from biomass (Reproduced with permission from Elsevier, Tang et al. 2020)

methyl esters (FAME) production from waste cooking oil using activated carbon developed from oil palm biomass as a catalyst. The synthesized AC catalyst exhibits a basicity of 11.21 mmol g^{-1} with substantial surface area and provides 98% of FAME yield under optimum reaction parameters. The reusability study showed that more than 76% of yield was achieved after five consecutive cycles. In a research work, Dejean et al. (2017) used shea nutshell as raw material to prepare an activated carbon-based catalyst for the production of ethanolic biodiesel. The X-ray diffraction (XRD) results confirmed that the presence of potassium carbonate in the catalyst was the main active potassium species responsible for catalytic activity. Recyclability tests showed that the catalyst had excellent cyclic stability and can be reused after a thermal post-treatment with superior catalytic activity.

The biochar-based solid heterogeneous catalyst gains more attention in the latest times due to their economic feasibility and simple method of preparation as well as environmentally safe nature. Generally, biochar is the blackened organic matter that is generated through the carbonization process and mainly it is the residual part of the fast pyrolysis from the woody mass and also the main product obtained upon slow pyrolysis. These are high in oxygen content (27–34 wt%) mostly in the form of phenolic and carboxylic acidic groups. The presence of phenolic, carboxylic, and sulfonic groups in biochar materials assists in improving the catalytic activity and also enhances the interaction of the reactant molecules on the surface of the catalyst (Liu et al. 2011). In a study, Aleman-Ramirez et al. (2021) prepared a heterogeneous catalyst from moringa leaves ash as a sustainable precursor for biodiesel production. The investigation published that inorganic carbonate minerals of dolomite, calcite, and $K_2Ca(CO_3)_2$ were the main components and enhances the transesterification reaction. The EDS analysis of the catalysts suggested that after the calcination process the amount of oxygen, potassium, calcium and magnesium increased to 59.57%, 9.87%, 10.09% and 5.92% respectively which provide significant catalytic activity toward transesterification. Basumatary et al. (2021) investigated the efficiency of a sustainable basic heterogeneous catalyst derived from heteropanax fragrans (Kesseru) for the synthesis of biodiesel from jatropha curcas oil. The elemental analysis showed that percentage of basic elements present in the uncalcined materials such as K (14.6%) and Ca (3.05%) increases after the calcination process. The high amount of potassium (19.2%) recorded after 550 °C along with various metals and that could be responsible for the high efficiency of the catalyst. Besides that, the calcined catalyst showed a maximum basicity of 0.423 mmol/g as compared to the uncalcined catalyst (0.298 mmol/g) and also displayed a high biodiesel yield of 90.22% in the third reaction cycle. Barros et al. (2020) synthesized a novel solid base catalyst from Pineapple (Ananás comosus) leaves ash for transesterification of soybean oil. The catalyst was prepared via calcinations of grounded leaves at 600 °C for 2 h and 900 °C for 30 min in a muffle furnace. The study reported a higher content of alkali or alkali metals (K, Ca, and Mg), about 85 wt% that could provide a major contribution to the high catalytic activity. The experimental results showed that a maximum oil to biodiesel conversion above 98% was recorded in presence of 4 wt% catalysts and oil to methanol molar ratio of 1:40 after 30 min. Gohain et al. (2020a, b) proposed calcined tectona grandis leave as an eco-friendly, renewable, and low-cost heterogeneous base catalyst for transesterification. The study investigated the efficiency of the catalyst towards biodiesel production and reported that the presence of alkali and alkaline earth metals creates well decorated basic surface sites. Arumugam and Sankaranarayanan (2020) utilized residual ash from sugarcane leaf as a heterogeneous catalyst for the synthesis of calophyllum inophyllum methyl esters. The catalyst was prepared by open-air burning and subjected to NaOH solution for the recovery and removal of silica followed by sonication. The mixture was filtered and the residual ash was washed with distilled water for several times to remove the remaining alkali. The calcination process generates the porous, spongy, and agglomerated structure of ash along with the production of metal oxides that can effectively catalyze the biodiesel production process. The major metal oxides identified were silicon dioxide, calcium oxide, and magnesium dioxide. The reusability study found that a maximum FAME yield of 97.85% was achieved up to six cycles. In a research work, Balajii and Niju (2020) studied the feasibility of a green heterogeneous base catalyst derived from banana peduncle ash for transesterification of non-edible ceiba pentandra oil. The experimental analysis reported that calcined banana ash composed of alkali oxide (K_2O), alkaline earth metal oxides (MgO, CaO), and metal oxide (SiO_2) by degrading the recalcitrant matrix of the biomass. The presence of alkali metal oxides or mixed metal oxides significantly enhances the basicity of catalyst which provides remarkable catalytic activity. It was also found that calcination provides a highly porous network which in turn increases the surface area of the catalyst that improves the activity of the ash catalyst. Under optimum process conditions such as 1.978 wt% of catalyst concentration, 9.20:1 ratio of methanol to oil, and 60 min reaction time, a maximum FAME yield of 99.36% was achieved. Nath et al. (2019) utilized a waste brassica nigra plant-derived green heterogeneous base catalyst for effective transesterification of soybean oil to synthesize biodiesel. The investigation found a high content of potassium about 56.13 wt% as the major component followed by calcium (26.04 wt%) in the form of oxide, carbonate, and chloride. The catalyst afforded a maximum yield of 98.79% in presence of 7 wt% of catalyst and a 12:1 ratio of methanol to oil in a short period of 25 min at 65 °C. Apart from

that, various biomass ash-based materials such as rice husk ash (Chen et al. 2013; Li et al. 2014), wood ash (Sharma et al. 2012), lignin (Guo et al. 2012a, b), waste date pits (Ala'a et al. 2018), corncob residue (Behera et al. 2020; Tang et al. 2020), defatted seed (Dawodu et al. 2014), etc. have been successfully employed as green sustainable precursors for the catalytic transesterification reaction to synthesize biodiesel.

Biomass based modified/functionalized basic heterogeneous catalyst

Much research work has been reported successful utilization of waste eggshell to develop a metal oxide or bimetallic mixed oxide catalyst for transesterification as it provides high natural abundance, low cost, eco-friendly sustainable route. Mansir et al. (2018) developed a bimetallic mixed oxide catalyst from waste eggshells to produce biodiesel from high free fatty acid content waste cooking oil. The powdered $CaCO_3$ was precarbonized to obtain CaO powder in a furnace at a temperature of 900 °C for 5 h. An appropriate amount of $Mn(NO_3)_2{\cdot}4H_2O$ and ZrO_4H_4 in the ratio of 3:2 was mixed with CaO powder and placed in a furnace at 650 °C for 5 h to get the resultant bimetallic doped CaO catalyst. The prepared catalyst showed a high biodiesel yield of 92.1% under the optimized reaction conditions and can be reused in five cycles without any significant loss activity. Chowdhury and his team (2019) investigated the biodiesel synthesis from Madhuca indica oil with waste egg shell-derived heterogeneous catalyst. The synthetic process was optimized by the Taguchi approach. The modified egg shell-based catalyst was prepared by using impregnation of sodium nitrate aqueous solution at a temperature of 800 °C for 3 h. The experimental analysis found BET-specific surface area of 2.83 $m^2\ g^{-1}$ for CaO eggshell catalyst without impregnation and 12.67 $m^2\ g^{-1}$ for impregnated catalyst, whereas the pore volume area was found to be 0.1098 and 0.2335 $cm^3\ g^{-1}$ for unimpregnated and impregnated catalyst respectively. Following that, the study concluded that metal-doped egg shell-derived catalyst enhancing the catalytic activity due to the modifications of surface texture. Khatibi et al. (2021) derived Na and K doped CaO from calcined eggshells for biodiesel production via transesterification of canola oil. The powdered eggshells were calcined at three different temperatures prior the impregnation process. The impregnation of Na–K was performed by using $NaNO_3$ and K_2SO_4 at 60 °C under constant stirring followed by calcinations at 600 °C for 5 h. BET analysis found that Na doped CaO experienced a lower surface area as compared with that for CaO while K doped one showed a higher surface area than that of CaO. On the other hand, both Na–K doped CaO had an average pore volume and specific surface area in between the values for Na–CaO and K–CaO catalysts and displayed a maximum biodiesel yield. The study clearly experienced that there is no linear relationship between the catalyst surface area and pore size distribution with the FAME yield. However, the investigation revealed the linear relationship between the biodiesel yield and the number of basic sites on the surface of the catalyst. The highest FAME yield of 97.6% was achieved under the catalyst loading of 3 wt% with methanol to oil molar ratio of 9:1 and 3 h of reaction time.

Nisar et al. (2017) investigated the modified animal bones with KOH as a heterogeneous base catalyst for transesterification of non-edible Jatropha oil. The calcined powder bones obtained at variable temperature ranges (500–1100 °C) in a furnace were soaked with different concentrations of potassium hydroxide solutions to synthesize a modified CaO catalyst. The experimental results also found that 900 °C is the most suited and optimum temperature for the calcinations as it offers the best catalytic performance of the catalyst. Farid et al. (2017) investigated the fatty acid methyl esters (FAME) production from waste cooking oil using activated carbon developed from oil palm biomass as a catalyst. The activated carbon was prepared by using a two-step method. Initially, a carbonization step was carried out at 700 °C for 2 h then an appropriate amount of KOH was impregnated followed by activation at 700 °C for another 2 h under a continuous flow of N_2. The obtained AC was further impregnated with K_3PO_4 followed by subsequent calcination for another 3 h under a continuous flow of N_2 at 500 °C. The study reported that the surface area and pore size distribution of the AC were decreased after calcination and K_3PO_4 immobilization due to the sequential spread of K_3PO_4 inside the capillary pores. However, they used KOH as an activating agent to improve the surface area and pore structure of the mesoporous carbon. The synthesized catalyst exhibits a basicity of 11.21 mmol g^{-1} with substantial surface area and provides 98% of FAME yield under optimum reaction parameters. The reusability study showed that more than 76% of yield was achieved after five consecutive cycles. In a study, Ayoob and Fadhil (2020) developed waste tires based activated carbon for biodiesel production from a mixture of non-edible oils. AC was prepared followed by a pyrolytic conversion of the waste tire at a temperature of 500 °C. The obtained pyrolytic char sample was purified with n-hexane and finally, the activation was carried out at 800–900 °C for 2 h under a stream of steam. Further, the as-prepared AC was utilized for the synthesis of carbon-based solid base catalyst through the wet impregnation method with different aqueous solutions of KOH and calcined at 400 °C for 2 h under a flow of N_2 gas, to obtain the desire carbon-based catalyst. In another study, they prepared lithium supported on activated carbon derived from scrap tires for transesterification of a mixture of non-edible oils. Although the impregnated LiOH-AC experienced a lower surface area as compared

with parent AC, the basicity increases significantly with rising the LiOH% in the impregnation solution and that plays an energetic role in the catalytic action. The catalyst reusability was also investigated and exhibited superior activity after being four times recycled with more than 80% FAME content (Ayoob and Fadhil 2019). Akinfalabi et al. (2019) synthesized AC based catalyst from kenaf seed cake to produced biodiesel from palm fatty acid distillate (PFAD). At optimum reaction parameters, a free fatty acid (FFA) conversion of 98.7% and yield of fatty acid methyl esters about 97.9% was achieved. The synthesized catalyst showed excellent catalytic activity and maintaining the yield of methyl esters and free fatty acid conversion of more than 90% up to five consecutive cycles.

Abdullah et al. (2021) developed a highly mesoporous activated carbon derived from palm kernel shell for biodiesel production from waste cooking oil. Hydrothermal carbonization (HTC) was carried out in an autoclave heated up to 240 °C for 24 h and NaOH was used as an activating agent to increase the active sites and improve the porous texture of the carbon structure. The obtained HTC based activated carbon was further impregnated with K_2CO_3 and CuO to achieve bifunctional characteristics that are suitable for simultaneous esterification and transesterification processes. The investigation concluded that the chemical treatment of NaOH significantly increased the surface area of AC from 3.57 to 3368.60 $m^2\ g^{-1}$. On the other hand, it was found that the impregnation of AC with a favourable amount of K_2CO_3 and CuO provides a higher amount of basicity. In a research work, Changmai et al. (2021a, b) developed a magnetic nano-sized solid catalyst from bio-waste Citrus sinensis peel ash for the synthesis of biodiesel from waste cooking oil (WCO). The developed magnetic catalyst afforded a maximum biodiesel yield of 98% under the reaction conditions of 6:1 methanol to oil molar ratio, 6 wt% of catalyst at 65 °C in 3 h. Besides that, the catalyst exhibited high physical stability and sustain the catalytic reactivity up to nine consecutive cycles. In a study, Madai et al. (2020) used banana peel ash-derived catalyst loaded with a metal oxide to fast rate synthesis of biodiesel from neem seed oil. The experimental analysis confirms the presence of potassium carbonate (K_2CO_3), a calcium magnesium silicate ($CaMgSiO_4$), and potassium sodium sulfate ($KNaSO_4$) and that contributes to raising the basicity of the catalyst up to 11.09. In a study conducted by Chen et al. (2013) reported a Li-doped rice husk ash catalyst. The calcined rice husk ash was mixed with an appropriate amount of Li_2CO_3 to obtain a Li-modified heterogeneous catalyst. The chemical treatment results in the conversion of the crystalline phase of the rice husk ash to the Li_2SiO_3 and a few Li_4SiO_4. It was reported that Li_2SiO_3 reacted with atmospheric CO_2 to form Li_2CO_3 that appears on the catalyst surface which exceeded the basic strength of the catalyst. The reaction conditions and the modification process of some biomass derived basic heterogeneous catalysts are illustrated in Table 3.

Biomass based modified/functionalized acidic heterogeneous catalyst

The sulfonated carbon material contains a higher amount of acidic groups at its surface than that of precursor activated carbon due to the insertion of various functional groups at the activated carbon surface. Moreover, the attached sulfonic groups ($–SO_3H$) helps to protonate the neighboring weakly acidic groups (e.g., –COOH, –OH) that will initiate the esterification or transesterification reaction by the attack of the alcohol on the carbocation. In a study, Tang et al. (2020) conducted an experiment to produce biodiesel from palm fatty acid distillate through the catalytic performance of papaya seed, empty fruit bunch (EFB), and corncob biomass waste-derived based activated carbons. The biomass materials were impregnated with H_3PO_4 to obtain activated carbon after that subjected for sulfonation by arylation of 4-BDS (4-benzene diazonium sulfonate). The study found that the synthesized AC exhibited a high porous structure as the carbonization process leads to the elimination of volatile materials during thermal treatment and also the use of the activation pretreatment step by H_3PO_4 as the activating agent. A well-developed porous structure of AC was significant to create a larger surface for the implantation of sufficient active sites and to grant access for the reactants into the inner surface. The experiment showed that corncob waste-derived sulfonated AC catalyst exhibited the highest FAME yield of 72.09% and FFA conversion of 93.49%. A study conducted by Konwar et al. (2014a, b) reported oilcake waste-derived catalysts in biodiesel production from acid oils. The reported catalyst exhibited high thermal stability and was successfully recycled in five consecutive experiments. The study found that the catalytic activity of the prepared solid acid catalyst was well comparable with an equivalent amount of H_2SO_4 under similar reaction conditions. Rocha et al. (2019) developed sulfonated activated carbon from corn cobs as heterogeneous catalysts to produce biodiesel from soya bin oil using microwave-assisted transesterification. The corncob-based AC was prepared with phosphoric acid via thermal treatment and sulfonation was done by using 4-benzenediazoniumsulfonate (BDS) as a sulfonating agent. The study demonstrated that after the sulfonation the specific surface area of the activated carbon slightly decreased, but maintains well-decorated mesopores for use as solid acid catalyst. The experimental facts concluded that a pure biodiesel phase with a yield of 88.7% was attained with 20% of catalyst concentration and a 6:1 ratio of alcohol-to-oil at microwave variable power of 0–600 W or 20 min. The study also reported the five subsequent reaction cycles of the catalyst without loss of its catalytic activity. In

Table 3 The reaction parameters and the functionalization process of some biomass based basic heterogeneous catalysts

Source	Catalyst type	Activation/calcination			Impregnation/sulfonation			BET-Surface area ($m^2\ g^{-1}$)	Basisity (mmol g^{-1})	FAME yield (%)	References
		Agent	*T* (°C)	*T* (h)	Agent	*T* (°C)	*T* (h)				
Snail shell	CaO	–	900	4	–	–	–	7	12.2–15	98	Laskar et al. (2018)
River snail Shell	CaO	–	800	3	–	–	–	3.495	15.0–18.4	98.5	Roschat et al. (2016)
Waste egg shell	Doped-CaO	–	900	5	$Mn(NO_3)_2{\cdot}4H_2O$ and ZrO_4H_4	650	5	12.6	–	92.1	Mansir et al. (2018)
Waste egg shell	CaO	Sodium nitrate	800	3	–	–	–	–	–	81.56	Chowdhury et al. (2019)
Waste egg shell	CaO	–	900	2	–	900	3	66.7	2.572	93.5	Farooq et al. (2018)
Waste egg shell	Doped-CaO	–	900	3	$NaNO_3$ and K_2SO_4	600	5	22.4	15.9	97.6	Khatibi et al. (2021)
Ostrich–eggshell	CaO	–	1000	4	–	–	–	71.0	–	96	Tan et al. (2015)
Ostrich bone	CaO	–	900	4	–	–	–	3.61	13.6	90.56	Khan et al. (2020)
Chicken bones	CaO	–	900	4	–	–	–	108.74	0.757	89.33	Farooq et al. (2015)
Palm kernel shell	CaO	–	800	2	–	–	–	–	0.516	0.516	Kostić et al. (2016)
Turbonilla striatula	CaO	–	900	4	–	–	–	8.359	–	93.3	Boro et al. (2011)
Waste tires	Activated carbon support	–	800–900	2	KOH	400	2	209.15	15–18.4	94.50	Ayoob and Fadhil (2020)
Scrap tires	Activated carbon support	–	800–900	3	LiOH	130	4	306.10	15–18.4	92.23	Ayoob and Fadhil (2019)
Palm kernel shell	Activated carbon support	NaOH	600	3	(K_2CO_3 and $Cu(NO_3)_2$	105	24	69.62	5.73	95.36	Abdullah et al. (2021)
Banana peel	Modified ash	–	650	3	$Li–CaO/Fe_2(SO_4)_3$	–	–	411.2	11.09	99.8	Madai et al. (2020)
Rice husk	Modified ash	–	900	4	Li_2CO_3	900	4	–	15	99.5	Chen et al. (2013)
Wood ash	Modified ash	–	800	–	K_2CO_3	800	3	12	12.7	97	Sharma et al. (2012)
Waste date pits	Modified ash	–	500	4	Calcium nitrate tetrahydrate	450	4	255.8	–	98.2	Ala'a et al. (2018)

a study, Niu and his team synthesized bamboo-based activated carbon for the esterification of oleic acid to produce biodiesel. Derived heterogeneous acid catalyst exhibits the well-developed mesoporous microstructure with a surface area of 225.71 $m^2\ g^{-1}$ (Niu et al. 2018). Bora et al. (2018) investigated the synthesis of heterogeneous carbonaceous catalysts from waste mesua ferrea linn (MFL) shells for esterification of mesua ferrea linn (MFL) oils. The study investigated the optimization of the biodiesel synthesis process based on four parameters viz. reaction time, temperature, catalyst loading, and methanol to oil ratio. A maximum of 95.57% of FFA conversion was recorded at optimum conditions including 10 wt% of catalyst, 6:1 ratio of methanol to oil, and 2 h of reaction at 55 °C.

Lathiya et al. (2018) prepared a solid acid catalyst from waste orange peels to investigate cost-effective biodiesel production. The orange peel AC was sulfonated by using concentrated H_2SO_4. Activated carbon was prepared through hydrothermal carbonization and KOH was used as an activation agent to promote the carbonization process as well as the formation of a mesoporous structure. Sulfonation was carried out in a teflon coated autoclave reactor at 200 °C for 24 h. The mechanism suggested that treatment of KOH with surface carbons leads to the formation of K_2CO_3 and after carbonization, the materials comprise of K metal, K_2O, CO, CO_2. The experimental analysis confirmed the attached $–SO_3H$ groups on ACs surface and increased sulfur content after sulfonation. A maximum biodiesel conversion of 91.68% was obtained from corn acid oil under optimized conditions using Box–Behnken Design (BBD). In an experiment, Ezebor et al. (2014) derived solid acid catalysts from Oil palm trunk and sugarcane bagasse for rapid esterification of fatty acids and moisture-assisted transesterification of oils using pseudo-infinite methanol. They investigated the effect of pseudo-infinite methanol in increasing the rate of esterification and transesterification reactions over oil palm trunk (OPT) and sugarcane bagasse (SCB) derived solid acid catalysts. The study found that under optimal reaction conditions, the process provides the FAME yields of 93% and 94% in 45 min for OPT and SCB catalysts, respectively. Fadhil et al. (2016) utilized waste polyethylene terephthalate (PET) to prepare activated carbon acid catalyst for biodiesel production from *Silybum marianum* L. seed oil. The catalyst reusability study reported that the catalytic activity gradually decreases upon recycling and reached 60% at the fifth cycle. Chellappan et al. (2018) also used concentrated sulfuric acid to introducing $–SO_3H$ groups in the surface of sawdust-derived biochar. The BET analysis showed that sulfonated biochar catalyst has a higher surface area and pore volume as compared to biochar. Moreover, sulfonation leads to functionalized biochar surfaces containing various functional acidic groups such as weak acidic –OH groups, strong acidic –COOH, and $–SO_3H$ groups. These functional groups provide a remarkable contribution to enhanced catalytic activity and increase the reactants' accessibility towards acidic sites for simultaneous esterification and transesterification.

In a study Yu et al. (2021) applied waste ginger straw as an efficient heterogeneous acid catalyst for biodiesel production. The acidic catalyst was synthesized by partial carbonization of the raw materials followed by sulfonation under sulphuric acid at optimized preparation conditions. The catalyst exhibits an amorphous carbon structure having an $–SO_3H$ group density of 1.05 mmol/g and provides excellent thermal stability up to 200 °C and satisfactory catalytic performance (93.2%) under the optimized reaction conditions of 9:1 M ratio of methanol to oleic acid and 7 wt% catalyst concentration at 64 °C for 210 min. Malani et al. (2018) used Rubber De-Oiled Cake as Heterogeneous Acid Catalyst source in Biodiesel Production by using Mixed Non-Edible Oil Feedstock. The acid catalyst was prepared through the direct sulfonation process by using Sulfuric acid and Chloro-sulfonic acid. The acidity of the catalysts was determined via titration techniques and total acidic site density was found to be 2.92 and 3.76 mmol/g for sulfonated and chloro–sulfonated catalyst respectively. The study reported a maximum biodiesel yields of $91.2 \pm 1.1\%$ and $93.7 \pm 1.3\%$ were achieved at 8.18 wt% catalyst loading and 12.8:1 molar ratio at 63 °C in single–step process and two-step process respectively. Wang et al. (2018) reported a mesoporous solid acid derived from biodegradable biomass materials through a mild and environmental friendly process. The experimental investigation revealed that a maximum 96.7% biodiesel yield was attained at 80 °C with in 3 h under 4 wt% catalyst dosage and 15:1 molar ratio of oleaic acid to methanol. It was found that the presence of the $–SO_3H$ and NH_3^+ sites on the magnetic catalyst plays a significant rule for effective esterification of high acid value oleaic acid with methanol. The reaction parameters and the functionalization process of some biomass based acidic heterogeneous catalysts are illustrated in Table 4.

Nanocatalysts from biomass resources

Apart from biomass based heterogeneous acidic and basic catalysts, biomass derived nanocatalysts have shown tremendous potential owning to their larger surface area, higher selectivity, and excellent catalytic activity. Researchers are now attracting towards the preparation of novel nanocatalysts with size ranging from 1 to 100 nm from biowaste materials due to their high surface areas, higher catalytic activity, and longer stability and at the same time it offers economic feasibility and environment friendly. Numerous methods have been reported for the synthesis of nanocatalysts such as wet impregnation method, combustion method, co-precipitation method, precipitation method, hydrothermal

Table 4 The reaction parameters and the functionalization process of some biomass based acidic heterogeneous catalysts

Source	Catalyst type	Activation/Calcination			Impregnation/Sulfonation			BET-Surface area ($m^2 g^{-1}$)	Basisity (mmol g^{-1})	FAME yield (%)	References
		Agent	T (°C)	T (h)	Agent	T (°C)	T (h)				
Oil palm Biomass	Activated carbon support	KOH	700	2	K_3PO_4	500	3	680	–	98	Farid et al. (2017)
Kenaf seed cake	Activated carbon support	H_3PO_4	400	2	H_2SO_4	150	12	365.63	–	97.9	Akinfalabi et al. (2019)
Corn cob	Activated carbon support	H_3PO_4	500	1	4-benzenediazoniumsulfonate	–	–	730.8	–	88.7	Rocha et al. (2019)
Oil-cake waste	Activated carbon support	H_3PO_2	500	1	4-benzenediazoniumsulfonate	–	–	696	–	71	Konwar et al. (2014a, b)
Orange peel	Activated carbon support	KOH	180	6	H_2SO_4	200	24	44	–	91.68	Lathiya et al. (2018)
Corncob	Activated carbon support	H_3PO_4	900	2	4-benzenediazoniumsulfonate	–	–	721.71	–	72.09	Tang et al. (2020)
Sugarcane bagasse	Activated carbon support	–	400	8	H_2SO_4	150	15	52. 13	–	94	Ezebor et al. (2014)
Murumuru kernel shell	Sulfonated ash	–	600	1	H_2SO_4	200	4	–	–	91.8	Bastoset al. (2020)
Sawdust	Sulfonated ash	–	400–600	4	H_2SO_4	–	–	3.3	–	95.6	Chellappan et al. (2018)
Tea waste	Sulfonated ash	H_3PO_4	700	2	H_2SO_4	160	6	122	–	97	Rashid et al. (2019)

method, sol–gel method,, and self-polymerization based grafting technique. Many researchers showed that several biowaste materials can be effectively utilized for the preparation of efficient nanocatalyst such as waste leaves, waste seeds, snail shell, waste eggshell, waste mussel shell, chicken bone, animal bone etc. as illustrated in Table 5. Zik et al. (2020) investigated the catalytic activity of nano-crystal cellulose and nano CaO derived from coconut residue and chicken bone for biodiesel production from waste cooking oil (WCO). The nanocatalysts were prepared by calcination process at different temperatures for different periods of time viz. 700, 800, and 900 °C for 4, 5, and 6 h, respectively. They reported the catalyst recyclability test and found the biodiesel yield was more than 90% after the fourth cycle. In a study, Krishnamurthy et al. (2020) reported the synthesis of snail shell based CaO nanocatalyst for biodiesel production by using *Hydnocarpus wightiana* oil and dairy scum. The hydrothermally prepared CaO nanocatalyst showed the average crystallite size of 40 nm having a surface area of 9.37 $m^2 g^{-1}$, and the average pore volume and pore diameter were found to be 0.0538 $cm^3 g^{-1}$ and 2.29 nm respectively. Borah et al. (2019) utilized the waste eggshell for the synthesis of CaO nanocatalyst for biodiesel production from WCO and found that the catalyst provides a satisfactory biodiesel yield after five consecutive cycles in presence of optimum conditions. Erchamo et al. (2021) investigated the catalytic performance of eggshell based CaO nanocatalyst for biodiesel synthesis from waste cooking oil. Since the use of ethanol in the transesterification reaction arises with various problems such as emulsification and difficulty in the separation process, in the transesterification reaction, they used a mixture of methanol–ethanol as ethanol provides better solvability as compared to methanol, while presence of methanol reduces the emulsification effect of ethanol. The experimental results found that a biodiesel yield of 92% was obtained under the optimized parameters like 2.5 wt% catalyst amount, 12:1 ratio of mixed methanol–ethanol (8:4) to oil for 120 min at 60 °C.

In a study, Yatish et al. (2021) employed the *Terminalia chebula* plant leaves and seeds as a green source for the preparation of copper oxide nanoparticles (CuO) and biodiesel production respectively. By using the prepared CuO nanocatalysts a maximum 97.1% biodiesel yield was achieved in presence of 3 wt% catalyst loads and 9:1 of methanol to oil molar ratio for the reaction time of 60 min at 60 °C. Dutta et al. (2019) investigated biodiesel synthesis from fish waste lipid by using zinc oxide nanocatalyst derived from banana (*Musa* spp.) corm (rhizome) extract. Figure 5 shows the SEM images of ZnO nanocatalysts. Dawood et al. (2021) demonstrated a green method for the preparation of nickel oxide nanocatalyst from an aqueous latex extract of the Ficus elastic. The diameter of the spherical-cubic shaped NiO nanocatalysts was found to be

Table 5 Method of preparation and characteristics of some biomass based nanocatalysts

Source	Nanocatalyst	Methods	Size (nm)	Surface area ($m^2 g^{-1}$)	References
Terminalia chebula leaves	CuO	Solution combustion Leaf extract was mixed with $Cu(NO_3)_2$, stirred and finally calcined at 400 °C	100	11.92	Yatish et al. (2021)
Cinnamomum tamala leaves	CuO	Leaf extract was mixed with $CuSO_4$, stirred at 70 °C and finally centrifuged, washed with water and ethanol	20	–	Suresh et al. (2021)
Razma seeds	ZnO	Seeds powder was mixed with $Zn(NO_3)_2$, heated to form gel, calcined at 500 °C for 3 h	50	–	Reddy Yadav et al. (2018)
Banana rhizome	ZnO	Banana rhizome extract was mixed with $ZnSO_4$ under microwave irradiation, washed and calcined at 400 °C for 3 h	372	–	Dutta et al. (2019)
Ficus elastic latex	NiO	Latex extract was mixed with $NiSO_4$ solution, heated upto 200 °C, centrifuged and finally calcined at 300 °C for 3 h	22–26	–	Dawood et al. (2021)
Castor leaf	Iron nanoparticles	Castor leaf extract was mixed with ferric chloride solution, centrifuged and dried	10–35	–	Rengasamy et al. (2016)
Egg shell	CaO	Eggshells were powdered and calcined at 900 °C for 3 h, refluxed in water at 60 °C, dried and calcined at 870 °C for 3 h	75	16.4	Pandit and Fulekar (2017))
Oil-palm empty fruit	K_2O	Burned in open air, milled and finally calcined at 600 °C for 4 h	150	–	Husin et al. (2018)
Egg shell	Zn–CaO	Egg shell was calcined at 900 °C for 3 h, mixed with aqueous solution of zinc acetate, filtered and finally calcined at 900 °C for 3 h	30–42	–	Borah et al. (2019)
Snail shell	CaO	Dry shells were crushed and washed with nitric acid, hydrothermal treatment with water at 120 °C for 3 h, finally calcined at 900 °C for 4 h	40	9.37	Krishnamurthy et al. (2020)
Waste eggshell	CaO	Crushed and dried egg shells were calcined at 900 °C, reflux in water at 60 °C, finally calcined at 870 °C for 3 h	23.65	64.51	Ahmad et al. (2020)
Eggshell	CaO	Crushed and dried egg shells were calcined at 900 °C for 3 h, reflux in water at 60 °C, finally calcined at 800 °C for 3 h	13.53–21.3	–	Erchamo et al. (2021)
Chicken bone	CaO	Dry bone powder was calcined at 700, 800, and 900 °C for 4, 5 and 6 h	50.34	–	Zik et al. (2020)
Palm kernel shell	K_2CO_3–CuO	Hydrothermal carbonization, chemical activation with NaOH, calcined at 600 °C for 3 h, functionalized with K_2CO_3 and $Cu(NO_3)_2$	–	3368.60	Abdullah et al. (2021)
Citrus sinensis peel	CSPA@Fe_3O_4	Burned in open air to make ash, water extract of ash was mixed with $FeSO_4.7H_2O$ and $FeCl_3$, stir for 3 h	12–13	15.55	Changmai et al. (2021a, b)
Croton macrostachyus leaves	Metal oxides	Sol–gel-thermal oxidation method	23.8	126.3	Kasirajan et al. (2022)
Citrullus colocynthis fruit	MgO	Co-precipitation method	1–5	147.4	Khan et al. (2022)

Table 5 (continued)

Source	Nanocatalyst	Methods	Size (nm)	Surface area (m^2 g^{-1})	References
Buxus papillosa leaf	CdO_2	Leaf extract was mixed with $CdSO_4$ followed by calcination	45	–	Arshad et al. (2023)

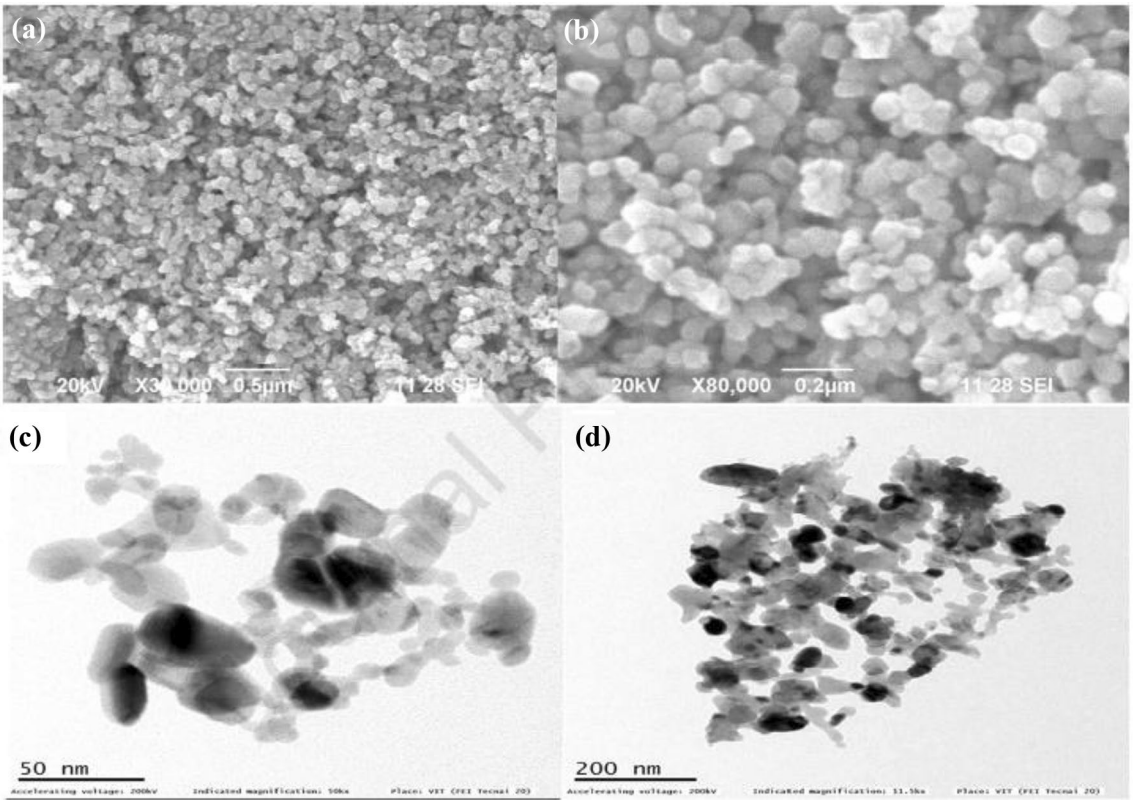

Fig. 5 SEM (**a**, **b**) and TEM (**c**, **d**) images of CuO nanocatalyst (Reproduced from with permission from Elsevier, Suresh et al. 2021)

22–26 nm and provides a highest biodiesel yield of 97.5% at optimum conditions. Rengasamy et al. (2016) investigated the catalytic effects of iron nanoparticles derived by using castor leaf extract in the transesterification of castor oil. The size of the iron nanoparticles was found to be 10–35 nm and the transesterification reaction yielded about 86% biodiesel in presence of 1 wt% of catalyst and 1:9 molar ratio of castor oil and methanol at 65 °C within 150 min. Cholapandian et al. (2022) investigated the biodiesel production from waste cooking oil by using CaO nanocatalyst synthesized from Acalypha indica leaves. The experimental investigation found 94.74% biodiesel yield under optimum process parameters like 2.4 wt% of catalyst load, 11.8:1 ratio of methanol to oil molar at 63.7 °C of reaction temperature for 70 min of reaction time. Kasirajan et al. (2022) utilized croton macrostachyus leaves for the preparation of metal oxides nano-catalyst via sol–gel–thermal oxidation method and the seeds as a potential non edible oil resource for biodiesel production by ultrasound-supported transeserification process. The prepared nanocatalyst exhibits superior basic sites with a high surface area of 126.3 m^2 g^{-1} and the particle size was 23.8 nm. They achieved a maximum yield of 98.85 ± 0.99 wt% by using 1.23 wt% of catalyst concentration with 1:9.13 molar ratio of oil to methanol within 36 min at a reaction temperature of 55.48 °C.

Biomass based magnetic nanocatalysts

Biomass materials loaded with ferrite ion that usually known as magnetic biochar catalyst has garnered tremendous attention in recent years. Typically, the magnetic biochar catalyst was prepared by impregnation of ferrite ion containing reagent into biomass materials followed by the thermal treatment. The usage of biomass impregnated magnetic

catalysts provides the economically sustainable approach as it enhance the recovery and reusability property of solid magnetic biochar catalyst in the biodiesel production. Furthermore, this helps to eliminate dependence of the time-consuming mechanical work and involvement of electrical instruments like centrifuge for the recovery of solid catalyst (Quah et al. 2019). The reaction conditions and recyclability yield of some biomass derived heterogeneous catalysts are summarized in Table 6.

Guo et al. (2012a, b) reported that magnetic catalyst can be recovered 1.7 times faster than non-magnetic catalyst. Besides that, nanomagnetic catalyst exhibits high specific surface area that leads the higher active sites on the catalyst surface which enhances the catalytic activity. It was also stated that the impregnation of Fe particles on the catalyst helps to elimination of volatile matters like H_2O and CO_2 during biomass pyrolysis process which in turn increases the surface area and pore volume of the catalyst particles. Moreover, the magnetic catalyst displayed tremendous stability and reusability after several cycles without any loss of catalytic activity. Ibrahim et al. (2019) prepared a carbonaceous solid acid magnetic catalyst using empty fruit bunch for biodiesel production from palm fatty acid distillate (PFAD). The synthesis process comprised of three consecutive steps like chemical activation-doping-sulphonation. Chemical activation was performed to increase the surface active site of the precursor material while the doping of Fe was carried out at different concentrations such as 2, 5, 10 and 15 (%) followed by sulphonation to obtain AC-$Fe_{(x)}$-SO_3Cl. The prepared magnetic catalyst had a high magnetic properties (HC = 344.14G) with higher surface area of 20.42 m^2/g and acidity of 29,520 µmol/g. The catalyst also showed excellent catalytic activity with 98.6% conversion of high free fatty acid at 100 °C in presence of 4 wt% catalyst and 16:1 methanol to PFAD ratio within 3 h. The synthesized magnetic catalyst could be effectively recovered as shown in Fig. 6. and showed superior esterification activity upto six continuous cycles without any further treatment. In another study, Araujo et al. (2021) derived a magnetic acid catalyst by using simple impregnation process followed by calcination at different temperatures and functionalization with sulphuric acid. In their study, red mud was used as Fe precursor for the synthesis of magnetic catalyst. The impregnation process was done at several ratios of red mud and acai seed powder followed by thermal treatment in a tubular furnace at 400, 500 and 600 °C which converts the hematite phase to magnetite phase. The obtained material was further functionalized with concentrated sulfuric acid for 180 min at 80 °C to get desired magnetic catalyst. It was observed that the optimum ratio of acai seed powder to red mud was 1:1 and the calcination temperature was 400 °C for 3 h. The prepared magnetic catalyst presented 88% yield of methyl oleate under 5 wt% catalyst concentrations and a 1:12 molar ratio of oleic acid to methanol at 100 °C. Quah et al. (2020) reported waste palm kernel shell derived magnetic acid catalyst via impregnation method. The dry biomass powder was mixed with an appropriate amount of iron chloride solution and placed for pyrolysis to form magnetic biochar and the acidity of the biochar was introduced by treating with concentrated sulphuric acid which leads to form the covalent linkages of sulfonic groups (–SO_3H) onto the surface of the mesoporous magnetic carbon. The analysis showed that the magnetic biochar prior to sulfonation possessed high magnetisation saturation of 37.655 emu/g and after sulfonation the magnetism was reduced to 8.458 emu/g. However, it was able to provide satisfactory magnetic response which was sufficient to recover the magnetic catalyst from reaction media effectively by using an external magnetic field.

On the other hand, Changmai et al. (2021a, b) derived a magnetically separable silica support acidic nanocatalyst for biodiesel production. The magnetic Fe_3O_4 was synthesised through co-precipitation method which was coated with silica nanoparticles to get Fe_3O_4@SiO_2 and finally functionalized with sulfonic acid to obtain Fe_3O_4@SiO_2–SO_3H core@shell nanoparticulate acid catalyst. The derived catalyst had a stronger magnetic saturation of 30.94 emu $g^{-1}$and displayed a surface area and pore diameter of 32.88 m^2 g^{-1} and 3.48 nm respectively. In other study, they also synthesized *Citrus sinensis* peel ash coated magnetic basic catalyst via a simple one step process. Magnetic Fe_3O_4 nanoparticles were synthesized via traditional co-precipitation method followed by the dropwise addition of basic extract prepared from *Citrus sinensis* peel ash (CSAP). The basicity and surface area of the catalyst was found to be 0.170 mmol g^{-1} and 15.55 m^2 g^{-1} respectively which showed significant reactivity in the formation of biodiesel. The vibrating sample magnetometer (VSM) analysis provides the existence of magnetism on derived Fe_3O_4 and CSPA@Fe_3O_4 are 37.74 and 31.56 emu/g respectively. The drop in magnetism of CSPA@Fe_3O_4 states the successful impregnation of ash materials on the surface of the highly magnetic Fe_3O_4 nanoparticles (Changmai et al. 2020). They also demonstrated a reaction mechanism based on diffusion–adsorption model on the magnetic catalyst surface Fig. 7. Since the magnetic particles surface was loaded with the basic oxides of the biomass substances, the O^{2-} species on catalyst surface helps to generate the methoxide ion which further attacks the electron deficient centre of triglyceride and form a tetrahedral intermediate followed by the rearrangement to methyl ester or biodiesel and diglyceride anion. Afterwards the diglyceride anion abstracts the hydrogen from catalyst to form diglyceride and similarly the process was repeated and generates one mole of glycerol and three moles of methyl ester.

Wang et al. (2018) reported a novel magnetically recyclable solid acid catalyst utilizing chitosan. They prepared a double shell hollow structured acid catalyst for the green

Table 6 The reaction conditions and recyclability yield of some biomass derived heterogeneous catalysts

Feedstock	Catalyst	Main elements/components	Reaction conditions				Yield%	Catalyst run	Recyclablity yield%	References
			MeOH/Oil	Catalyst (wt%)	T(h)	T(°C)				
Palm oil	Capiz shell	CaO	8:1	3	6	60	93	3	–	Suryaputra et al. (2013)
Soybean oil	Snail shell	CaO	6:1	3	7	RT	98	8	91	Laskar et al. (2018)
Waste cooking oil	Egg shell	CaO	15:1	3	3	80	92.1	5	79	Mansir et al. (2018)
Date seed oil	Chicken egg shell	CaO	12:1	5	1.5	65	93.5	6	80	Farooq et al. (2018)
Waste cooking oil	Ostrich bone	CaO	15:1	5	4	60	90.56	6	75	Khan et al. (2020)
Waste cooking oil	Chicken bones	CaO	15:1	5	4	65	89.33	4	80	Farooq et al. (2015)
Sunflower oil	Palm kernel shell	CaO	9:1	3	4	65	99	3	96.2	Kostić et al. (2016)
Mustard oil	Turbonilla striatula	CaO	9:1	3	3	65	93.3	3	50	Boro et al. (2011)
Waste cooking oil	Scallop shell	CaO	6:1	5	2	65	86	5	65	Sirisomboonchai et al. (2015)
Soybean oil	Banana trunk ash	K_2O	6:1	5	6	RT	98.39	5	61	Rajkumari and Rokhum (2020)
Soybean oil	Moringa leaves	O, Ca, K	6:1	6	2	65	86.7	3	53.11	Aleman-Ramirez et al. (2021)
Jupati oil	Murumuru kernel shell	C, O	30:1	6	4	135	91.8	4	80	Bastos et al. (2020)
Pongamia pinnatta oil	Sawdust	C, O, S	9:1	2	2	85	95.6	3	85.7	Chellappan et al. (2018)
Soybean oil	Pineapple leaves	K, Ca, Mg	40:1	4	0.5	80	98.2	4	85	Barros et al. (2020)
Waste cooking oil	Citrus sinensis peel	K_2O, CaO	6:1	6	3	65	98	9	91	Changmai et al. (2021a, b)
Neem seed oil	Banana peels	K, Si	8:1	1.7	1	60	99.8	5	75	Madai et al. (2020)
Calophyllum inophyllum oil	Sugarcane leaf	SiO_2, CaO, MgO	19:1	5	3	64	97	6	85	Arumugam and Sankaranarayanan (2020)
Waste palm oil	Coconut coir husk	C, O	12:1	10	3	130	89.8	4	77	Thushari et al. (2019)
Soybean oil	Brassica nigra plant	K, Ca	12:1	7	0.5	65	98.79	3	96	Nath et al. (2019)
Date seed oil	Waste date pits	CaO	12:1	4.5	2	70	98.2	6	82	Ala'a et al. (2018)
Soybean oil	Rice husk ash	Si, O	24:1	4	3	65	99.5	5	86	Chen et al. (2013)

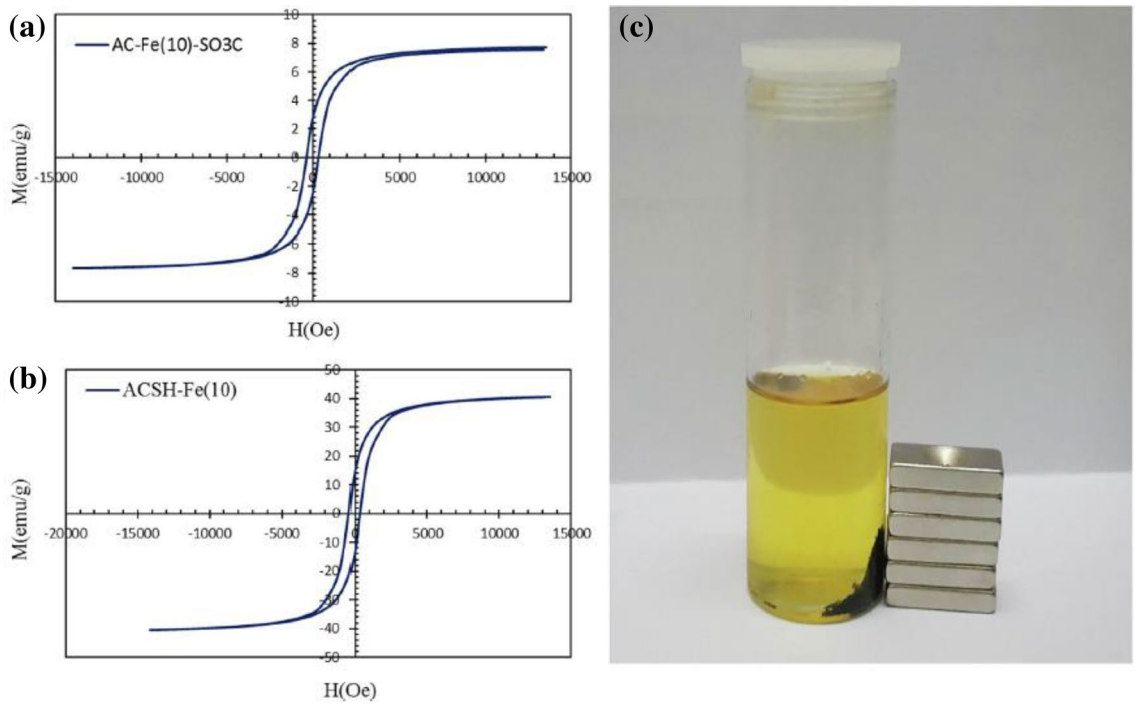

Fig. 6 VSM magnetization curves of magnetic catalyst (**a**, **b**) and magnetic separation of the catalyst (**c**) (Reproduced with permission from Elsevier, Ibrahim et al. 2019)

production of biodiesel as illustrate in Fig. 8. At first the Fe_3O_4 nanoparticles was prepared as the center of microsphere followed by the introduction of chitosan layer above the magnetic nanospheres. The obtained Fe_3O_4@chitosan was treated with tetraethyl orthosilicate (TEOS) under continuous stirring to get chitosan coated Fe_3O_4@chitosan@SiO_2 and the above identical procedure was repeated to form the double shell structure. The acidic functional groups were introduced on the surface of the double shell microspheres using *p*-toluenesulfonic acid. The incorporated double shell hollow structure provides several advantages on catalytic activity such as preventing the magnetic materials from etching and improvement on surface area and active sites on catalyst surface. The experimental analysis showed that the hollow structure of Fe_3O_4@Chitosan-Hollow-Chitosan (FCHC) offers a high biodiesel yield of 96.7% whereas non hollow Fe_3O_4@Chitosan-SO_3H catalyst offered only 75.1%. The Fe_3O_4@Chitosan-Hollow-Chitosan (FCHC) catalyst exhibited a strong magnetism of 18.9 emu/g and a remarkable recyclability rate (84.1% biodiesel yield) even after five cycles.

In another study, Liu et al. (2018) reported the utilization of bamboo charcoal for the synthesis of bifunctional magnetic solid base catalyst in biodiesel production. The synthesis process involves the wet impregnation of bamboo charcoal precursor with γ-Fe_2O_3 through an in-situ method followed by the saturation using KNO_3 solution. After that the magnetic bamboo charcoal substances placed for calcination at 500 °C for 3 h. The experimental investigation revealed the characteristic mesoporous structure of the magnetic catalyst having high specific surface area of 28.7m^2/g along with strong magnetism of 35.4 emu/g due to stable impregnation of γ-Fe_2O_3 particles onto the carbon skeleton of bamboo charcoal. The as prepared catalyst provides 98.0% of biodiesel yield under 2.5 wt% catalysts loading and 8:1 ratio of methanol to oil at 60 °C. Moreover, it also demonstrated the excellent recovery yield of more than 94% even after four consecutive cycles. Zhang et al. (2016) also derived a magnetic base catalyst from bamboo powder supported with nickel and sodium silicate (Na_2SiO_3@Ni/C). In their study, the magnetic precursor was synthesized by using the mixture of nickel nitrate solution, solid urea and bamboo powder followed by calcination at high temperature to get Ni/C particles. Finally, the Ni/C particles were mixed with sodium silicate solution through reflux and then calcinated at 400 °C to obtain the final magnetic catalyst. The existence of Ni element in the synthesized catalyst displayed a strong magnetism (15.7 emu/g) and also provided excellent catalytic activity for the conversion of glycerol to hydrogen. Apart from that, comparatively a high biodiesel yield (98.1%) was achieved in the fresh cycle followed by the reusability yield of greater than 93% after four cycles.

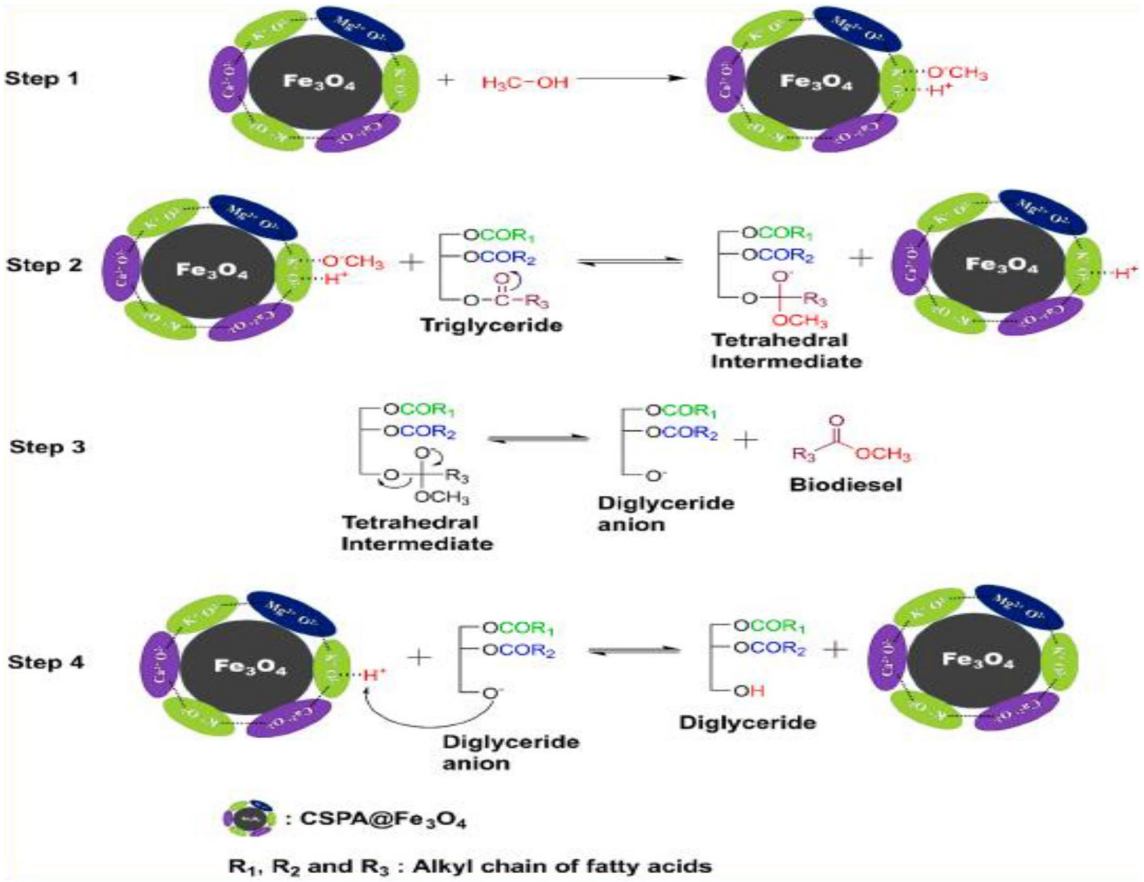

Fig. 7 Probable mechanism of CSPA@Fe_3O_4 catalyzed transesterification reaction (Reproduced with permission from Elsevier, Changmai et al. 2020)

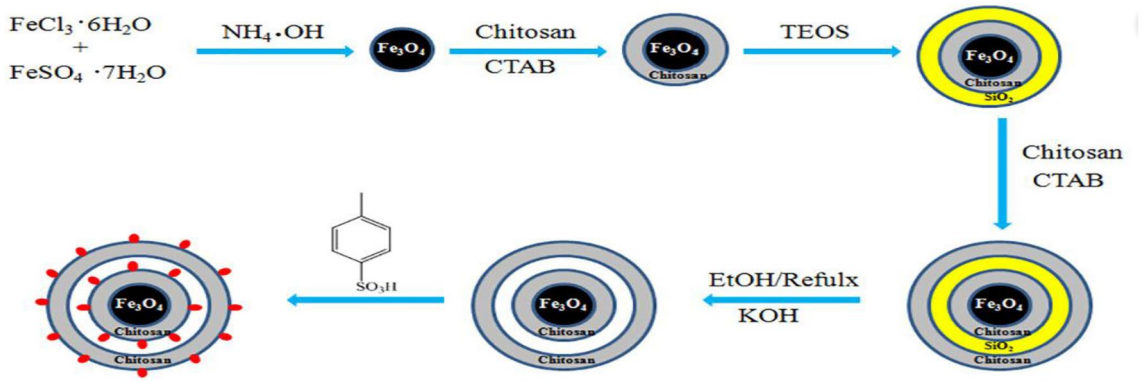

Fig. 8 Schematic illustration for the synthesis of FCHC-SO_3H catalyst (Reproduced with permission from Elsevier, Wang et al. 2018)

Critical analysis of the catalysts

The biomass based heterogeneous catalysts provides numerous advantages over the chemical based catalysts including the biodegradable, non-toxic and high abundant nature. However, the catalytic activity of biomass originated catalysts depends upon the elemental compositions (like potassium, calcium, magnesium etc.) and the crystalline components (like K_2CO_3, K_2O, CaO, MgO etc.) of the catalysts which are the significant factor for the reactivity of transesterification reaction. The presence of high concentrations of alkali and alkaline elements or compounds makes the biomass materials extremely basic in natures that are suitable to carry out a transesterification reaction. Moreover,

the catalytic activity of the catalysts depends upon the nature of feedstock used for transesterification. The basic catalysts are suitable for low FFA (< 3%) content feedstock due to their tendency towards soap formation in presence of high FFA. The acid catalyzed transesterification is unaffected by the high FFA as it also esterifies to their respective methyl esters and increases the overall biodiesel yield. This review also found that not only basicity and acidity can control the transesterification reaction and biodiesel yield but also the catalysts size and surface area are quite significant. Small sized and high surface area catalysts offer sufficient accessibility to reactant molecules for catalysts surface active site which ultimately enhance the biodiesel yield. However, there is no linear relationship is established well between the biodiesel yield and the surface area of the biomass based catalysts. The basic functionalized catalysts are more effective for biodiesel synthesis as it requires short reaction time as compared to the acidic catalysts. Besides that, the magnetic functionalized heterogeneous basic catalysts are more superior due to their rapid and easy separable nature from the reaction medium which enhances the catalyst reusability up to certain repeated cycles.

Conclusions and perspectives

Production of biodiesel via transesterification of triglycerides is mainly influenced by the active sites and basicity of catalyst as well as amount of catalyst, molar ratio of methanol to oil, reaction times, and temperatures. This review revealed that the utilization of biomass derived heterogeneous catalyst is found as one of the most potential heterogeneous catalysts for biodiesel synthesis. Catalysts derived from various renewable biomasses such as egg shells, fish scales, biomass ash and animal bones have shown promising effect for biodiesel production which is easily available in nature. The consumption of biomass or waste as the source of catalyst may reduce the associated cost for commercially available solid catalyst as well as provide new applications and utilization for the waste. However, solid heterogeneous catalysts often struggle with poisoning and active site leaching in the reaction medium. Thereby, to develop a more efficient design, robust and catalytically stable catalysts is still an important challenge which can improve the overall quality of biodiesel production process. It is important to maintain the porosity and hydrophilic/hydrophobic sites on catalyst surface so that mass transport can be enhanced with limited diffusion and catalyst deactivation. Apart from that, single step or in-situ route for catalyst preparation is encouraged to avoid the complex multistep grafting process. The basic functionalized catalysts are more effective for low FFA content feedstock whereas acidic catalysts are more favourable for high FFA feedstock for biodiesel synthesis. Besides that, the magnetic functionalized heterogeneous catalysts are more superior due to their rapid and easy separable nature from the reaction medium which enhances the catalyst reusability up to certain repeated cycles. Nevertheless, further investigation and development of biomass derived heterogeneous catalyst are necessary to explore more efficient and highly active heterogeneous catalyst that can improve the overall catalytic performance in biodiesel production as well as other chemical processes.

Availability of data and materials No datasets are used.

Declarations

Conflict of interest There is no conflict of financial or personal interest.

Ethical statements Not applicable.

References

Abdullah SHYS, Hanapi NHM, Azid A, Umar R, Juahir H, Khatoon H, Endut A (2017) A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renew Sustain Energy Rev 70:1040–1051

Abdullah RF, Rashid U, Ibrahim ML, Hazmi B, Alharthi FA, Nehdi IA (2021) Bifunctional nano-catalyst produced from palm kernel shell via hydrothermal-assisted carbonization for biodiesel production from waste cooking oil. Renew Sustain Energy Rev 137:110638

Ahmad S, Chaudhary S, Pathak VV, Kothari R, Tyagi VV (2020) Optimization of direct transesterification of *Chlorella pyrenoidosa* catalyzed by waste egg shell based heterogenous nano-CaO catalyst. Renew Energy 160:86–97

Akinfalabi SI, Rashid U, Shean TYC, Nehdi IA, Sbihi HM, Gewik MM (2019) Esterification of palm fatty acid distillate for biodiesel production catalyzed by synthesized kenaf seed cake-based sulfonated catalyst. Catalysts 9(5):482

Alaa H, Jamil F, Al-Haj L, Myint MTZ, Mahmoud E, Ahmad MN, Hasan AO, Rafiq S (2018) Biodiesel production over a catalyst prepared from biomass-derived waste date pits. Biotechnol Rep 20:e00284

Aleman-Ramirez JL, Moreira J, Torres-Arellano S, Longoria A, Okoye PU, Sebastian PJ (2021) Preparation of a heterogeneous catalyst from moringa leaves as a sustainable precursor for biodiesel production. Fuel 284:118983

Araujo RO, Santos VO, Ribeiro FC, Chaar JDS, Pereira AM, Falcão NP, de Souza LK (2021) Magnetic acid catalyst produced from acai seeds and red mud for biofuel production. Energy Convers Manage 228:113636

Arshad S, Ahmad M, Munir M, Sultana S, Zafar M, Dawood S, Alghamdi AM, Asif S, Bokhari A, Mubashir M, Chuah LF (2023) Assessing the potential of green CdO_2 nano-catalyst for the synthesis of biodiesel using non-edible seed oil of Malabar Ebony. Fuel 333:126492

Arumugam A, Sankaranarayanan P (2020) Biodiesel production and parameter optimization: an approach to utilize residual ash from sugarcane leaf, a novel heterogeneous catalyst, from *Calophyllum inophyllum* oil. Renewable Energy 153:1272–1282

Atabani AE, Badruddin IA, Badarudin A, Khayoon MS, Triwahyono S (2014) Recent scenario and technologies to utilize non-edible oils for biodiesel production. Renew Sustain Energy Rev 37:840–851

Ayodeji AA, Modupe OE, Rasheed B, Ayodele JM (2018) Data on CaO and eggshell catalysts used for biodiesel production. Data Brief 19:1466–1473

Ayoob AK, Fadhil AB (2019) Biodiesel production through transesterification of a mixture of non-edible oils over lithium supported on activated carbon derived from scrap tires. Energy Convers Manage 201:112149

Ayoob AK, Fadhil AB (2020) Valorization of waste tires in the synthesis of an effective carbon based catalyst for biodiesel production from a mixture of non-edible oils. Fuel 264:116754

Ayoola AA, Fayomi OSI, Usoro IF (2018) Data on PKO biodiesel production using CaO catalyst from Turkey bones. Data Brief 19:789–797

Azad AK, Ameer Uddin SM (2013) Performance study of a diesel engine by first generation bio-fuel blends with fossil fuel: an experimental study. J Renew Sustain Energy 5(1):013118

Balajii M, Niju S (2019a) A novel biobased heterogeneous catalyst derived from *Musa acuminata* peduncle for biodiesel production—process optimization using central composite design. Energy Convers Manage 189:118–131

Balajii M, Niju S (2019b) Biochar-derived heterogeneous catalysts for biodiesel production. Environ Chem Lett 17(4):1447–1469

Balajii M, Niju S (2020) Banana peduncle—a green and renewable heterogeneous base catalyst for biodiesel production from *Ceiba pentandra* oil. Renew Energy 146:2255–2269

Barros SDS, Junior WAP, Sá IS, Takeno ML, Nobre FX, Pinheiro W, Manzato L, Iglauer S, de Freitas FA (2020) Pineapple (*Ananás comosus*) leaves ash as a solid base catalyst for biodiesel synthesis. Biores Technol 312:123569

Bastos RRC, da Luz Corrêa AP, da Luz PTS, da Rocha Filho GN, Zamian JR, da Conceição LRV (2020) Optimization of biodiesel production using sulfonated carbon-based catalyst from an amazon agro-industrial waste. Energy Convers Manage 205:112457

Basumatary S, Nath B, Kalita P (2018) Application of agro-waste derived materials as heterogeneous base catalysts for biodiesel synthesis. J Renew Sustain Energy 10(4):043105

Basumatary S, Nath B, Das B, Kalita P, Basumatary B (2021) Utilization of renewable and sustainable basic heterogeneous catalyst from *Heteropanax fragrans* (Kesseru) for effective synthesis of biodiesel from *Jatropha curcas* oil. Fuel 286:119357

Behera B, Dey B, Balasubramanian P (2020) Algal biodiesel production with engineered biochar as a heterogeneous solid acid catalyst. Biores Technol 310:123392

Betiku E, Ajala SO (2014) Modeling and optimization of *Thevetia peruviana* (yellow oleander) oil biodiesel synthesis via *Musa paradisiaca* (plantain) peels as heterogeneous base catalyst: a case of artificial neural network vs. response surface methodology. Ind Crops Prod 53:314–322

Betiku E, Akintunde AM, Ojumu TV (2016) Banana peels as a biobase catalyst for fatty acid methyl esters production using Napoleon's plume (*Bauhinia monandra*) seed oil: a process parameters optimization study. Energy 103:797–806

Bohlouli A, Mahdavian L (2019) Catalysts used in biodiesel production: a review. Biofuels 12(8):885–898

Bora AP, Dhawane SH, Anupam K, Halder G (2018) Biodiesel synthesis from *Mesua ferrea* oil using waste shell derived carbon catalyst. Renew Energy 121:195–204

Borah MJ, Das A, Das V, Bhuyan N, Deka D (2019) Transesterification of waste cooking oil for biodiesel production catalyzed by Zn substituted waste egg shell derived CaO nanocatalyst. Fuel 242:345–354

Boro J, Thakur AJ, Deka D (2011) Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. Fuel Process Technol 92(10):2061–2067

Capuano L (2020) International Energy Outlook. U. S. Energy Information Administration (EIA), pp 1–7

Catarino M, Ramos M, Dias AS, Santos MT, Puna JF, Gomes JF (2017) Calcium rich food wastes based catalysts for biodiesel production. Waste Biomass Valor 8(5):1699–1707

Changmai B, Vanlalveni C, Ingle AP, Bhagat R, Rokhum L (2020) Widely used catalysts in biodiesel production: a review. RSC Adv 10(68):41625–41679

Changmai B, Rano R, Vanlalveni C, Rokhum L (2021a) A novel *Citrus sinensis* peel ash coated magnetic nanoparticles as an easily recoverable solid catalyst for biodiesel production. Fuel 286:119447

Changmai B, Wheatley AE, Rano R, Halder G, Selvaraj M, Rashid U, Rokhum SL (2021b) A magnetically separable acid-functionalized nanocatalyst for biodiesel production. Fuel 305:121576

Chellappan S, Nair V, Sajith V, Aparna K (2018) Synthesis, optimization and characterization of biochar based catalyst from sawdust for simultaneous esterification and transesterification. Chin J Chem Eng 26(12):2654–2663

Chen KT, Wang JX, Dai YM, Wang PH, Liou CY, Nien CW, Wu JS, Chen CC (2013) Rice husk ash as a catalyst precursor for biodiesel production. J Taiwan Inst Chem Eng 44(4):622–629

Cholapandian K, Gurunathan B, Rajendran N (2022) Investigation of CaO nanocatalyst synthesized from *Acalypha indica* leaves and its application in biodiesel production using waste cooking oil. Fuel 312:122958

Chowdhury S, Dhawane SH, Jha B, Pal S, Sagar R, Hossain A, Halder G (2019) Biodiesel synthesis from transesterified *Madhuca indica* oil by waste egg shell-derived heterogeneous catalyst: parametric optimization by Taguchi approach. Biomass Conv Bioref 11(4):1171–1181

Correia LM, Saboya RMA, de Sousa Campelo N, Cecilia JA, Rodríguez-Castellón E, Cavalcante CL Jr, Vieira RS (2014) Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sunflower oil. Biores Technol 151:207–213

Corro G, Sánchez N, Pal U, Bañuelos F (2016) Biodiesel production from waste frying oil using waste animal bone and solar heat. Waste Manage 47:105–113

Dawodu FA, Ayodele OO, Xin J, Zhang S (2014) Application of solid acid catalyst derived from low value biomass for a cheaper biodiesel production. J Chem Technol Biotechnol 89(12):1898–1909

Dawood S, Koyande AK, Ahmad M, Mubashir M, Asif S, Klemeš JJ, Bokhari A, Saqib S, Lee M, Qyyum MA, Show PL (2021) Synthesis of biodiesel from non-edible (*Brachychiton populneus*) oil in the presence of nickel oxide nanocatalyst: parametric and optimisation studies. Chemosphere 278:130469

Dejean A, Ouédraogo IW, Mouras S, Valette J, Blin J (2017) Shea nut shell based catalysts for the production of ethanolic biodiesel. Energy Sustain Dev 40:103–111

Demirbaş A, Arslan G, Pehlivan E (2006) Recent studies on activated carbons and fly ashes from Turkish resources. Energy Source A 28(7):627–638

Dhawane SH, Kumar T, Halder G (2018) Recent advancement and prospective of heterogeneous carbonaceous catalysts in chemical and enzymatic transformation of biodiesel. Energy Convers Manage 167:176–202

Dossin TF, Reyniers MF, Berger RJ, Marin GB (2006) Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. Appl Catal B 67(1–2):136–148

Dutta S, Jaiswal KK, Verma R, Basavaraju DM, Ramaswamy AP (2019) Green synthesis of zinc oxide catalyst under microwave

irradiation using banana (Musa spp.) corm (rhizome) extract for biodiesel synthesis from fish waste lipid. Biocatal Agric Biotechnol 22:101390

Endut A, Abdullah SHYS, Hanapi NHM, Hamid SHA, Lananan F, Kamarudin MKA, Umar R, Juahir H, Khatoon H (2017) Optimization of biodiesel production by solid acid catalyst derived from coconut shell via response surface methodology. Int Biodeterior Biodegradation 124:250–257

Erchamo YS, Mamo TT, Workneh GA, Mekonnen YS (2021) Improved biodiesel production from waste cooking oil with mixed methanol–ethanol using enhanced eggshell-derived CaO nano-catalyst. Sci Rep 11(1):1–12

Ezebor F, Khairuddean M, Abdullah AZ, Boey PL (2014) Oil palm trunk and sugarcane bagasse derived solid acid catalysts for rapid esterification of fatty acids and moisture-assisted transesterification of oils under pseudo-infinite methanol. Biores Technol 157:254–262

Fadhil AB, Aziz AM, Al-Tamer MH (2016) Biodiesel production from *Silybum marianum* L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification. Energy Convers Manage 108:255–265

Farabi MA, Ibrahim ML, Rashid U, Taufiq-Yap YH (2019) Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo. Energy Convers Manage 181:562–570

Farid MAA, Hassan MA, Taufiq-Yap YH, Ibrahim ML, Othman MR, Ali AAM, Shirai Y (2017) Production of methyl esters from waste cooking oil using a heterogeneous biomass-based catalyst. Renew Energy 114:638–643

Farooq M, Ramli A, Naeem A (2015) Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. Renew Energy 76:362–368

Farooq M, Ramli A, Naeem A, Mahmood T, Ahmad S, Humayun M, Islam MGU (2018) Biodiesel production from date seed oil (*Phoenix dactylifera* L.) via egg shell derived heterogeneous catalyst. Chem Eng Res Des 132:644–651

Faruque MO, Razzak SA, Hossain MM (2020) Application of heterogeneous catalysts for biodiesel production from microalgal oil—a review. Catalysts 10(9):1025

Gohain M, Devi A, Deka D (2017) *Musa balbisiana* Colla peel as highly effective renewable heterogeneous base catalyst for biodiesel production. Ind Crops Prod 109:8–18

Gohain M, Laskar K, Paul AK, Daimary N, Maharana M, Goswami IK, Hazarika A, Bora U, Deka D (2020a) *Carica papaya* stem: a source of versatile heterogeneous catalyst for biodiesel production and C-C bond formation. Renew Energy 147:541–555

Gohain M, Laskar K, Phukon H, Bora U, Kalita D, Deka D (2020b) Towards sustainable biodiesel and chemical production: multifunctional use of heterogeneous catalyst from littered *Tectona grandis* leaves. Waste Manage 102:212–221

Guo F, Xiu ZL, Liang ZX (2012a) Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Appl Energy 98:47–52

Guo P, Huang F, Zheng M, Li W, Huang Q (2012b) Magnetic solid base catalysts for the production of biodiesel. J Am Oil Chem Soc 89(5):925–933

Husin H, Asnawi TM, Firdaus A, Husaini H, Ibrahim I, Hasfita F (2018) Solid catalyst nanoparticles derived from oil-palm empty fruit bunches (OP-EFB) as a renewable catalyst for biodiesel production. IOP Conf Ser Mater Sci Eng 358(1):012008

Ibrahim NA, Rashid U, Taufiq-Yap YH, Yaw TCS, Ismail I (2019) Synthesis of carbonaceous solid acid magnetic catalyst from empty fruit bunch for esterification of palm fatty acid distillate (PFAD). Energy Convers Manage 195:480–491

Kasirajan R, Jiru EB, Girma E, Ancha VR, Sadasivam S, Jayakumar M, Manivasagan R (2022) Synthesis of bio-based oxides nano-composites catalyst from croton macrostachyus leaves for biodiesel production from croton macrostachyus seed oil. Fuel 325:124900

Khan HM, Iqbal T, Ali CH, Javaid A, Cheema II (2020) Sustainable biodiesel production from waste cooking oil utilizing waste ostrich (*Struthio camelus*) bones derived heterogeneous catalyst. Fuel 277:118091

Khan UN, Inayat A, Shah GM, Hassan HM, Zaki ME, Alanazi AA, El-Zahhar AA, Noureen S, Abbas SM (2022) Green synthesis of magnesium oxide nanosheets by using *Citrullus colocynthis* fruit extract and its use in biofuel production. Biomass Bioenerg 167:106640

Khatibi M, Khorasheh F, Larimi A (2021) Biodiesel production via transesterification of canola oil in the presence of Na–K doped CaO derived from calcined eggshell. Renew Energy 163:1626–1636

Konwar LJ, Boro J, Deka D (2014a) Review on latest developments in biodiesel production using carbon-based catalysts. Renew Sustain Energy Rev 29:546–564

Konwar LJ, Das R, Thakur AJ, Salminen E, Mäki-Arvela P, Kumar N, Mikkola JP, Deka D (2014b) Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste. J Mol Catal A Chem 388:167–176

Kostić MD, Bazargan A, Stamenković OS, Veljković VB, McKay G (2016) Optimization and kinetics of sunflower oil methanolysis catalyzed by calcium oxide-based catalyst derived from palm kernel shell biochar. Fuel 163:304–313

Krishnamurthy KN, Sridhara SN, Kumar CA (2020) Optimization and kinetic study of biodiesel production from *Hydnocarpus wightiana* oil and dairy waste scum using snail shell CaO nano catalyst. Renew Energy 146:280–296

Kumar P, Aslam M, Singh N, Mittal S, Bansal A, Jha MK, Sarma AK (2015) Characterization, activity and process optimization with a biomass-based thermal power plant's fly ash as a potential catalyst for biodiesel production. RSC Adv 5(13):9946–9954

Laskar IB, Rajkumari K, Gupta R, Chatterjee S, Paul B, Rokhum L (2018) Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil. RSC Adv 8(36):20131–20142

Lathiya DR, Bhatt DV, Maheria KC (2018) Synthesis of sulfonated carbon catalyst from waste orange peel for cost effective biodiesel production. Bioresour Technol Rep 2:69–76

Lee SL, Wong YC, Tan YP, Yew SY (2015) Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. Energy Convers Manage 93:282–288

Li M, Zheng Y, Chen Y, Zhu X (2014) Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk. Bioresour Technol 154:345–348

Li C, Hu X, Feng W, Wu B, Wu K (2018) A supported solid base catalyst synthesized from green biomass ash for biodiesel production. Energy Source A Recov Util Environ Effects 40(2):142–147

Lim S, Yap CY, Pang YL, Wong KH (2020) Biodiesel synthesis from oil palm empty fruit bunch biochar derived heterogeneous solid catalyst using 4-benzenediazonium sulfonate. J Hazard Mater 390:121532

Liu WJ, Zeng FX, Jiang H, Zhang XS (2011) Preparation of high adsorption capacity bio-chars from waste biomass. Bioresour Technol 102(17):8247–8252

Liu K, Wang R, Yu M (2018) An efficient, recoverable solid base catalyst of magnetic bamboo charcoal: preparation, characterization, and performance in biodiesel production. Renew Energy 127:531–538

Madai IJ, ChandeJande YA, Kivevele T (2020) Fast rate production of biodiesel from neem seed oil using a catalyst made from banana peel ash loaded with metal oxide (Li-CaO/$Fe_2(SO_4)_3$). Adv Mater Sci Eng 2020:1–11

Malani RS, Sardar H, Malviya Y, Goyal A, Moholkar VS (2018) Ultrasound-intensified biodiesel production from mixed nonedible oil feedstock using heterogeneous acid catalyst supported on rubber de-oiled cake. Ind Eng Chem Res 57(44):14926–14938

Maneerung T, Kawi S, Wang CH (2015) Biomass gasification bottom ash as a source of CaO catalyst for biodiesel production via transesterification of palm oil. Energy Convers Manage 92:234–243

Maneerung T, Kawi S, Dai Y, Wang CH (2016) Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. Energy Convers Manage 123:487–497

Mansir N, Teo SH, Rabiu I, Taufiq-Yap YH (2018) Effective biodiesel synthesis from waste cooking oil and biomass residue solid green catalyst. Chem Eng J 347:137–144

Mbaraka IK, Shanks BH (2006) Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. J Am Oil Chem Soc 83(2):79–91

Miladinović MR, Zdujić MV, Veljović DN, Krstić JB, Banković-Ilić IB, Veljković VB, Stamenković OS (2020) Valorization of walnut shell ash as a catalyst for biodiesel production. Renew Energy 147:1033–1043

Mohadesi M, Gouran A, Dehnavi AD (2021) Biodiesel production using low cost material as high effective catalyst in a microreactor. Energy 219:119671

Mohammed NI, Kabbashi NA, Alade AO, Sulaiman S (2017) Advancement in the utilization of biomass-derived heterogeneous catalysts in biodiesel production. Green Sustain Chem 8(1):74–91

Nath B, Das B, Kalita P, Basumatary S (2019) Waste to value addition: utilization of waste *Brassica nigra* plant derived novel green heterogeneous base catalyst for effective synthesis of biodiesel. J Clean Prod 239:118112

Nisar J, Razaq R, Farooq M, Iqbal M, Khan RA, Sayed M, Shah A, ur Rahman, I., (2017) Enhanced biodiesel production from Jatropha oil using calcined waste animal bones as catalyst. Renewable Energy 101:111–119

Niu S, Ning Y, Lu C, Han K, Yu H, Zhou Y (2018) Esterification of oleic acid to produce biodiesel catalyzed by sulfonated activated carbon from bamboo. Energy Convers Manage 163:59–65

Ooi HK, Koh XN, Ong HC, Lee HV, Mastuli MS, Taufiq-Yap YH, Alharthi FA, Alghamdi AA, AsikinMijan N (2021) Progress on modified calcium oxide derived waste-shell catalysts for biodiesel production. Catalysts 11(2):194

Pandit PR, Fulekar MH (2017) Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology. J Environ Manage 198:319–329

Quah RV, Tan YH, Mubarak NM, Khalid M, Abdullah EC, Nolasco-Hipolito C (2019) An overview of biodiesel production using recyclable biomass and non-biomass derived magnetic catalysts. J Environ Chem Eng 7(4):103219

Quah RV, Tan YH, Mubarak NM, Kansedo J, Khalid M, Abdullah EC, Abdullah MO (2020) Magnetic biochar derived from waste palm kernel shell for biodiesel production via sulfonation. Waste Manage 118:626–636

Rajkumari K, Rokhum L (2020) A sustainable protocol for production of biodiesel by transesterification of soybean oil using banana trunk ash as a heterogeneous catalyst. Biomass Conv Bioref 10(4):839–848

Rashid U, Ahmad J, Ibrahim ML, Nisar J, Hanif MA, Shean TYC (2019) Single-pot synthesis of biodiesel using efficient sulfonated-derived tea waste-heterogeneous catalyst. Materials 12(14):2293

Reddy Yadav LS, Raghavendra M, Manjunath K, Nagaraju G (2018) Photocatalytic, biodiesel, electrochemical sensing properties and formylation reactions of ZnO nanoparticles synthesized via eco-friendly green synthesis method. J Mater Sci Mater Electron 29(10):8747–8759

Rengasamy M, Anbalagan K, Kodhaiyolii S, Pugalenthi V (2016) Castor leaf mediated synthesis of iron nanoparticles for evaluating catalytic effects in transesterification of castor oil. RSC Adv 6(11):9261–9269

Risso R, Ferraz P, Meireles S, Fonseca I, Vital J (2018) Highly active Cao catalysts from waste shells of egg, oyster and clam for biodiesel production. Appl Catal A 567:56–64

Rocha PD, Oliveira LS, Franca AS (2019) Sulfonated activated carbon from corn cobs as heterogeneous catalysts for biodiesel production using microwave-assisted transesterification. Renewable Energy 143:1710–1716

Roschat W, Siritanon T, Kaewpuang T, Yoosuk B, Promarak V (2016) Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method. Bioresour Technol 209:343–350

Sai BA, Subramaniapillai N, Mohamed MSBK, Narayanan A (2020) Optimization of continuous biodiesel production from rubber seed oil (RSO) using calcined eggshells as heterogeneous catalyst. J Environ Chem Eng 8(1):103603

Sharma M, Khan AA, Puri SK, Tuli DK (2012) Wood ash as a potential heterogeneous catalyst for biodiesel synthesis. Biomass Bioenerg 41:94–106

Singh V, Sharma YC (2017) Low cost guinea fowl bone derived recyclable heterogeneous catalyst for microwave assisted transesterification of *Annona squamosa* L. seed oil. Energy Convers Manage 138:627–637

Sirisomboonchai S, Abuduwayiti M, Guan G, Samart C, Abliz S, Hao X, Kusakabe K, Abudula A (2015) Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. Energy Convers Manage 95:242–247

Smith SM, Oopathum C, Weeramongkhonlert V, Smith CB, Chaveanghong S, Ketwong P, Boonyuen S (2013) Transesterification of soybean oil using bovine bone waste as new catalyst. Biores Technol 143:686–690

Suresh T, Sivarajasekar N, Balasubramani KJRE (2021) Enhanced ultrasonic assisted biodiesel production from meat industry waste (pig tallow) using green copper oxide nanocatalyst: comparison of response surface and neural network modelling. Renew Energy 164:897–907

Suryaputra W, Winata I, Indraswati N, Ismadji S (2013) Waste capiz (*Amusium cristatum*) shell as a new heterogeneous catalyst for biodiesel production. Renew Energy 50:795–799

Tan YH, Abdullah MO, Nolasco-Hipolito C, Taufiq-Yap YH (2015) Waste ostrich-and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance. Appl Energy 160:58–70

Tang ZE, Lim S, Pang YL, Shuit SH, Ong HC (2020) Utilisation of biomass wastes based activated carbon supported heterogeneous acid catalyst for biodiesel production. Renew Energy 158:91–102

Thangaraj B, Solomon PR, Muniyandi B, Ranganathan S, Lin L (2019) Catalysis in biodiesel production—a review. Clean Energy 3(1):2–23

Thushari I, Babel S, Samart C (2019) Biodiesel production in an autoclave reactor using waste palm oil and coconut coir husk derived catalyst. Renew Energy 134:125–134

Vadery V, Narayanan BN, Ramakrishnan RM, Cherikkallinmel SK, Sugunan S, Narayanan DP, Sasidharan S (2014) Room temperature production of jatropha biodiesel over coconut husk ash. Energy 70:588–594

Wang A, Li H, Pan H, Zhang H, Xu F, Yu Z, Yang S (2018) Efficient and green production of biodiesel catalyzed by recyclable biomass-derived magnetic acids. Fuel Process Technol 181:259–267

Wei Z, Xu C, Li B (2009) Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresour Technol 100(11):2883–2885

Yatish KV, Prakash RM, Ningaraju C, Sakar M, Geetha Balakrishna R, Lalithamba HS (2021) *Terminalia chebula* as a novel green source for the synthesis of copper oxide nanoparticles and as feedstock for biodiesel production and its application on diesel engine. Energy 215:119165

Yu H, Cao Y, Li H, Zhao G, Zhang X, Cheng S, Wei W (2021) An efficient heterogeneous acid catalyst derived from waste ginger straw for biodiesel production. Renew Energy 176:533–542

Zabeti M, Daud WMAW, Aroua MK (2009) Activity of solid catalysts for biodiesel production: a review. Fuel Process Technol 90(6):770–777

Zeng D, Liu S, Gong W, Wang G, Qiu J, Chen H (2014) Synthesis, characterization and acid catalysis of solid acid from peanut shell. Appl Catal A 469:284–289

Zhang F, Wu XH, Yao M, Fang Z, Wang YT (2016) Production of biodiesel and hydrogen from plant oil catalyzed by magnetic carbon-supported nickel and sodium silicate. Green Chem 18(11):3302–3314

Zhang F, Tian X, Shah M, Yang W (2017) Synthesis of magnetic carbonaceous acids derived from hydrolysates of *Jatropha hulls* for catalytic biodiesel production. RSC Adv 7(19):11403–11413

Zik NAFA, Sulaiman S, Jamal P (2020) Biodiesel production from waste cooking oil using calcium oxide/nanocrystal cellulose/polyvinyl alcohol catalyst in a packed bed reactor. Renew Energy 155:267–277